KINETICS AND MECHANISM OF UREA - FORMALDEHYDE AND RELATED REACTIONS

THESIS SUBMITTED TO THE UNIVERSITY OF COCHIN IN PARTIAL FULFILMENT OF THE REQUIREMENTS OF THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
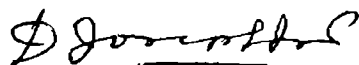
By

B. RAVEENDRAN NAIR, M. Sc.

DEPARTMENT OF APPLIED CHEMISTRY

UNIVERSITY OF COCHIN, COCHIN - 682022

DECEMBER 1981

TO MY PARENTS

CERTIFICATE

This is to certify that this thesis bound
herewith is an authentic record of the research work
carried out by the author under my supervision in
partial fulfilment of the requirements of the Degree
of Doctor of Philosophy of the University of Cochin
and further that no part thereof has been presented
before for any other degree.

Dr. D. Joseph Francis
(Supervising Teacher)
Professor and Head
Cochin-22, ⎱
Department of Polymer Science
and Rubber Technology
29-12-1981. ⎰
University of Cochin.

ACKNOWLEDGEMENTS

i

CONTENTS

PREFACE

The Urea-Formaldehyde resins find numerous
applications in adhesive, textile finishing and moulded
plastic industries etc. However, the chemical processes
involved have not been clearly established and the
chemistry of the formation of the higher homologues are
still uncertain.

Unlike in the case of phenol-formaldehyde
reaction, the products of the reactions of urea with
formaldehyde are complex and pH dependent, because the
functionality of urea is four and the initial reaction
products formed are not quite stable. So the properties
of the final products are largely determined by the rea-
ction conditions and an understanding of the different
factors influencing the reaction may be achieved by follow-
ing the reaction quantitatively.

The main objective of this work was to chara-
cterise the intermediate species formed in the reactions
of urea and its related compounds with formaldehyde in
acid, alkaline and neutral media and to study the kinetics

of the various steps occurring in the course of the reaction.
It was also of interest to study the effect of different
substituent groups viz., methyl, phenyl etc. as well as the
effects of concentrations of the reactants and concentra-
tions of the acid and alkali on the nature and rate of the
reactions.

It was necessary to develop a suitable thin-
layer chromatographic method to carry out qualitative and
quantitative analysis of the reaction products.

The subject matter of the thesis is discussed in
seven separate chapters.

Chapter I is a brief review of the earlier investi-
gations done on the reactions of urea with formaldehyde.
Preparation of materials and experimental details are discussed
in chapter II. The thin-layer chromatographic methods and
spraying reagent systems developed for the qualitative and
quantitative analysis of the reactions are described in
chapter III.

The preliminary experimental studies on the various
reactions are discussed in chapter IV. This includes the
isolation of the reaction steps for the kinetic studies and

a quantitative analysis of the reaction products. In

chapter V the reactions of urea with formaldehyde leading to

the formation of monomethylolurea under acid, alkaline and

neutral media at different temperatures and concentrations

of the reactants are described. The decomposition of mono-

methylolurea at different pH values and temperatures is also

discussed.

Chapter VI is a description of the reactions of

monomethylolurea with formaldehyde leading to the formation

of dimethylolurea. Both the formation and dissociation of

dimethylolurea have been studied at various pH values and

temperatures.

Chapter VII deals with the various routes for

methylene bridge formation in the urea-formaldehyde reaction.

Self condensation of methylols and intercondensation of

methylols and methylols with urea have been described at

various acid concentrations and temperatures. The forma-

tion of higher homologues has been discussed separately.

Study of the reaction of methylenediurea with formaldehyde

has also been included in this chapter.

Chapter VIII contains the studies of the reactions

of methyl- and phenylureas with formaldehyde and chapter IX

describes the studies on the reactions of acetamide and benzamide with formaldehyde.

Chapter X is a discussion of the results presented in the foregoing chapters and the interpretation of the results. A possible mechanism for the initial steps in the urea-formaldehyde reaction is proposed.

The results of this study are published/under publication as follows:

i) "A Thin-Layer Chromatographic Technique for the Separation and Determination of the Products of the Reactions of Amides with Formaldehyde", J. Chromatogr., 195 (1), 158-161 (1980).

ii) "Kinetics and Mechanism of Urea-Formaldehyde Reactions", Presented in a 'Symposium on Polymer Science' held at the Chemistry Department of the Sardar Patel University, Gujarat, during February 1981, 'Symposium on Polymer Science',p.1 (1981).

iii) "Kinetics and Mechanism of the Reactions of Urea and its Related Compounds with Formaldehyde", (Under publication).

CHAPTER I

INTRODUCTION

Urea-formaldehyde resins find numerous applications in adhesive, textile finishing and moulded plastic industries. These resins came into prominence, since they possess such desirable characteristics as freedom from colour, good clarity and adhesive quality. Like phenolic resins, urea-formaldehyde resins are, in the finished product crosslinked, insoluble and infusible materials. A low molecular weight resin is first formed which is crosslinked in the final fabrication process. Compared to phenolic resins, urea-formaldehyde products are cheaper, light in colour, odourless and have better resistance to electrical tracking, but have inferior heat resistance and higher water absorption.

The first reported work on the reaction of formaldehyde with amide hydrogens was by Tollens[1], in 1884. He isolated monomethylolurea, the simplest addition product of urea and formaldehyde. Gold Schmidt[2] (1896) used various amounts of urea and formaldehyde in acid solutions of various strengths and obtained insoluble, white, granular deposits, which were analysed and found to correspond to the empirical formula $C_5H_{10}N_4O_3$.

This so-called "Gold Schmidt's Compound" had the formula

$$[CH_2\!=\!NCONHCH_2NHCONHCH_2OH]_x$$
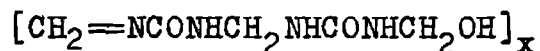
I

Einhorn and Hamburger[3-4](1904) conducted further research that led to the isolation of dimethylolurea. Einhorn and Hamburger[3-6](1908) using mild alkaline reaction conditions isolated various white, crystalline, easily soluble products, that melted at about $126^{\circ}C$, formed amorphous substances on further heating at $137^{\circ}C$, and finally decomposed at $260^{\circ}C$. They also pointed out the unusual nature of the urea formaldehyde products when reaction was induced beyond the methylol stage in comparison with the products obtained from other simple amides and alkyl substituted ureas. Slightly alkaline conditions were required for the formation of methylolureas at ordinary temperature. Practical application of urea-formaldehyde resins were reported by John[7](1920), Pollak[8](1920), Ellis[3](1935), Walter[9](1963), Dixon[10](1918), Henkel and Cie[11](1935) and others. The research by these investigators contributed to the growth of urea-formalde-hyde resin industry in the 1920's. The first effort at making a urea-formaldehyde resin is recorded in the patent to John[7] Urea was reacted with excess of

formaldehyde by application of heat and the product was
concentrated. The initial product proved water soluble
and John suggested its use as an adhesive and textile
impregnant. When reacted beyond a certain point, the
concentrate formed a transparent insoluble gel which could
be hardened by further heating. Pollak[12](1923) reduced
the formaldehyde/urea molar ratio to less than 3 1 and
added a base, ammonia, to control the reaction. Ripper[13]
(1923) used sodium acetate to retard gelatinization.

Other investigators (Scheiber et al. 1928)[14]
found that in acid solution these methylolureas were
converted into insoluble substances, similar to "Gold
Schmidt's Compound". From monomethylolurea in glacial
acetic acid they isolated low molecular weight poly-
methyleneurea and polymethyleneurea acetate.

$$[CH_2 = N\ CO\ NH_2]_{12} \cdot H_2O \qquad [CH_2 = N\ CO\ NH_2]_{12} \cdot CH_3COOH$$
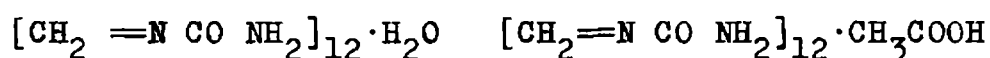
$$II \qquad\qquad\qquad III$$

It was generally assumed that condensates of urea
and formaldehyde consisted of urea fragments (in one way or
another) interlinked by methylene ($-CH_2-$) groups and having
a number of methylol groups distributed over the structure.
Details of this structure were not known. Often the

condensates were assumed to have a three dimensional structure with the occurrence of six membered rings. The reactions of urea and formaldehyde leading to these condensates were considered as a polycondensation by Kadowaki[15](1936) and Widmer and Frey[16](1939). According to Marvel[17](1946) the condensate may be partially the result of a polymerisation (trimerisation) of primarily formed methyleneurea.

Kadowaki[15](1936) described 1, 1'-methylenebisurea which he made by the acid reaction of urea and formaldehyde. He also reacted this dimer with formaldehyde and by step-wise means prepared and identified the next higher linear polymers, including the hexamer, all with methylene linkages.

Marvel et al.[17](1946) held the view that the primary reaction product of urea and formaldehyde led to the formation of methyleneurea (NH_2 CO $N{=}{=}CH_2$), which polymerized instantly to its trimer, forming a ring of the trimethylenetriamine type. In the second stage, by the formation of methylenebisamides, this ring would produce the polymeric urea-formaldehyde resin. The formula for this cured resin was given as in structure IV.

$$3(NH_2CON{=}CH_2) \longrightarrow$$

CO—NH$_2$

N

H$_2$C   CH$_2$

N   N

H$_2$N—CO   CO—NH$_2$

C

H$_2$

$$\xrightarrow{\quad CH_2O \quad}$$

NH————CH$_2$————NH

CO   CO

N   N

H$_2$C   CH$_2$ H$_2$C   CH$_2$

—NH-CO—N   N—CO   CO—N   NCO-NH-CH$_2$—

C   NH   NH   C

H$_2$ CH$_2$ CH$_2$ H$_2$

H$_2$ NH   NH   H$_2$

C   CO   CO   C

—NH-CO—N   N—CO   CO—N   N-CO-NH-CH$_2$—

H$_2$C   CH$_2$ H$_2$C   CH$_2$

N   N

CO-NH-CH$_2$—   CO-NH-CH$_2$—   (1)

IV
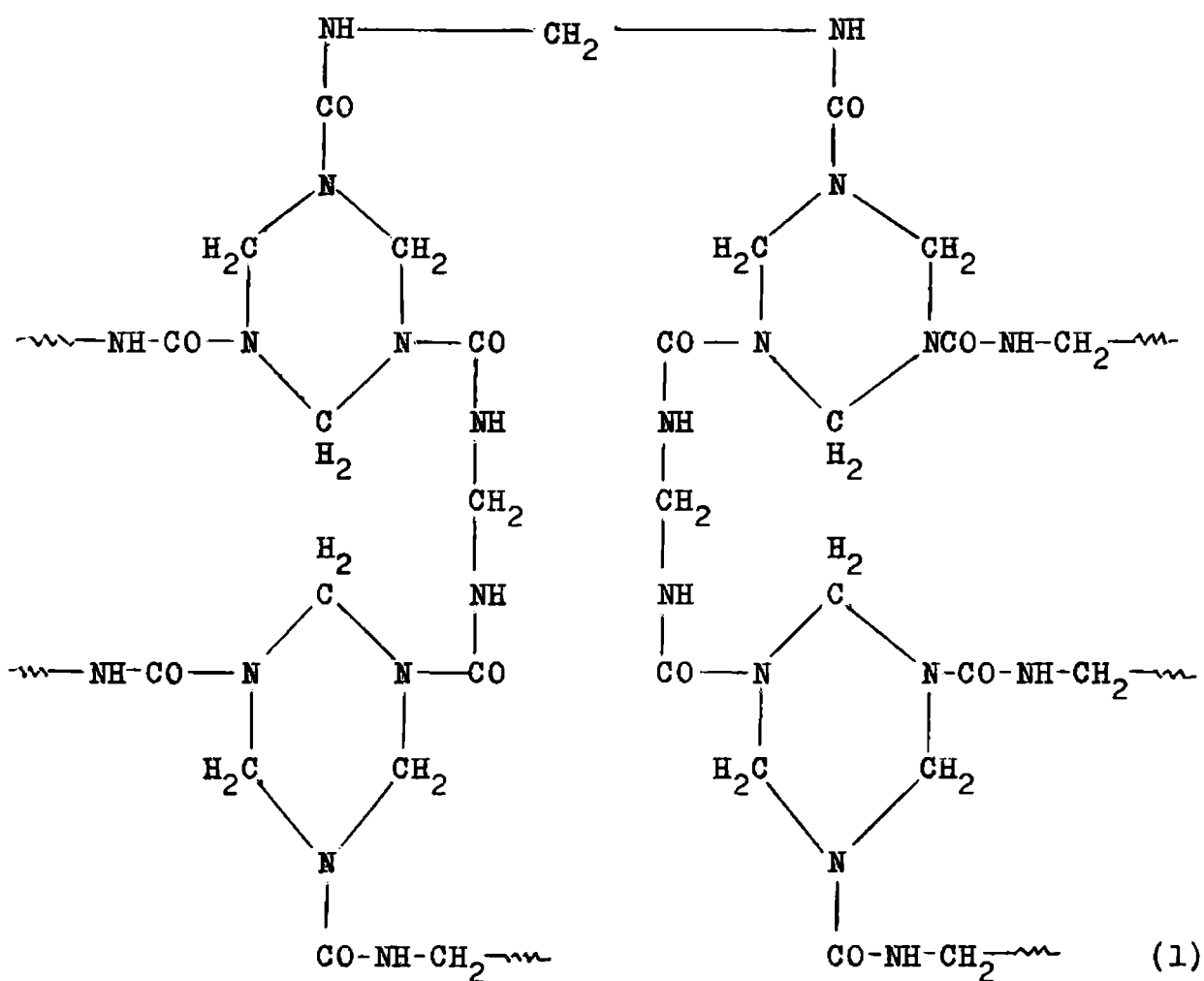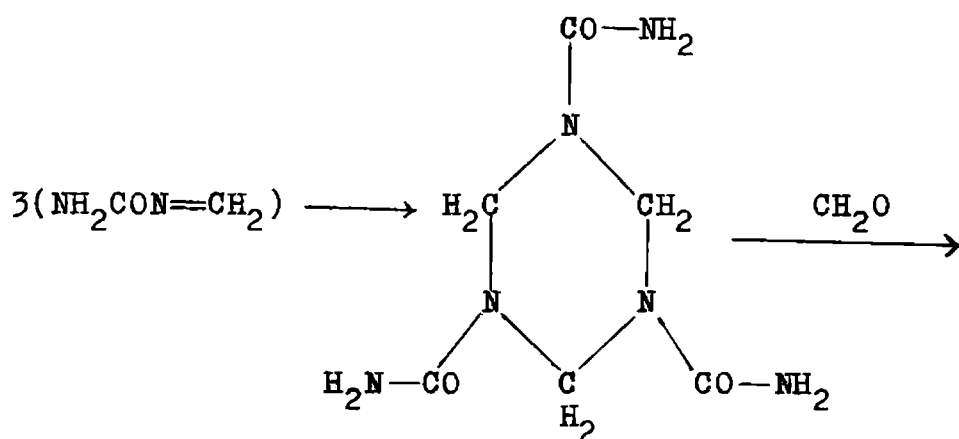
J.I. de Jong and J. de Jonge[18](1953) prepared some condensates of urea and formaldehyde in solution at pH 2-7 at temperatures 20-70°C. These products were analysed with respect to their content of methylene groups, methylol groups and urea groups. The average molecular weight could be estimated. The analytical data agreed with the presence of methylene bridges between urea fragments. They reported that "methyleneurea" may be a mixture of condensates with an average molecular weight of 300-500 and are formed by a step-wise condensation reaction.

Owing to the complexity of the polymer structure, numerous analytical methods have been developed to get better insight into the chemical composition of this kind of resins. Most methods involved the determination of the amount of free formaldehyde[19-43] and methylol groups[44-47]. Later these observations were further confirmed by spectroscopic analysis[48-52]

The question of molecular weights attained by intermediate and fully cured condensation products has been treated by various authors. It has been shown that products precipitated in the course of the reaction at 25°C and pH 1.7 in F/U = 1 have an average degree of polymerisation (DP) of 7. Products precipitated from this system[18] at 76°C and pH 6.6 were only slightly different

with $\overline{DP}$ of 6. The growth of the condensate was considered to be limited by their solubility. Kadowaki[15](1936) synthesized by step-wise growth, linear chains with a $\overline{DP}$ upto 6. In an earlier study it was shown that condensation product could also be precipitated by reaction in the ratio F/U = 2 at room temperature. Rather low molecular weights (< 350) were assigned to them through determination by cryoscopy and $-NH_2$ group estimation[9] Urea-formaldehyde condensates existing in the dispersed state for which molecular weight from 10,000 to 20,000 were originally assigned, were later shown to be dialisable and have only low molecular weight[53]

Kinetic studies

A few kinetic studies have been reported on the reaction of urea and related compounds with formaldehyde. The rates of the initial reaction with aqueous formaldehyde were determined in the early stages by measuring the consumption of formaldehyde. The reversible nature of the reaction was demonstrated by several workers.

$$H_2NCONH_2 + CH_2O \rightleftharpoons H_2NCONHCH_2OH \qquad (2)$$
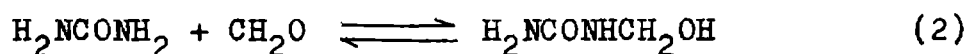
The reaction rates were affected by ionic strength and the presence of alcohols which retarded the reaction. Generally

second-order kinetics was observed, Smythe[54,55](1947,1951) and Bettelheim and Cedwall[56](1948) studied the urea-formaldehyde reaction in 2-4 molar aqueous solutions. Ignoring a very rapid initial reaction during the first 20-40 percent conversion, the further decrease in formaldehyde was found to be in reasonable harmony with a second order reaction equation. Using a polarographic method for determining free formaldehyde, Cowe and Lynch[57](1948) found the reaction between urea and formaldehyde to be reversible in a strongly alkaline solution; the formation of monomethylolurea being bimolecular and the decomposition monomolecular. Donally[58](1950) found the decomposition of monomethylolurea in dilute hydrochloric acid (pH = 2.3-0.7) to follow first order kinetics, the reaction rate being directly proportional to the H^+ ion concentration.

The rate of reaction of urea with formaldehyde was studied extensively by de Jong and de Jonge[59](1952). Though their reaction conditions were only partly identical in a small pH and temperature range, numerically the results differed from those obtained by Cedwall and Lynch, and led to a somewhat different reaction mechanism. Also the value for the rate constant as obtained by Donally appeared to be about one-third of the value found in the work of de Jong and de Jonge. The authors showed that in neutral, acid and

basic aqueous solutions, the forward reaction was bimolecular in the early stages. The reverse reaction was monomolecular. Data were obtained at pH 2-11 in 0.045 to 0.2 $\underline{M}$ solution at 25-59°C.

de Jong and de Jonge[59,60](1952) found that the reactions producing both substances (monomethylolurea and dimethylolurea) showed a close resemblence to each other. In both cases equilibrium was reached from both sides. Although the formation of both of the substances appeared to be bimolecular, the decomposition of dimethylolurea proved to be monomolecular. The rates of formation of both were found to be directly proportional to the concentration of the hydroxyl- and hydrogen ions, which had a catalytic influence. Activation energies for the reaction were found to be 14 k cal/mole for the forward reaction and 19 k cal/mole for the reverse reaction.

An investigation by the same authors[61](1953) on the kinetics of formation of methylene linkages in solutions of urea and formaldehyde in 1-3 $\underline{M}$ aqueous solutions at a pH of 4.1-4.4 indicated that the reactions involved were all bimolecular; hydrogen ions catalysed the reactions between an aminomethylol group and an amino group, leading to the formation of methylene linkages between urea fragments.

$$-NHCH_2OH + -NH_2 \longrightarrow -NHCH_2NH- + H_2O \qquad (3)$$
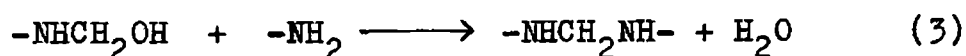
Lanquist[62-65](1957) studied the reaction rate of urea and formaldehyde at 20°C. He utilised a spectrophoto-metric method to determine the concentrations of monomethylol-urea and dimethylolurea. The method was based on a colour reaction between these compounds and p-dimethylaminobenzal-dehyde in the presence of methanolic hydrochloric acid.

The kinetics of the reaction between urea and formaldehyde were studied in the presence of various amounts of sulphuric acid at various temperatures by Shenai and Manjeshwar[66](1974). The reaction was shown to follow first order kinetics. The activation energy increased from 12.51 k cal/mole for 5 percent sulphuric acid (catalyst) to 14.59 k cal/mole for 45 percent sulphuric acid. The base catalysed reaction of urea and formaldehyde, leading to the formation of monomethylolurea, has an activation energy of 15.4 k cal/ mole.

Fractionation of Resins

Ito[67](1961) characterised the products of the base catalysed reaction of urea and formaldehyde. Paper chromato-graphic techniques were applied to resolve the reaction mixtures into mono-, di-, tri- and tetra methylolureas. Although previous authors indicated that tetramethylolurea was not produced, Ito presented some evidence to indicate its

formation. Significant quantities appeared to be obtained under the conditions he chose.

A series of reactions were done at 30°C utilising N_F/N_U ratio from 2/1 to 20/1 in presence of 0.005 $\underline{M}$ NaOH gave, initially at least, only unreacted urea, mono-, and dimethylolureas. At higher molar ratios trimethylolurea was formed as the reaction proceeded. At temperature of 60°C and with a tenfold increase of the catalyst to 0.05 $\underline{M}$ NaOH, tetramethylolurea was observed chromatographically even in the initial stages of the reaction. As the reaction proceeded, larger concentrations of tetramethylolurea were noted.
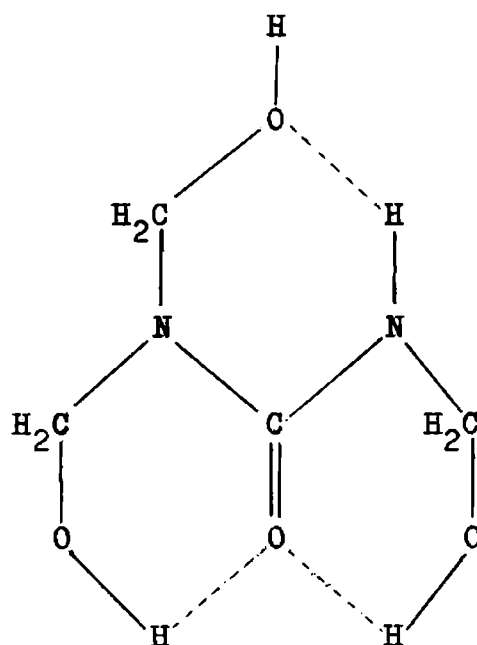
Ito[68](1961) isolated a product from urea-formaldehyde reaction mixture by solvent fractionation technique, which corresponded to chromatographic assignments for trimethylolurea. The substance was further characterised by the formation of its trimethylether and of thioether derivatives. Therefore, based on this characterisation, Ito confirmed his chromatographic assignments for trimethylolurea.

At higher temperatures and high base concentrations, with increasing N_F/N_U, he also obtained some chromatographic

evidence for formation of tetramethylolurea.

The need for more stringent conditions required to form tetramethylolurea, was explained by Ito as owing to hydrogen-bonding in the trimethylolurea as shown below.

$$
\begin{array}{c}
\text{H} \\
| \\
\text{O} \cdots \\
\diagup \quad \diagdown \\
\text{H}_2\text{C} \qquad \text{H} \\
| \qquad\qquad | \\
\text{N} \qquad\qquad \text{N} \\
\diagup \quad \diagdown \quad \diagup \quad \diagdown \\
\text{H}_2\text{C} \qquad \text{C} \qquad \text{H}_2\text{C} \\
| \qquad \| \qquad | \\
\text{O} \quad \text{O} \quad \text{O} \\
\diagdown \cdots \diagup \cdots \diagdown \\
\text{H} \qquad\qquad \text{H}
\end{array}
$$

V

The only available aminohydrogen for further reaction with formaldehyde could be involved in a six membered hydrogen bonded ring structure.

More recently instrumental methods were applied to the fractionation and analysis of urea-formaldehyde

resins. Kambanis and Vasishth[69](1971) reported the 60

MHz-H'-NMR of a resin, derivatized with acetic anhydride

in acetic acid. The spectrum showed absorption only for

-NH-and -NH$_2$ groups, whereas the rest of the spectrum

consisted of one broad peak. A few authors have used

GPC in order to obtain information on the molecular weight

distribution in the resin. Armonas[70](1970) obtained a

fair separation in the high molecular weight part by

using the system Sephadex LH 20/aqueous (2 percent) DMF.

An extensive study was made by Stark et al.[71](1973).

Three types of gels (Sephadex, Bio-Bead and Merckogel)

were swollen in appropriate solvents. It was found that

the combination Merckogel OR 1500/DMF gave a good separation

between urea, monomethylolurea and dimethylolurea. To

improve the solubility of the resins in organic solvents,

Braun and Bayersaorf[72](1972) silylated the resin prior to

analysis. Wim Dankelman[73](1976) and co-workers described

a method for analysing low molecular weight part of the

resin by GLC as well as the resin as a whole by 220 MHz H'-NMR

and for the ratio of low to high molecular weight material

in the resin by GPC.

Braun and Bayersdorf[74](1980) suggested that

alkylenediureas react with formaldehyde under formation

of homologous series of oligomers having an even number

of urea units. These oligomers possess very similar
solvation properties and degrees of methylolation compared
with urea-formaldehyde reactions. Therefore they are well
suited for the calibration of gel-permeation-chromatography
systems used for the investigation of urea-formaldehyde
resins with dimethylformamide as eluent. The dependence
of molecular weight[75] distribution from pH value and feed
ratios was estimated by comparison with calibration
condensates. Oligomer growth is slow with alkaline
catalysis, and catalyst type only determines the degree
of urea methylolation. The reduced condensation rate is
attributed to an unfavourable mechanism involving Schiff-
base intermediate. Highly reduced condensation caused by
increasing alkyl substitution of the urea unit is regarded
as evidence for the intermediate base.

Oligomers are observed having degree of condensation
upto 20 urea units in neutral or acid reaction conditions
and multi-stage condensations at elevated temperature. A
portion of monomer urea is converted to higher oligomers
during resin aging. Some technical resins contain globular
particles consisting of agglomerated primary particles
having diameters between 2-3 microns.

Reactions of Substituted Ureas (Acetamide and Benzamide)
with Formaldehyde

George A. Crowe Jr. and Cecil C. Lynch[76](1950)
studied the reversible reactions of acetamide-formaldehyde

and benzamide-formaldehyde polarographically. Kinetic studies showed that the equilibrium constants and energies of activation were about the same as that for urea-formaldehyde reaction to form monomethylolurea. The forward reactions are bimolecular and the rate of formaldehyde-acetamide reaction is about the same as that for urea-formaldehyde reaction at pH 12.7 and 25°C, the benzamide-formaldehyde reaction is 3-4 times as rapid.

The rate of reaction of formaldehyde with aliphatic and aromatic amides (benzamide and acetamide) were studied in aqueous solutions by Irma Tarvainen and Jouko Koskikallio[77,78](1970,1974). Both general acid and general base catalysis were observed. Uncatalysed hydrolysis was interpreted as a general acid catalysis by water.

Need for a Kinetic Investigation of the Urea-Formaldehyde and Related Reactions

A study of the literature on the reaction of urea and substituted ureas with formaldehyde under acidic, alkaline and neutral conditions reviewed above, shows that so far no kinetic investigation has been carried out with a view to isolate the various initial reactions leading to resinification. Because of the complexity of the reaction between

urea and formaldehyde it is not very easy to control the
reaction so that expected product alone is formed, which
will enable the study of its formation and dissociation
separately. The reported analytical methods were found
unsuitable to separate and estimate the initial reaction
products formed in the aqueous reaction mixtures for
kinetic studies. Hence it was desirable to develop a
simple analytical method suitable for the above purpose.

All the earlier workers used sulphite method,
taking rosolic acid as the indicator to estimate the amount
of free formaldehyde in the reaction mixtures. Assuming
that the consumed formaldehyde was completely utilized for
the formation of the desired product, rates were determined
and mechanisms were suggested. Also the end-point in the
estimation of formaldehyde by the sulphite method using
rosolic acid as the indicator was found to be not quite
sharp in reaction mixtures containing excess of sodium
sulphite. Therefore, it was planned to use the sulphite
method, using thymolphthalene as the indicator for the
estimation of free formaldehyde since it gives sharper
end-points.

Object and Scope of the Thesis

The main objectives of the investigations reported
in the present thesis are the following:

(1) Developing a suitable method for the study of the initial reactions of urea and related compounds with formaldehyde.

(2) Isolation of various reaction steps involved in the initial stages of the reaction.

(3) A critical comparison of the results obtained with those of the earlier workers.

(4) To determine the rates of the individual reactions in the formation of resins, and to elucidate the mechanism of the reaction.

CHAPTER II

MATERIALS AND EXPERIMENTAL PROCEDURE

Preparation of Materials

1. Urea (U)

BDH (Poole, Great Britain), analytical reagent grade, recrystallised from water (m.p. $133^{o}C$).

2. Formaldehyde (F)

BDH analytical reagent grade, aqueous solution (38 percent) containing less than 2 percent of methanol was used.

3. Monomethylolurea (MMU)

It was prepared according to the method given by Ludlam.[79] One gram of disodiumhydrogenorthophosphate was dissolved in 39.5 ml of aqueous formaldehyde. To the solution was added 60 g of urea and stirred the mixture while maintaining the temperature below $25^{o}C$ by running water round the reaction vessel. When the urea dissolved completely (about 2 hrs) the reaction vessel was placed in a refrigerator at a temperature of $0^{o}C$ for 15-24 hours

by then the reaction mixture solidified. The mass was
broken up and made a slurry with about 20 ml of methylated
spirit containing 1 percent (V/V) of a 10 percent (m/V)
aqueous solution of disodiumhydrogenorthophosphate,
filtered and recrystallised twice from ethanol containing
disodiumhydrogenorthophosphate.

Thin-layer chromatography described below
indicated that the monomethylolurea prepared by the above
method was free from urea and other urea derivatives.
Melting point obtained by the capillary method was 110-111°C.

4. Dimethylolurea (DMU)

A modified method described by Ludlam[79] was used.
One gram of disodiumhydrogenorthophosphate was dissolved
in 158 ml of formaldehyde and 60 g of urea was added. The
mixture was stirred while maintaining the temperature below
25°C by running water round the reaction vessel. When the
exothermic reaction subsided (about 2 hours) the reaction
vessel was placed in a refrigerator at a temperature of 0°C
for 15-24 hours. The crude product was filtered off and
recrystallised twice from methylated spirit.

Thin-layer chromatography showed that the dimethylol-
urea prepared by this method was free from urea and other

urea derivatives. The melting point determined was 132°C
by the capillary method. Values given in the literature
range from $126-139^{\circ}$C.

5. Methylenediurea (MeDU)[79]

Urea (400 g) was stirred with 300 ml of water,
53 ml of aqueous formaldehyde and 1.2 ml of orthophosphoric
acid until all the urea dissolved. After leaving it to
stand for 24 hours at room temperature the solution was
cooled to 0°C and left for further 24 hours. The crude
methylenediurea was filtered and crystallised twice from
water.

The major impurity present along with methylene-
diurea was dimethylenetriurea. This contaminant was removed
during recrystallisation. Thin-layer chromatography showed
that the methylenediurea was free from urea, dimethylene-
triurea and other urea condensation products. Melting
poiht was found to be $207-208^{\circ}$C.

6. Dimethylenetriurea (DMeTU)[80]

Urea (80 g) and formaldehyde (13 ml) were stirred
well in the presence of 0.5 ml of orthophosphoric acid.
The mixture became homogeneous and a white solid separated

after 1 hour. The precipitate was filtered, washed with
cold water and crystallised repeatedly from water until
completely free from higher homologues (m.p. 243°C). Thin-
layer chromatographic method showed that it was completely
free from urea and other higher homologues.

7. Trimethylenetetraurea (TMeTeU)

This was prepared by the method reported by
Kadowaki with modifications.[80] Formaldehyde (78 ml) and
urea (100 g) were added to 300 ml of water and the pH was
adjusted to 2.5 by adding hydrochloric acid. The mixture
was kept for one day, then the solidified mass was stirred
with hot water and filtered. The filtrate on cooling
yielded a white solid which was crystallised repeatedly
until the TMeTeU was free from dimethylenetriurea and its
higher homologues. Thin-layer chromatographic method
showed that the compound was free from impurities (m.p.248°C).

8. Monomethylolmethylenediurea (MMMeDU)

It was prepared by the method suggested by Ludlam.[79]
Methylenediurea (1.3 g) was dissolved in 25 ml of hot water
containing 0.1 g of disodiumhydrogenorthophosphate. The
solution was quickly cooled and before the methylenediurea

crystallised out, 0.6 g of formaldehyde (36 percent solution) was added. The resulting solution was stirred overnight at room temperature and then evaporated it to dryness, at a temperature not exceeding $30^{\circ}C$ by passing a jet of air over the solution in an evaporating basin. The residue contained dimethylolmethylenediurea as an impurity and also a considerable amount of methylenediurea. The methylenediurea was removed by dissolving the above substance in water-alcohol mixture (4:1 V/V) and cooling quickly. The methylol compound alone precipitated out.

9. Dimethylolmethylenediurea (DMMeDU)

It was also prepared by the method of Ludlam[79] MeDU (1.3 g) was dissolved in 25 ml of hot water containing 0.1 g of disodiumhydrogenorthophosphate. The solution was quickly cooled and before the methylene diurea crystallised out, 1.7 g formaldehyde solution was added. The solution was stirred overnight at room temperature and then evaporated to dryness at a temperature not exceeding $30^{\circ}C$ by passing a jet of air over the solution in an evaporating basin. The solid thus obtained contained some MMMeDU and some unchanged MeDU. The latter compound could be removed by dissolving the solid in 30 ml of hot water alcohol mixture (4:1 V/V) and cooling quickly. The methylol alone precipated.

10. Methylurea (MeU)

BDH (Poole, Great Britain), analytical reagent grade, recrystallised from water (m.p. 102°C).

11. Monomethylolmethylurea (MMMeU)[80]

Methylurea (7.4 g) and formaldehyde (8 ml) were mixed by stirring with potassium carbonate to bring the pH to 9. The reaction mixture was kept at room temperature for 2 hours and then in a refrigerator at 0°C. After 48 hours crystals of MMMeU were formed. The viscous liquid was decanted and recrystallised from alcohol twice (m.p. 122-125°C).

12. Phenylurea (PhU)

BDH (Poole, Great Britain), analytical reagent grade, recrystallised from alcohol (m.p. 147°C).

13. Methylenebisphenylurea (MeBPhU)[80]

Phenylurea (13.6 g) was dissolved in 100 ml 1,4-dioxane. It was stirred with formaldehyde (4 ml) and 0.5 ml of concentrated hydrochloric acid. After 30 minutes, a white solid mass separated which was filtered, washed with water and recrystallised from 1,4-dioxane (m.p. 268°C).

14. Acetamide (A)

BDH (Poole, Great Britain), analytical reagent grade, recrystallised from water (m.p. 81°C).

15. Monomethylolacetamide (MMA)[80]

Acetamide (12 g), formaldehyde (15.3 ml) and potassium carbonate (1 g) were mixed and warmed gently and the viscous liquid was kept aside in a vacuum desiccator. The solid mass was extracted with methanol. The filtrate on evaporation yielded a hygroscopic solid (m.p. 51°C).

16. Methylenebisacetamide (MeBA)[80]

Acetamide (23 g) was weighed into a 100 ml conical flask and stirred with formaldehyde (15.3 ml) and concentrated hydrochloric acid for 15 hours. The precipitated compound was filtered and crystallised repeatedly from ethanol, giving crystalline needles (m.p. 199-201°C).

17. Benzamide (B)

BDH (Poole, Great Britain), analytical reagent grade (m.p. 130°C).

18. Monomethylolbenzamide (MMBA)[80]

Benzamide (12 *g*) was dissolved in the minimum volume of methanol and stirred with formaldehyde (15.3 ml) in the presence of potassium carbonate (1 *g*) for 24 hours. The reaction mixture was cooled in ice. The crystals separated were filtered and recrystallised from ethanol, giving plates (m.p. 108-110°C).

19. Methylenebisbenzamide (MeBB)[80]

Benzamide (12 *g*) was dissolved in minimum volume of methanol and stirred with formaldehyde (3.8 ml) and concentrated hydrochloric acid (1 ml) for 24 hours. The solvent was evaporated and the precipitated compound was filtered and recrystallised from hot ethanol (m.p. 222-224°C).

The IR spectra of these compounds were taken on a Perkin Elmer Spectrophotometer and the nuclear magnetic resonance spectra, were taken on a varian A60 instrument operating at 100 MHz at 25°C in deuterated dimethylsulphoxide in the presence of anhydrous calcium chloride. The spectra corresponded to the structures given above.

Experimental Procedure

The experimental procedure adopted for all the kinetic studies were as given below.

The reactions were carried out in a 250 ml four
necked flask fitted with a mercury sealed stirrer, a water
condenser, sensitive thermometer, and a vacuum-sampling
device. The flask was heated in a thermostat, which was
maintained at the required temperature within ± 0.1°C.

The urea solution at the desired concentration
was first introduced into the reaction vessel. After the
required temperature was attained, catalyst was added
followed by the measured amount of formaldehyde solution
so that the expected volume, concentration and pH of the
final reaction mixture was attained. For reactions involv-
ing addition of formaldehyde to methylol derivatives,
formaldehyde was first taken in the reaction vessel to
which the methylolurea was added. Soon after the complete
addition, an aliquot sample was withdrawn using the vacuum
sampling device and cooled in ice-cold water to slow down
the reaction. From this the unreacted formaldehyde and
the products of reaction were estimated.

For chromatographic analysis of the products
the reaction was arrested as described in chapter IV.

Unreacted formaldehyde alone was estimated by
the sulphite method[87,82] or hydroxylamine hydrochloride
method[83,84] and sum of the free formaldehyde and methylols
of urea were estimated by the iodimetric method.

In the reaction of acetamide with formaldehyde, the free formaldehyde was estimated by the hydroxylamine hydrochloride method. In the sulphite method large amount of sodium hydroxide was liberated when the free formaldehyde reacted with sodium sulphite solution, which hydrolysed the acetamide and its compounds to acetic acid. Hence in this case sulphite method was not tried. In all other cases sulphite method was used.

During the course of the reaction, aliquots were withdrawn at various intervels, cooled in ice-cold water and free formaldehyde and compounds of urea were estimated as described below.

Estimation of Formaldehyde

Sulphite Method

The reaction mixture (5 ml) was pipetted out into a clean 100 ml conical flask. To this was added 5 drops of thymolphthalein indicator (0.1 g of the indicator per 100 ml of ethanol) followed by 5 ml of sodium sulphite solution (1 $\underline{M}$). A known excess of dilute hydrochloric acid (0.1 $\underline{N}$) was added to destroy the liberated NaOH. The excess acid was back titrated using carbonate-free standard sodium hydroxide solution from a micro-burette. End-point was the appearance

of a faint blue colour. A blank was also done under
identical conditions. The amount of alkali liberated,
equivalent to the free formaldehyde present was obtained.

Owing to the presence of excess sodium sulphite,
the commonly used resolic acid did not give sharp end point.
Thymol=phthalein was found to be a better indicator than
rosolic acid.

Hydroxylamine Hydrochloride Method

To 5 ml of the reaction sample, a few drops of
bromophenol blue indicator were added and it was neutralised
by careful addition of N/100 hydrochloric acid or sodium
hydroxide as the case may be. The end-point was a colour
change from violet to greenish yellow, or vice-versa. To
the neutralised solution 5 ml of 10 percent hydroxylamine
hydrochloride solution was added and the mixture was allowed
to stand for 5 minutes. The hydrochloric acid liberated by
the action of hydroxylamine hydrochloride with formaldehyde
according to the equation

$$CH_2O + H_2NOH \cdot HCl \longrightarrow CH_2 = NOH + HCl + H_2O \quad (4)$$
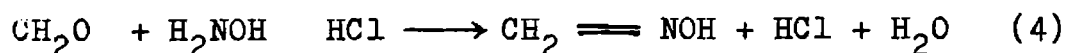
was titrated against carbonate-free standard sodium
hydroxide solution from a microburette. To correct for

the free hydrochloric acid present in hydroxylamine
hydrochloride solution, 5 ml of the latter was titrated
against standard sodium hydroxide solution and this blank
titre value was subtracted from the earlier one. The
equivalent weight of formaldehyde according to the above
equation is its molecular weight. From the titre values
the strength of formaldehyde was calculated.

The sulphite method was found to be better than
the hydroxylamine hydrochloride method for the estimation
of formaldehyde. The indicator used, thymolphthalein
in the sulphite method showed a sharp colour change at the
end point even when very dilute formalin solutions were
used and also in reaction mixtures containing free urea.

Determination of the sum of Free Formaldehyde and
Methylols

The iodimetric method of Romijin[85,86] was modi-
fied and used for the estimation of the sum of free formal-
dehyde and methylols. This method is based on the oxidation
of formaldehyde by hypoiodite formed when sodium hydroxide
is added to a solution of formaldehyde to which a known
excess of standard iodine solution has been added. The
excess iodine is back titrated after acidification.

Reaction mixture (5 ml) was pipetted out into 50 ml of iodine solution (0.1 $\underline{N}$) kept in an iodine flask, followed by 10 ml of sodium hydroxide solution (2$\underline{N}$). The mixture was kept for sixty to seventy minutes at room temperature and acidified with 20 ml of sulphuric acid solution (2$\underline{N}$). The liberated iodine was titrated against a standard solution of sodium thiosulphate (0.05$\underline{N}$) using starch as the indicator. A blank was also done. The amount of iodine reacted is equivalent to the formaldehyde present free and as methylols.

Quantitative analysis of the reaction products, namely methylols and methylenes of urea and its related compounds, was carried out using thin-layer chromatographic technique. The details of the procedure are given in chapter III.

CHAPTER III

THIN LAYER CHROMATOGRAPHIC TECHNIQUES FOR THE
SEPARATION AND ESTIMATION OF THE PRODUCTS OF
THE REACTIONS OF UREA AND RELATED COMPOUNDS
WITH FORMALDEHYDE

A few methods have been reported in literature

for the chromatographic separation of the reaction products

of urea and formaldehyde. So far no method is available for

the separation of the products of the reaction of formaldehyde

with methylurea, phenylurea, acetamide and benzamide.

Ito[67](1961) was the first to employ paper chroma-

tographic technique in studying the urea formaldehyde

reaction. The author carried out the reaction under differ-

ent conditions in presence of alkali and studied the

resultant methylol compounds with the help of two-dimensional

paper chromatography. The formation of trimethylolurea and

tetramethylolurea was established using methanol and pyridine-

chloroform-water solvent systems. Varying concentrations of

urea and formaldehyde were mixed under different alkali

concentrations. The separated spots were detected using

Tollen's reagent.

W.Y. Lee[87](1973) used both thin-layer chromato-
graphy and paper chromatography for the separation of the
methylols and methylene ureas and compared their Rf values
with the two techniques. The author showed that cellulose
thin layers gave better separation for methylols, than
silica gel thin-layers. p-Dimethylaminobenzaldehyde in
ethanol-hydrochloric acid mixture was used for the detection
of free amino groups in methylene urea and chromotropic acid
in concentrated sulphuric acid for detecting methylols.

Next year P.R. Ludlam[79](1973) published two
papers on thin-layer chromatography of simple urea-formaldehyde-
methanol reaction products. The methyl ethers were separated
on thin layers of Kieselgel using ethylacetate-methanol-
ammonia system. Spots were detected by chlorination followed
by spraying with 5 percent solution of o-toluidine in glacial
acetic acid. Intensities of the spots were compared with
standard spots and percentage amounts of mono- and dimethylol
ureas were determined.

The above methods of separation and analysis of
the products of urea and formaldehyde were found to be
unsuitable for a quantitative study. Hence a new analytical
method was necessary for the study of urea-formaldehyde
reaction for the following reasons.

An important point to be considered in the
chromatographic separation of urea-formaldehyde reaction
products is their instability.[80,87] In general they are
reactive materials, they may polymerise, disproportionate,
or decompose readily. The methylol compounds, even if
prepared in a pure state and stored at normal temperatures,
show indications of decomposition after a few weeks and,
in aqueous or alcoholic solution can show some indication
of decomposition or reaction after a few hours. The ethers
are more stable, both in solution and as solids, than the
methylol compounds and can be stored for many months at
room temperature without decomposition.

The reactions of methylol compounds and, to a
lesser extent, the ethers, are catalysed strongly by
hydrogen ions.[79,80,87] Therefore, if their solutions are
applied to the chromatographic plate and developed with
acidic solvents, decomposition will occur. Methylenediurea
is stable in the solid form. It will however, hydrolyse in
aqueous solution, the reaction being catalysed by hydrogen
ions.

Detection Procedures Tried for TLC

Many spray reagents and detection procedures have
been examined in the course of this investigation. Some,

picric acid,[88] ninhydrin,[89-91] Schiff's reagent,[92] phenyl-hydrazine-Nickel sulphate, potassium permanganate in dilute sulphuric acid[93] and various concentrations of potassium dichromate in dilute sulphuric acid,[94] were found to be either very insensitive or very specific. For example, Schiff's reagent gave colours only with compounds that liberated formaldehyde. Some procedures were partially successful and were used for a time, often until a more suitable method was found. These reagents and procedures are reviewed below.

a) p-Dimethylaminobenzaldehyde in Ethanol[95-97] (1 percent solution)

The plate was sprayed with the reagent and placed for 5 minutes in a vessel saturated with hydrogen chloride. This reagent showed good sensitivity to urea and compounds containing primary amide groups. But secondary amido compounds were detected only at relatively high concentrations. The contrast between the spots and the background plate (yellow on white) was poor.

b) Chromotropic Acid-Sulphuric Acid[98]

One volume of 10 percent (w/V) aqueous chromotropic acid mixed with 5 volume of concentrated sulphuric acid and water (5:3 ratio V/V). The resulting mixture

was sprayed and chromatograms were heated at 100°C, for
5-10 minutes to develop violet spots. It showed colour
with compounds which could be oxidised to formaldehyde or
compounds having $-CH_2-$ group. Even though the reagent
is very sensitive, the background also became highly
violet and well defined spots were not obtained.

c) Dichlorofluoresceine Solution-Bromine Vapour

The plate was slightly moistened by spraying
with 0.05 percent dichlorofluorescein in 1 $\underline{N}$ sodium
hydroxide solution, exposed to bromine vapour until the
initial pink colour was discharged and finally sprayed
heavily with the dichlorofluorescein solution. Pink
spots were produced on a pale yellow background. This
procedure was sensitive, but the factors that are involved
in colour formation were not easily controlled and repro-
ducibility was found to be poor. Any ammonia or basic
materials remaining on the plate also interfered with
colour production. The sensitivity was found to be
about 0.2 μg for DMU.

d) Alkaline Potassium Pentacyanonitrosylferrate (III)
   (Potassium Nitroprusside) - Potassium Hexacyanoferrate
   (III) Solution[99-101]

Equal volumes of 10 percent solutions of the
above two materials and potassium hydroxide were mixed

and used immediately as the mixture is stable for only

half an hour, purple spots were produced on a brownish-

yellow background. Two main drawbacks were found with

this spray: it was fairly insensitive, as the minimum

amount of dimethylolurea that could be detected was

15 µg, and the colour faded within 5 minutes.

e) o-Toluidine-Chlorine[79,102-104]

In this method the plate was exposed to

chlorine gas and after allowing sufficient time for the

excess of the chlorine to disperse, the plate was sprayed

with a solution of an aromatic amine in glacial acetic

acid. Of the aromatic amines tested, o-toluidine was

the best. Eventhough the spots were stable even for

several weeks, this method of detection could not be

used for the subsequent analysis of the compounds thus

detected.

Chromatographic Technique Developed in the Present
Investigation

A thin-layer chromatographic method has been

developed for the effective separation of all the compounds

of urea and its derivatives with formaldehyde.[80] The

methylols and methylene ureas thus separated were detected

with a suitable spraying reagent system. The well-defined
spots were scraped out, the products were extracted with
suitable reagents, centrifuged and the extracts were used
for the chlorimetric estimation of the products.

Both cellulose and silica gel G TLC plates
were used for the separation of the initial reaction
products of urea and related compounds with formaldehyde.
All compounds except monomethylolurea, dimethylolurea,
monomethylolmethylenediurea and dimethylolmethylenediurea
were separated on silica gel G plates with suitable
developing solvent systems. The above four methylols were
not separated on silica gel G plates in any of the solvent
system tried. But they could be separated well on cellulose
plates.

Procedure

Silica gel G plates (BDH) and cellulose plates
(Loba) with layer thickness of 0.5mm each were used for
the separation. After air drying, the plates were heated
at 100-105°C, for 10 minutes for cellulose and 30 minutes
for silica gel G plates.

Cellulose plates were prepared by the following
procedure: 19 g of the microcrystalline cellulose was

weighed into a 500 ml beaker. 100 ml of distilled water was added and immediately stirred with a high speed mechanical stirrer for 60 seconds and spread on glass plates as usual.

The activated plates were always kept in a vacuum desiccator.

The tank used in this work measured 22x7x22 cms. Precautions were taken by using filter paper on the sides of the tank. The atmosphere in the tank was saturated with solvent.

Aqueous solutions (0.02 $\underline{M}$) of the reference compounds (5-30 μl) were spotted on the plates, dried and developed using the appropriate solvent system (vide infra). The dried plates were sprayed with the colouring reagent or viewed under UV light. The spots were marked, scraped off, extracted with suitable reagents, centrifuged and the absorbance of the extract was measured quantitatively using a spectrocolorimeter after suitable treatment.

Detection Method[80]

New spraying reagents have been developed for the detection of the methylols and methylene compounds of

urea and its derivatives on thin layers.

The spots corresponding to the compounds which
separated on silica gel and cellulose plates were first
of all sprayed with a 1 percent solution of phenylhydrazine
in 30 sulphuric acid. Then it was sprayed with a 0.1
aqueous solution of iron (III) chloride. The methylols
and methylene compounds were hydrolysed to free formal-
dehyde in presence of acid. Then it reacted with phenyl-
hydrazine giving the hydrazone of the aldehyde. The
hydrozone gave reddish-pink spots by complexing with
the iron (III) chloride. The free urea present in these
spots were then analysed quantitatively by the diacetyl-
monoxime method colorimetrically.[105] The phenyl hydrazone
colour is discharged and does not interfere with the
estimation of urea. Detection limit was 0.01-0.1 μg for
the compounds studied.

The spots corresponding to the reaction products
of benzamide and acetamide were estimated by the quanti-
tative colour reaction of formaldehyde liberated, the spots
being detected using UV light. The spots corresponding to
the benzamide derivatives could be quantitatively detected
by iodination also for qualitative purposes. The acetamide
derivatives could be detected qualitatively by the phenyl
hydrazine sulphate-ferric chloride reagent.

Estimation Method for the Compounds of Urea[80]

The reddish pink spots were scraped off separately
and centrifuged after the addition of 5 ml of reagent I
(see below). The clear solution was transferred completely
into a boiling tube. Reagent II (see below) (5 ml) was
added and the mixture, heated on a boiling water-bath for
20 minutes using an air condenser preferably in the dark.
It was then rapidly cooled in ice-cold water and diluted
to 25 ml and absorbance of the pink solution was measured
at 520 nm.

Reagent I: was prepared by dissolving 1.5 g of iron (III)
chloride hexahydrate in 30 ml of 85 percent phosphoric
acid and diluting with 15 ml water. This solution (0.5 ml)
was made upto 500 ml using 10 percent (V/V) sulphuric acid.

Reagent II: was prepared by dissolving 0.17 g of thiosemi-
carbazide in 100 ml water and mixing with a solution of
diacetyl monoxime (0.85 g) in 100 ml of warm water. The
mixture was made up to 500 ml and kept in amber-glass
bottles.

Estimation Method for the Compounds of Acetamide and
Benzamide[80]

Here the formaldehyde liberated on hydrolysis
was determined by its colour reaction with chromotropic
acid. The separated spots were located and marked in a

U-V chamber, scraped off separately, extracted with
water and centrifuged to remove silica gel. The clear
solutions were made up to 25 ml, mixed with 0.3 ml of
0.1 $\underline{M}$ aqueous chromotropic acid and carefully made up
to 50 ml with concentrated sulphuric acid[107] They
were then heated on a boiling water bath for 10 minutes,
cooled to room temperature and absorbance of the violet
solution measured at 570 nm.

In the case of the water insoluble compounds,
the spots were scraped off separately, extracted with
acetone, centrifuged, and the resulting solutions were
evaporated and then used for colour development.

Quantitative determinations were made from
Beer's law plots of absorbance versus concentration.
The Rf values of the compounds and λ_{max} values together
with molar absorptivities (ε) of the coloured extracts
are given in Table 1. The accuracy of the method is
±2 percent.

The details of the technique applied for the
individual compounds are given below.

Methylols of Urea and Methylenediurea

MMU, DMU, MMMeDU and DMMeDU were separated on
cellulose plates using pyridine-chloroform-water (40:16:5)

42

system. The plates were developed in the solvent mixture
for 60 minutes, during which time the solvent rose about
20 cms. The plate was then taken out, allowed to dry at
room temperature for 60 minutes after developing. Elevated
drying temperatures can cause decomposition of the compounds
leading to reduced spot intensities and unexpected spot
colours. After thorough drying, till the plates were
completely free from pyridine, it was sprayed with
phenylhydrazine in sulphuric acid solution followed by
iron (III) chloride solution. The reddish-pink spots
were identified using standard Rf values and estimated
by the diacetyl monoxime method as described before. The
wavelength corresponding to the maximum absorption (λ_{max})
together with their Rf values and molar extinction
coefficients (ε_{max}) are given in Table 1.

Methylenediurea and its Homologues

MeDU, DMeTU and TMeTeU were separated on silica
gel plates using isopropanol-toluene-water-acetic acid
(70:20:3:2) system. The compounds were spotted, dried
at room temperature and developed in the solvent system
for 60 minutes, during which time the solvent rose to
10 cms. The plates were taken out, dried for 15 minutes
and detected using the phenylhydrazine sulphate--FeCl$_3$

spraying reagent system. The reddish-pink spots were then analysed as described before by the diacetylmonoxime method. The λ_{max}, Rf values and ε_{max} are listed in Table 1.

On cellulose plates all the methylols and methylene ureas could be separated. But on silica gel only the methylenes could be separated, since the acid hydrolyses the methylols easily. It was also noted that the cellulose TLC had an advantage over the silica gel TLC. By the former method U, MMU and DMU could be resolved easily, as separate well defined spots. But on silica gel using the second solvent system the MMU and DMU are not resolved well. Trimethylolurea could be also detected easily on cellulose plates as a separate spot above the spot for dimethylolurea. However cellulose is difficult to remove by centrifuging after the colour is extracted. Hence for the separation and estimation of methylene diureas, silica gel plates were used and for methylol ureas cellulose plates were used.

Compounds of Methylurea and Phenylurea

The compounds were separated on silica gel G plates. MeU and MMMeU were separated using 1-butanol and PhU, MMPhU and MeBPhU were separated using ethyl acetate

as solvents. The compounds were spotted, dried at room

temperature and developed in suitable solvents. The

plates were dried for 15 minutes at room temperature,

and the spots were viewed in a U-V chamber or were

made visible by spraying the reagent. The located spots

were then estimated by the diacetylmonoxime method. The

λ_{max}, Rf values and ε_{max} of the compounds are given in

Table 1.

Compounds of Acetamide and Benzamide

Acetamide and benzamide compounds were separated

on silica gel TLC plates. A, MMA and MeBA were separated

using methanol-chloroform (3:2) mixture and B, MMB and

MeBB were separated using diethyl ether as solvents. For

quantitative determination the compounds were spotted,

dried at room temperature, and developed using appropriate

solvent systems. The developed plates were dried for

15 minutes, located the spots quantitatively in a U-V

chamber and estimated the methylols and methylenes as

formaldehyde by the chromotropic acid method as described

before. Rf values, λ_{max} and ε_{max} values are given in

Table 1.

In the above separation technique the free

urea compounds could be located as yellow spots using

Ehrlich's reagents[97] and the amides (A) and (B) could be

located as blue spots by chlorination followed by spraying
with potassium iodide-starch solution.[107]

Linear Relationship Between Concentration and
Absorbance

To test the linear relationship between concentra-
tion and absorbance at low concentrations (Beer's law),
compounds were spotted separately and in mixtures on the
plate using a micropipette. After the usual chromato-
graphic procedure, the absorbance of the solutions was
measured against a suitable blank at the wavelength
corresponding to maximum absorption for each compound.
When a compound was spotted alone or in mixtures there
was no difference in its absorbance values.

With proper control of conditions such as the
time of development, the time of drying, the amount of
substance spotted and the time for extraction and develop-
ment of colour, reproducible values could be obtained
within ±2 percent.

Table 1

Rf values of the various amides and their reaction products with formaldehyde and the λ_{max} and ε_{max} of their coloured extracts

Sl. No.	Compounds	Rf	λ_{max}	ε_{max} lit.mole^{-1}cm.$^{-1}$
1.	Monomethylolurea (MMU)	0.48	520	8359
2.	Dimethylolurea (DMU)	0.64	520	7782
3.	Methylenediurea (MeDU)	0.41	520	13040
4.	Monomethylolmethylene-diurea (MMMeDU)	0.22	520	12910
5.	Dimethylolmethylene-diurea (DMMeDU)	0.29	520	12860
6.	Dimethylenetriurea (DMeTU)	0.21	520	23060
7.	Trimethylenetetraurea (TMeTeU)	0.053	520	21100
8.	Monomethylolmethylurea (MMMeU)	0.31	520	8670
9.	Monomethylolphenylurea (MMPhU)	0.367	--	--
10.	Methylenebisphenylurea (MeBPhU)	0.90	525	14200
11.	Monomethylolacetamide (MMA)	0.64	570	14701
12.	Methylenebisacetamide (MeBA)	0.82	570	11034
13.	Monomethylolbenzamide (MMB)	0.40	570	14695
14.	Methylenebisbenzamide (MeBB)	0.72	570	12867
15.	Urea (U)	0.37	--	--
16.	Methylurea (MeU)	0.60	--	--
17.	Phenylurea (PhU)	0.58	--	--
18.	Acetamide (A)	0.43	--	--
19.	Benzamide (B)	0.47	--	--

CHAPTER IV

PRELIMINARY EXPERIMENTAL STUDIES

The preliminary experimental studies were aimed at finding out suitable methods to arrest the reactions and establishing conditions favourable for isolating the initial stages involved in the addition of formaldehyde to urea and its derivatives, for kinetic studies. The reactions were conducted as described in chapter II. The reactants and products were analysed at regular intervals of time by thin-layer chromatography [chapter III].

Method for Arresting the Reaction

Arresting of the reactions of urea and its compounds with formaldehyde was one of the major problems encountered in the kinetic studies.

In all kinetic studies aliquots were withdrawn using a vacuum sampling device, the receiver of which was cooled in ice to slow down the reaction. This reaction mixture could not be kept for a long time for further estimations. Because even at $0^{\circ}C$ for example, urea will react with formaldehyde giving monomethylolurea easily.

47

Hence immediately after the withdrawal of the sample, a fixed volume of the reaction mixture was arrested for the estimation of formaldehyde by the sulphite method or hydroxylamine-hydrochloride method.

The sulphite method used by Ogata and Okano[82] was found to be quite unsuitable for arresting the reaction for quantitative TLC analysis, because large amount of alkali was liberated equivalent to the amount of unreacted formaldehyde present. This alkali facilitated the dissociation of the methylols present in the reaction mixture. Hence such mixtures could not be kept for the TLC estimation.

The hydroxylamine hydrochloride method was also not suitable for arresting the reaction mixture for the TLC estimation. This is due to the fact that when hydroxylamine hydrochloride was added to the reaction mixture, formaldehyde reacted thus:

$$CH_2O + HONH_2HCl \longrightarrow CH_2 = NOH + HCl + H_2O \qquad (5)$$
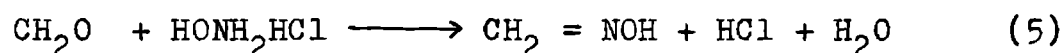
liberating an equivalent quantity of hydrochloric acid. This acid formed favoured the formation of condensation products between free amino groups and methylols present. Further, large amount of hydrochloric acid, if present, accelerated the backward reaction.

However, the above two methods did not affect
the formaldehyde estimation since the acid or alkali formed
was immediately neutralized. But in the TLC estimation of
products unless the conditions and time required were
properly controlled, reproducible results could not be
obtained. Hence for the TLC estimation, the reaction
mixture was arrested as follows:

Sodium bisulphite (saturated) solution was used
instead of sodium sulphite. Sodium bisulphite reacted with
formaldehyde resulting in the quantitative removal of the
latter. No acid or alkali is liberated in the reaction.

$$CH_2O + NaHSO_3 \longrightarrow CH_2OHSO_3Na \qquad (6)$$
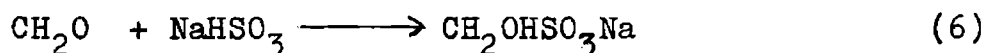
In the case of urea, intermediate compounds
formed (methylols) were found to dissociate even in the
absence of formaldehyde at neutral pH. But at nearly
zero degree centigrade the dissociation was very negligi-
ble and hence the reaction samples were first treated with
sodium bisulphite solution and were kept in a refrigerator
at zero to $5^{\circ}C$. The following was the procedure adopted.

Aliquots were withdrawn from the vessel using a
vacuum sampling device kept in ice to slow down the reaction.
Immediately 3 ml of the reaction mixture thus cooled was

taken in a test tube and the unreacted free formaldehyde
was destroyed by adding 1 ml of saturated sodium bisulphite
solution and kept at zero to $5^{\circ}C$. Estimation of the products
in the reaction mixture was done by the TLC method.

In order to check the above procedure and to
ascertain that no further reaction or dissociation has
taken place by this arresting method, the following experi-
ments were also done.

Dilute aqueous solutions of monomethylolurea
(0.05 M), urea (0.05 M) and formaldehyde (0.05 M)
reaction mixture arrested with sodium bisulphite solution,
were kept in a refrigerator. Analysis of the samples after
one hour and 5 hours by the TLC method showed that no
change in concentrations took place even after 5 hours.

Selection of Suitable Concentrations for Kinetic Studies

Urea:

Reaction of urea with formaldehyde was found to
be highly complicated. When urea is mixed with formalde-
hyde, depending on the molar ratios of the reactants, pH
and temperature different products were formed. With excess
of formaldehyde, large amounts of dimethylolurea and
trimethylolurea were found to be formed under alkaline and

neutral pH eventhough monomethylolurea was the initial product. On the other hand, with excess of urea, formation of methylenediurea predominated along with monomethylolurea even under alkaline conditions. It showed that selection of the ratio of the concentrations of reactants is a major criterion in the kinetic studies of urea-formaldehyde reaction.

When equal concentrations of urea and formaldehyde were used under various conditions, formation of MMU alone was the main reaction at the very initial stages of the reaction. At pH 7 and temperatures $20^{\circ}C$ to $40^{\circ}C$, the reaction was quite controllable. Hence investigation of the formation of MMU from urea and formaldehyde was made by selecting equal concentrations of the latter reactants (0.1 M, 0.25 M and 1 M each). For convenience major part of the reactions was conducted using 0.25 M each as the initial concentrations of urea and formaldehyde.

Reaction rate of urea and formaldehyde was also studied at 0.1 M and 1 M. concentrations. Under these concentrations similar kinetics was observed.

Reaction rates were studied under acidic, alkaline and neutral pH values. pH values in the range 4.5-8.5 were found to be quite suitable for the kinetic

studies of the formation of MMU. But increase of pH complicated the reaction due to the formation of higher methylols and decrease of pH complicated the reaction due to the formation of methylenediurea and its higher homologues.

In the study of the formation of dimethylolurea from monomethylolurea and formaldehyde, increase of formaldehyde concentration favoured trimethylolurea and decrease of formaldehyde favoured dissociation of MMU under alkaline conditions and neutral pH. Hence here also equal concentrations were selected which favoured the maximum formation of dimethylolurea.

In the formation of methylenediurea from monomethylolurea and urea increase of urea concentration did not favour the formation of side products. But when the urea concentration was reduced intercondensation reaction between MMU was predominant over the formation of MeDU. The formation of MeDU was favoured only in the acid pH range. But higher acid pH and also alkaline pH favoured the dissociation of methylols. Hence formation of MeDU was studied in the pH range 3.5-5 taking equal concentrations of MMU and urea.

Iodimetric estimation of sum of free formaldehyde and methylols and TLC estimations proved that methylene

linkages could be formed not only from monomethylolurea and urea, but also from the reaction between MMU and MMU, DMU and MMU and DMU and urea. Hence these reactions were also studied by taking equal concentrations in the pH range 4-5. Beyond this pH range dissociation of methylols was favoured.

Substituted Ureas:

In the reaction of phenyl- and methyl-ureas with formaldehyde also equimolar (0.25 M) concentrations were found to be suitable. Above pH 9 and 60°C formation of N,N dimethylols complicated the reaction. In strongly acidic pH, the products got precipitated. Since phenylurea is insoluble in water its reactions were conducted in dioxane-water mixture (1:2 V/V).

Acetamide and Benzamide:

Reactions of the amides with formaldehyde could not be carried out at alkaline pH because of hydrolysis. Under acid pH, methylols were the initial product formed. To prevent methylene bridge formation equal concentration of formaldehyde or excess of it was necessary. Rates of acetamide reaction are very slow, hence high temperatures

never complicated the reaction. Due to low solubility
of benzamide in water, dioxane-water mixture (1:10 V/V)
was selected as the medium. Methylols of benzamide and
methylenebisbenzamide do not dissociate to any appreciable
extent under the conditions studied.

CHAPTER V

REACTIONS OF UREA AND FORMALDEHYDE

a) Formation of MMU from Urea and Formaldehyde

Monomethylolurea is formed in the reversible
reaction:

$$H_2NCONH_2 + CH_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NH_2CONHCH_2OH \qquad (7)$$
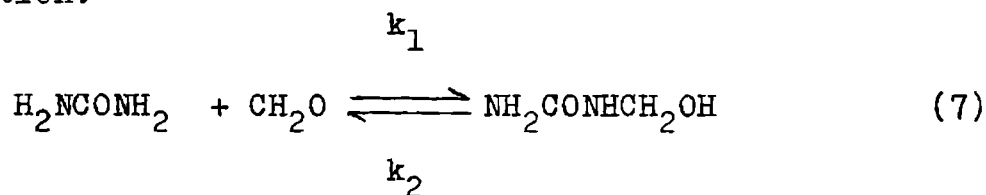
Rate of formation of MMU from urea and formaldehyde
was studied in neutral, acid and alkaline aqueous
solution. The product, MMU, formed in the reaction was
analysed by TLC according to the method described in
chapter III.

Rate of the Reaction

The reaction between 0.25$\underline{M}$ urea and 0.25$\underline{M}$
formaldehyde was carried out at $30^{o}C$ and pH 7 as described
in chapter II. Samples of the reaction mixture were
withdrawn at regular intervals of time, the unreacted
formaldehyde in the samples was determined titrimetri-
cally and the product, MMU, was estimated by the

quantitative TLC method described. The analytical data are given in Table 2. The forward reaction was found to follow second order kinetics in the early stages. The second order rate constants (k_1) listed in the last column have been calculated from the disappearance of formaldehyde.

Reaction conditions were so adjusted that no methylenediurea or dimethylolurea were formed in the initial stages. Monomethylolurea was the only product present in the TLC plate during early stages. The amount of formaldehyde reaction (determined by the sulphite method) agreed well with the amount of MMU formed (estimated by the quantitative TLC method). These two results were also checked by iodimetric method, which gave the total concentrations of methylols and free formaldehyde. The above results showed that no methylene-ureas were formed in the initial stages. Only after about 30 minutes (pH 7 and $30^{\circ}C$) minute amounts of DMU was found to be present.

Effect of Temperature on Reaction Rate

In order to evaluate the activation energy the reaction was studied also at 40, 50 and $60^{\circ}C$ using $0.25\underline{M}$ urea and $0.25\underline{M}$ formaldehyde at pH 7. The analytical

Table 2

Analytical Data on Urea-Formaldehyde Reaction
Urea: 0.25M, CH_2O: 0.25M, pH: 7, Temperature: $30^{\circ}C$

Time (min.)	CH_2O m/lx10^2	Decrease in CH_2O m/lx10^2	MMU m/lx10^2	k_1(second order) x10^4 lit.mol^{-1}sec^{-1}
0	25.00			
10	24.58	0.42	0.40	1.139
20	24.18	0.82	0.80	1.130
30	23.78	1.22	1.20	1.140
40	23.41	1.59	1.50	1.132
50	23.04	1.96	1.89	1.134
60	22.72	2.28	2.04	1.115
70	22.37	2.63	2.41	1.119
80	22.02	2.98	2.56	1.128
			Av:	1.130

data are presented in Tables 3-5. The activation energy
was found to be 10.5 k.cals/mole determined graphically
(Fig.1) by plotting the logarithm of the rate constants
against 1/T. Activation energies were also calculated
at different pH values, by conducting the reaction at
different temperatures. Activation energies obtained
at pH values 3, 3.5, 4.7, 9.4 and 10.5 in the temperature
range 20-60 C are listed in Tables 6-20. It was seen
that the activation energy increased with increase of acid
strength and alkali strength. The values at pH 3.5 and
10.5 were 13 and 18.3 respectively. This showed that
the reaction in alkaline medium has a higher energy of
activation than that in the acid medium. These values
agree well with the activation energy reported by Shenai
and Manjeshwar in the acid pH and Lanquist in the alkali pH.

It is seen from the tables that the rate of
formation of MMU increases with temperature. At pH 7
a three-fold increase in k_1 occurred by increasing the
temperature from 40 to 60°C. At pH 4.7 also the increase
was almost the same. But when the pH was reduced to 3,
the rate increased by more than 4 times for 20° rise of
temperature. Further when the pH was increased to 10.5,
nearly an eight-fold increase in the rate was observed
for the reaction due to the increase of temperature from
20 to 40°C. The reaction was quite controllable at

Table 3

Effect of Temperature on Urea-Formaldehyde Reaction

Urea: $0.25\underline{M}$, CH_2O: $0.25\underline{M}$, pH: 7, Temperature: $40^{\circ}C$

Time (min.)	CH_2O $m/1 \times 10^2$	Decrease in CH_2O $m/1 \times 10^2$	MMU $m/1 \times 10^2$	k_1(second order) $\times 10^4$ lit $mol^{-1} sec^{-1}$
0	25.00			
10	24.30	0.70	0.67	1.924
20	23.63	1.37	1.50	1.933
30	22.99	2.01	1.82	1.942
40	22.40	2.60	2.30	1.935
50	21.82	3.18	2.89	1.943
60	21.30	3.70	3.40	1.930
			Av:	1.935

Table 4

Effect of Temperature on Urea-Formaldehyde Reaction

Urea: $0.25\underline{M}$, CH_2O: $0.25\underline{M}$, pH: 7, Temperature: $50^{\circ}C$

Time (min.)	CH_2O $m/1 \times 10^2$	Decrease in CH_2O $m/1 \times 10^2$	MMU $m/1 \times 10^2$	k_1(second order) $\times 10^4$ lit $mol^{-1} sec^{-1}$
0	25.00			
10	23.85	1.15	1.05	3.215
20	22.80	2.20	2.15	3.216
30	21.80	3.20	2.95	3.181
40	20.91	4.09	3.80	3.250
50	20.18	4.82	4.59	3.185
60	19.45	5.55	5.02	3.170
			Av:	3.203

Table 5

Effect of Temperature on Urea-Formaldehyde Reaction

Urea: $0.25\underline{M}$, CH_2O: $0.25\underline{M}$, pH: 7, Temperature: $60^{o}C$

Time (min.)	CH_2O $m/1 \times 10^2$	Decrease in CH_2O $m/1 \times 10^2$	MMU $m/1 \times 10^2$	k_1(second order) $\times 10^4$ lit $mol^{-1}sec^{-1}$
0	25.00			
10	23.11	1.89	1.80	5.483
20	21.35	3.65	3.50	5.698
30	20.25	4.75	4.12	5.213
40	19.02	5.98	5.30	5.240
50	18.01	6.99	6.10	5.185
			Av:	5.362

Table 6

Effect of pH on Urea-Formaldehyde Reaction

Urea: $0.25\underline{M}$, CH_2O: $0.25\underline{M}$, pH: 4.7, Temperature: $40^{o}C$

Time (min.)	CH_2O $m/1 \times 10^2$	Decrease in CH_2O $m/1 \times 10^2$	MMU $m/1 \times 10^2$	k_1(second order) $\times 10^4$ lit $mol^{-1}sec^{-1}$
0	25.00			
10	24.20	0.80	0.80	2.204
20	23.45	1.55	1.50	2.203
30	22.67	2.33	2.30	2.278
40	22.10	2.90	2.55	2.170
50	21.70	3.30	2.70	2.100
			Av:	2.214

Table 7

Effect of pH on Urea-Formaldehyde Reaction
Urea: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 4.7, Temperature: 50°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMU m/1x10^2	k_1(second order) x10^{4}lit mol^{-1}sec^{-1}
0	25.00			
5	24.30	0.70	0.65	3.84
10	23.65	1.35	1.40	3.81
20	22.41	2.59	2.45	3.87
30	21.40	3.60	3.30	3.74
40	20.48	4.52	3.80	3.71
			Av:	3.79

Table 8

Effect of pH on Urea-Formaldehyde Reaction
Urea: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 4.7, Temperature: 60°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMU m/1x10^2	k_1(second order) x10^{4}lit mol^{-1}sec^{-1}
0	25.00			
5	23.80	1.20	1.20	6.722
10	22.68	2.32	2.20	6.819
15	21.72	3.28	3.10	6.711
20	20.80	4.20	3.57	6.730
25	20.05	4.95	4.25	6.583
			Av:	6.708

Table 9

Effect of pH on Urea-Formaldehyde Reaction
Urea: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 3.5, Temperature: 40°C

Time (min.)	CH_2O m/lx10^2	Decrease in CH_2O m/lx10^2	MMU m/lx10^2	k_1(second order) x10^4 lit mol^{-1}sec^{-1}
0	25.00			
5	24.20	0.80	0.75	4.408
10	23.41	1.59	1.52	4.528
20	21.99	3.01	2.85	4.562
30	20.83	4.17	3.99	4.448
40	19.77	5.23	4.90	4.409
			Av:	4.671

Table 10

Effect of pH on Urea-Formaldehyde Reaction
Urea: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 3.5, Temperature: 50°C

Time (min.)	CH_2O m/lx10^2	Decrease in CH_2O m/lx10^2	MMU m/lx10^2	k_1(second order) x10^4 lit mol^{-1}sec^{-1}
0	25.00			
5	23.54	1.46	1.42	8.27
10	22.25	2.75	2.62	8.24
15	21.07	3.93	3.73	8.29
20	20.05	4.95	4.72	8.23
25	19.10	5.90	4.98	8.24
			Av:	8.253

Table 11

Effect of pH on Urea-Formaldehyde Reaction

Urea: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 3.5, Temperature: 60°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMU m/1x10^2	k_1(second order) x10^{4}lit mol^{-1}sec^{-1}
0	25.00			
5	22.30	2.70	2.68	16.143
10	20.12	4.88	4.78	16.170
15	18.41	6.59	6.20	15.909
20	16.95	8.05	6.70	15.830
25	15.72	9.28	7.80	15.720
			Av:	15.954

Table 12

Effect of pH on Urea-Formaldehyde Reaction

Urea: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 3, Temperature: 40°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMU m/1x10^2	k_1(second order) x10^{4}lit mol^{-1}sec^{-1}
0	25.00			
10	22.00	3.00	2.97	9.091
20	19.59	5.41	5.35	9.205
30	17.88	7.12	6.92	8.849
40	16.34	8.66	8.41	8.833
50	15.16	9.84	8.90	8.650
			Av:	8.926

Table 13

Effect of pH on Urea-Formaldehyde Reaction

Urea: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 3, Temperature: 50°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMU m/1x10^2	k_1(second order) x10^{4}lit mol^{-1}sec^{-1}
0	25.00			
5	21.24	3.76	3.7	23.603
10	18.76	6.24	6.08	22.175
15	16.50	8.50	8.25	22.896
20	15.05	9.95	9.47	22.037
25	14.18	10.82	10.32	20.035
			Av:	22.149

Table 14

Effect of pH on Urea-Formaldehyde Reaction

Urea: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 3, Temperature: 60°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMU m/1x10^2	k_1(second order) x10^{4}lit mol^{-1}sec^{-1}
0	25.00			
5	19.06	5.94	5.86	41.553
10	15.40	9.60	8.90	41.558
15	13.04	11.96	10.89	40.763
20	11.36	13.64	11.84	40.023
25	10.06	14.94	12.47	39.602
			Av:	40.640

Table 15

Effect of pH on Urea-Formaldehyde Reaction

Urea: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 9.4, Temperature: 30°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMU m/1x10^2	k_1(second order) x10^4 lit mol^{-1}sec^{-1}
0	25.00			
5	24.55	0.45	0.45	2.448
15	23.75	1.25	1.23	2.339
30	22.66	2.34	2.30	2.294
45	21.62	3.38	3.05	2.316
60	20.58	4.42	4.00	2.386
			Av:	2.356

Table 16

Effect of pH on Urea-Formaldehyde Reaction

Urea: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 9.4, Temperature: 40°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMU m/1x10^2	k_1(second order) x10^4 lit mol^{-1}sec^{-1}
0	25.00			
10	22.72	2.08	2.00	6.69
20	20.80	4.20	4.00	6.73
30	19.25	5.75	5.50	6.64
40	17.95	7.05	6.89	6.546
50	16.80	8.92	8.15	6.510
60	15.72	9.28	8.25	6.559
			Av:	6.612

Table 17

Effect of pH on Urea-Formaldehyde Reaction

Urea: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 9.4, Temperature: 50°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMU m/1x10^2	k_1(second order) x10^{4}lit mol^{-1}sec^{-1}
0	25.00			
5	22.55	2.45	2.40	14.48
10	20.58	4.15	4.10	14.60
15	18.85	6.15	6.00	14.50
20	17.35	7.65	7.45	14.69
25	16.08	8.22	8.25	14.79
			Av:	14.61

Table 18

Effect of pH on Urea-Formaldehyde Reaction

Urea: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH:10.5, Temperature: 20°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMU m/1x10^2	k_1(second order) x10^{4}lit mol^{-1}sec^{-1}
0	25.00			
5	23.76	1.24	1.25	6.96
10	22.68	2.32	2.20	6.81
15	21.38	3.62	3.5	7.52
20	20.59	4.41	4.09	7.14
25	19.52	5.48	4.79	7.48
			Av:	7.18

Table 19

Effect of pH on Urea-Formaldehyde Reaction

Urea: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 10.5, Temperature: 30°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMU m/1x10^2	k_1(second order) x10^{4}lit mol^{-1}sec^{-1}
0	25.00			
5	21.84	3.16	3.2	19.57
10	19.42	5.58	5.4	19.16
15	17.28	7.72	7.26	19.85
20	15.71	9.30	8.50	19.71
30	13.42	11.58	9.81	19.17
40	11.42	13.58	11.00	19.82
			Av:	19.546

Table 20

Effect of pH on Urea-Formaldehyde Reaction

Urea: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 10.5, Temperature: 40°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMU m/1x10^2	k_1(second order) x10^{4}lit mol^{-1}sec^{-1}
0	25.00			
5	17.80	7.2	6.80	53.93
10	14.48	10.52	9.70	48.43
15	11.02	13.98	10.00	56.38
20	9.08	15.92	13.20	58.44
25	8.01	16.98	14.70	56.66
			Av:	54.77

Fig.1 ACTIVATION ENERGY FOR THE REACTION OF UREA AND FORMALDEHYDE AT DIFFT. PH VALUES

A PH: 7.0
B PH: 4.7
C PH: 3.5
D PH: 9.4
E PH: 3.0
F PH: 10.5
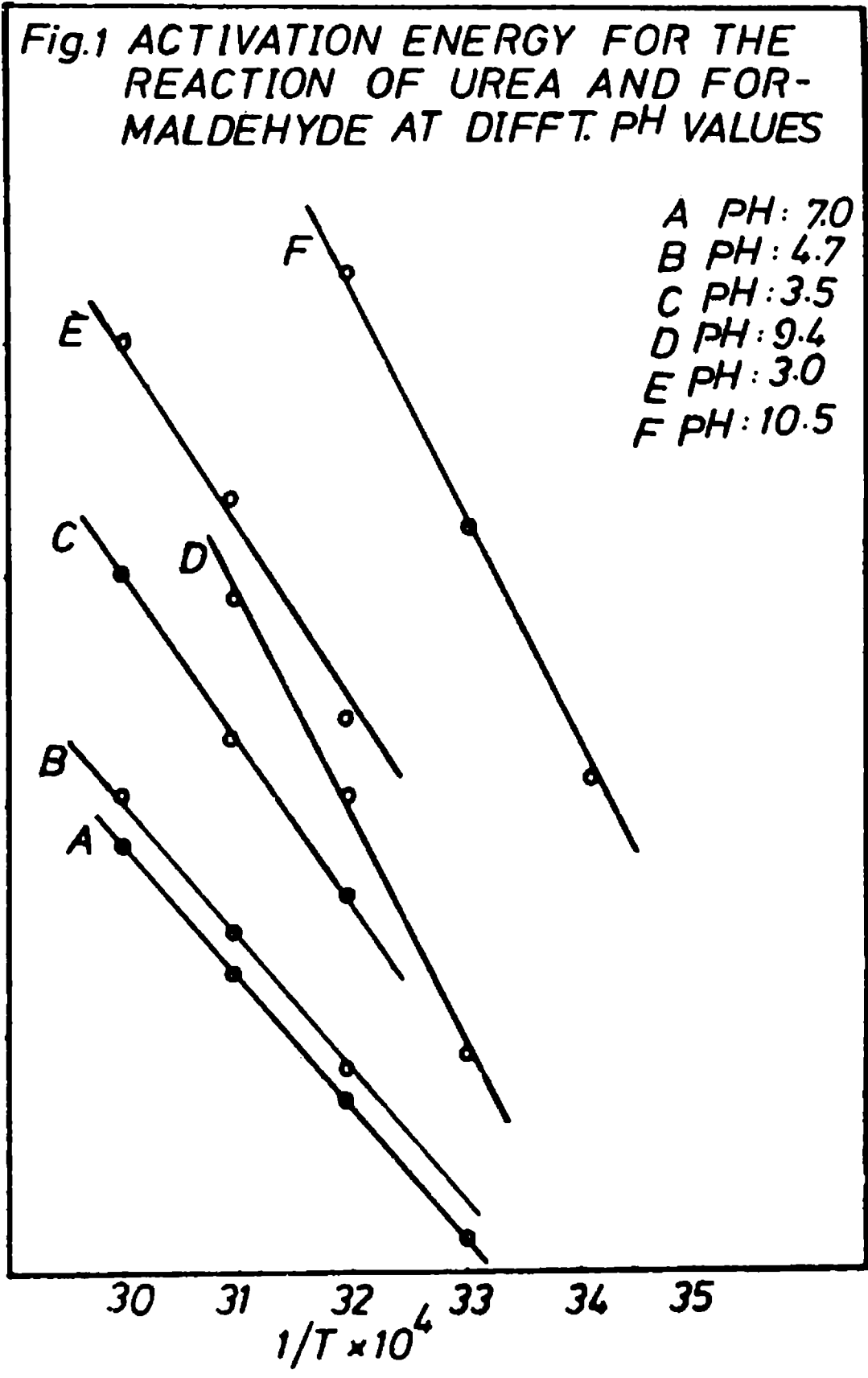
neutral pH, upto 60°C. But at higher acid and alkali
concentrations (beyond pH 3 and 10.5) deviation from second
order kinetics was observed even at 50°C from the very
beginning of the reaction.

The formation of MMU was doubled by an increase
of 10°C and its concentration reached a maximum earlier
at a high temperature and then decreased due to condensation.
Typical values collected at pH 4.7 for the temperatures
40, 50 and 60°C are plotted (Fig.2). The deviation from
second order kinetics of the reaction at higher tempera-
tures is due to the fact that methylenediurea and dimethylol-
urea are formed as side products at an earlier stage of the
reaction in acid and alkali solutions respectively.

Effect of Concentration of the Reactants

Formation of MMU from urea and formaldehyde was
also studied at different concentrations by taking 0.1$\underline{M}$,
0.25$\underline{M}$ and 1$\underline{M}$ each of urea and formaldehyde at pH 9.8 and
40°C. The results are tabulated in Tables 21-23.

Effect of pH on the Reaction

Monomethylolurea formation was studied in the
pH range 10.5 to 3 and temperatures 30 to 60°C. At all
temperatures the rate constants pass through a minimum

Fig.2   FORMATION OF MONOMETHYLOL UREA AT DIFFERENT TEMPARATURE, Urea 0.25M, F 0.25M, PH 4.7 A 40°C, B 50°C, C·60°C
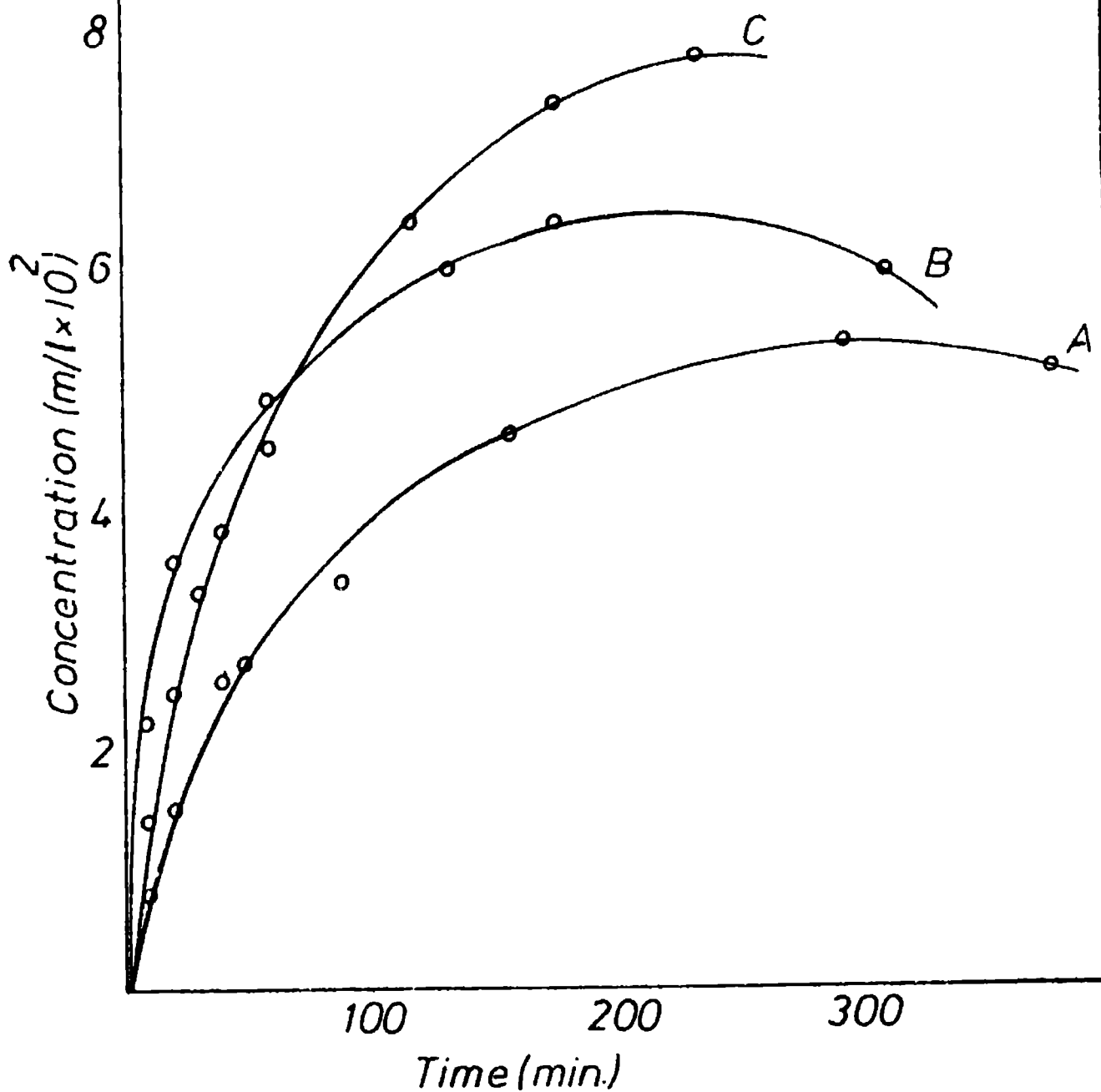
Table 21

Effect of Concentration on Urea-Formaldehyde Reaction
Urea: $0.1\underline{M}$, CH_2O: $0.1\underline{M}$, pH: 9.8, Temperature: $40^{o}C$

Time (min.)	CH_2O $m/1 \times 10^2$	Decrease in CH_2O $m/1 \times 10^2$	MMU $m/1 \times 10^2$	k_1(second order) $\times 10^4$ lit $mol^{-1} sec^{-1}$
0	10.00			
10	9.52	0.48	0.500	8.40
20	9.09	0.91	0.890	8.34
30	8.70	1.30	1.270	8.30
40	8.34	1.66	1.550	8.29
50	7.98	2.02	1.880	8.44
			Av:	8.35

Table 22

Effect of Concentration on Urea-Formaldehyde Reaction
Urea: $0.25\underline{M}$, CH_2O: $0.25\underline{M}$, pH: 9.8, Temperature: $40^{o}C$

Time (min.)	CH_2O $m/1 \times 10^2$	Decrease in CH_2O $m/1 \times 10^2$	MMU $m/1 \times 10^2$	k_1 (Second order) $\times 10^4$ lit $mol^{-1} sec^{-1}$
0	25.00			
10	22.12	2.88	2.85	8.68
20	19.94	5.06	5.10	8.46
30	18.03	6.97	6.85	8.59
40	16.43	8.52	8.37	8.62
50	15.45	9.55	9.20	8.24
60	14.37	10.63	9.69	8.22
			Av:	8.47

Table 23

Effect of Concentration on Urea-Formaldehyde Reaction

Urea: $1\underline{M}$, CH_2O: $1\underline{M}$, pH: 9.8, Temperature: $40^{\circ}C$

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMU m/1x10^2	k_1(second order) x10^{4}lit mol^{-1}sec^{-1}
0	100.00			
5	79.55	20.55	20.40	8.569
10	65.80	34.20	34.00	8.662
20	49.50	50.50	51.00	8.519
30	39.10	60.50	58.90	8.653
40	32.34	67.66	65.20	8.720
50	28.00	72.00	70.10	8.570
60	24.41	75.59	72.00	8.601
			Av:	8.613

in the pH range 4.5 to 8.5 (Fig.3). Below 4.5 and above
8.5 pH the rate constants increase rapidly proving thereby
catalysis by H_3O^+ and OH^-. At pH 7 and low temperatures
(30 and 40°C) rate of formation of MMU from urea and formal-
dehyde was quite controllable. It was found that upto 60
minutes no side products were formed to affect the rate of
formation of MMU at pH 7 and 30°C. When the pH was changed
to 3, nearly a five-fold increase in rate was observed. But,
for an increase of pH from 7 to 10.5, the rate increased
25 times. This showed that catalysis by OH^- ions favoured
the MMU formation more than that by H_3O^+ ions.

Eventhough MMU was the only initial product formed
at the very early stages of the reaction, with the increase
of acid concentrations condensation was favoured at an
earlier stage. Thus formation of methylenediurea by the
reaction of MMU with free urea, was observed at pH 3.5 and 3
and high temperatures. Hence the rate constant decreased
slightly with time, at acid pH and high temperatures due to
the additional consumption of urea as MeDU. At pH 3 and
temperature 60°C precipitate started separating from the
reaction mixture at 50 minutes due to the formation of
higher methyleneureas.

Fig. 3   REACTION OF UREA AND FORMALDEHYDE AT DIFFERENT PH VALUES. Urea: 0.25M, F: 0.25M. A: 30°C, B: 40°C, C: 50°C, D: 60°C.
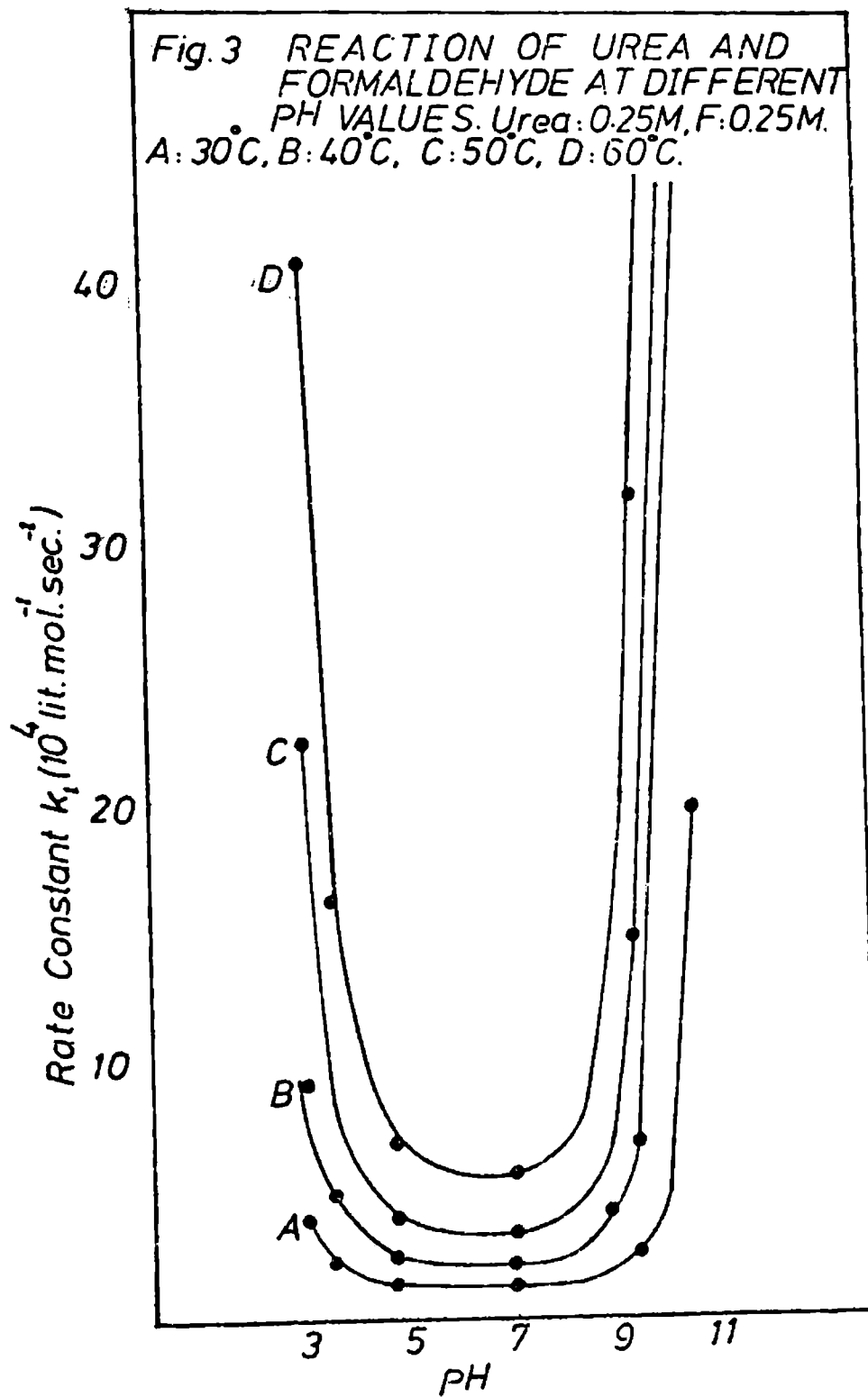
At pH 10.5 methyleneureas were not formed during
initial stages of the reaction. But formation of dimethylol-
urea started at an earlier stage when the reaction was done
at 50°C. Hence at this pH the reaction was conducted at
20-40°C. Since formaldehyde was consumed more due to the
formation of small amounts of DMU, the rate increased slightly
with time at higher temperatures for pH 10.5. At later
stages of the reaction minute amounts of trimethylolurea,
methylenediurea and other two higher homologues were detected.

The energy of activation E and the entropy of
activation $\Delta S^{\neq}$ for the reaction at pH values 3-10.5 were
calculated and are given in Table 24.

b) Dissociation of MMU

The dissociation of MMU was studied at 0.25M in
pH ranges 3.5 to 10.5 and temperatures 30 to 50°C. The
reaction was followed by determining the amount of free
formaldehyde formed by decomposition of MMU, using sulphite
method. Iodimetric method was also used to check that no
methylene linkage was produced during the initial stages
of the reaction. The reaction was found to follow first
order kinetics.

7

Table 24

Activation Energy and Entropy of Activation
for the Urea-Formaldehyde Reaction

pH	E Cals/mol	$\Delta S^{\neq}$ at 25°C
3.0	17160	-18.96
3.5	13070	-33.47
4.7	11440	-40.29
7.0	10500	-43.96
9.4	16700	-22.06
10.5	18300	-12.4

In order to find the effect of temperature, the reaction was studied at 40, 50 and 60°C at the same concentrations of the reactants at pH 7. The data are presented in Tables 25,26 and 27. The activation energy is found to be 12 k cals/mole (Fig.4). The rate of decomposition was found to increase three-fold for 20°C rise of temperature.

Dissociation was also studied at pH 3.5 and 10.5 and temperature 50°C. Results are given in Tables 28 and 29. At acid pH, eventhough the rate was quite controllable at the initial stages, it became complicated at the later stages due to the formation of methylene linkages by intercondensation between the free $-NH_2$ group of one MMU and $-CH_2OH$ group of another MMU. This may be also possible due to the condensation between monomethylolurea and free urea formed by decomposition. The rate increased 2.5 times for a change of pH from 7 to 3.5. Dissociation of MMU was found to be more favoured in alkaline pH. After 40 minutes the deviation from first-order kinetics was observed. No DMU or MeDU were found to be formed during the reaction in alkaline medium. The rate of dissociation increased 17 times for a change in pH from 7 to 10.5 at 50°C.

Calculation of k_1 and k_2 from Equilibration Data

Alternatively k_1 and k_2 could be calculated from the equilibrium concentrations of reactants and products.

Table 25

Analytical Data on the Dissociation of MMU
MMU: 0.25M, pH: 7, Temperature: 40°C

Time (min.)	CH_2O formed m/l x 10^2	Unreacted MMU m/l x 10^2	Estimated MMU m/lx10^2	k_2(first order) x 10^6 sec^{-1}
0		25.00		
60	0.48	24.52	24.30	5.11
120	0.88	24.12	24.00	4.89
180	1.35	23.65	23.57	5.13
240	1.75	23.25	23.04	5.03
300	2.20	22.80	22.50	5.10
360	2.71	22.29	22.00	5.24
			Av:	5.08

Table 26

Effect of Temperature on the Dissociation of MMU
MMU: 0.25M, pH: 7, Temperature: 50°C.

Time (min.)	CH_2O formed m/l x 10^2	Unreacted MMU m/l x 10^2	Estimated MMU m/lx10^2	k_2(first order) x 10^6 sec^{-1}
0		25.00		
30	0.37	24.63	24.50	8.20
60	0.76	24.24	24.30	8.51
120	1.45	23.55	23.50	8.22
180	2.17	22.83	22.70	8.42
240	2.82	22.18	22.10	8.28
300	3.55	21.45	22.32	8.49
			Av:	8.35

Table 27

Effect of Temperature on the Dissociation of MMU

MMU: 0.25$\underline{M}$, pH: 7, Temperature: 60°C

Time (min.)	CH_2O formed m/l x 10^2	Unreacted MMU m/lx10^2	Estimated MMU m/lx10^2	k_2(first order) x 10^5sec^{-1}
0		25.00		
30	0.65	24.35	24.30	1.458
60	1.30	23.70	23.60	1.490
120	2.45	22.55	22.50	1.420
180	3.60	21.40	21.30	1.440
240	4.75	20.25	20.05	1.460
300	5.90	19.10	19.00	1.490
			Av:	1.460

Fig.4 ACTIVATION ENERGY FOR THE DISSOCIATION OF MONOMETHY-LOLUREA AT pH 7. MMU 0·25M.
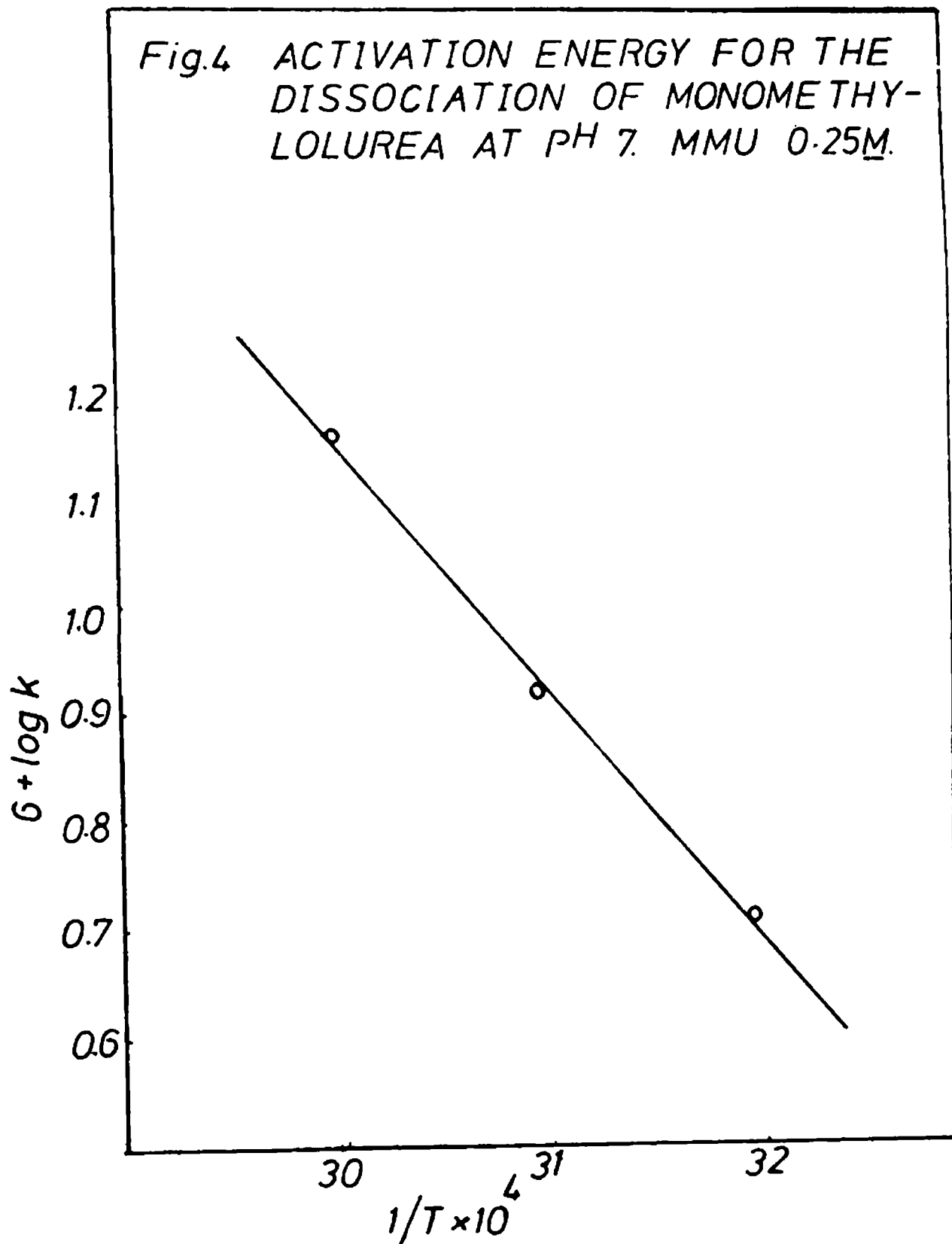
Table 28

Effect of pH on Dissociation of MMU

MMU: 0.25$\underline{M}$, pH: 3.5, Temperature: 50°C

Time (min.)	CH_2O formed m/l x 10^2	Unreacted MMU m/lx10^2	Estimated MMU m/lx10^2	k_2(first order) x 10^5sec^{-1}
0		25.00		
5	0.17	24.83	24.75	2.149
15	0.48	24.52	24.50	2.073
30	0.95	24.05	23.9	2.134
45	1.42	23.58	23.42	2.158
60	1.85	23.15	23.00	2.136
75	2.30	22.70	22.40	2.139
			Av:	2.132

Table 29

Effect of pH on Dissociation of MMU

MMU: 0.25$\underline{M}$, pH: 10.5, Temperature: 50°C

Time (min.)	CH_2O formed m/l x 10^2	Unreacted MMU m/lx10^2	Estimated MMU m/lx10^2	k_2(first order) x 10^4 sec^{-1}
0		25.00		
5	0.998	24.02	24.00	1.343
10	1.990	23.01	22.90	1.392
15	2.950	22.05	21.87	1.389
20	3.700	21.30	21.04	1.337
25	4.500	20.50	20.08	1.319
			Av:	1.357

Thus k   for the formation of monomethylolurea

$$U \; + \; F \; \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \; MMU \qquad (8)$$

$$(a-x) \quad (a-x) \qquad\qquad x$$
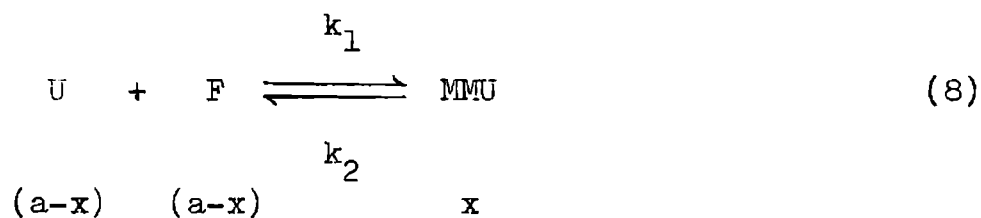
is given by[108]

$$k_1 = \frac{x_e}{t(a^2 - x_e^2)} \; \log_e \frac{x_e(a^2 - xx_e)}{a^2(x_e - x)} \qquad (9)$$

where x and x_e are the amounts of MMU at time t and at
equilibrium.   Similarly k   for the decomposition of MMu
MMU is given

$$MMU \; \underset{k_1}{\overset{k_2}{\rightleftharpoons}} \; U \; + \; F \qquad (10)$$

$$(a-x) \qquad\qquad x \qquad x$$
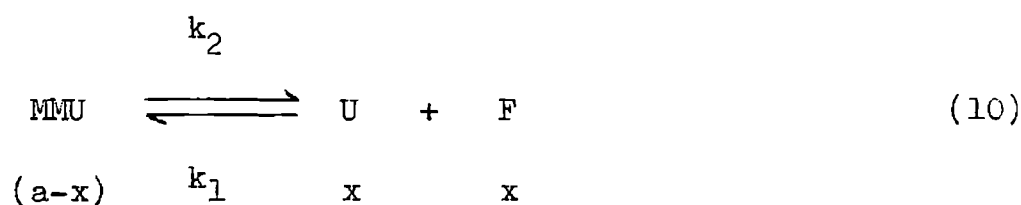
by[108]

$$k_2 = \frac{x_e}{t(2a - x_e)} \; \log_e \frac{ax_e + x(a - x_e)}{a(x_e - x)} \qquad (11)$$

where x and x_e are the amounts of U or F at time t and at
equilibrium. The values of k_1 and k_2 so calculated agreed

well with those obtained by the earlier isolation method
(Table 30). In the pH range studied the equilibrium constant
was found to be independent of pH. The equilibrium in
equation (8) shifts to the left with increasing temperature.
In more acid solution it varied with pH probably due to
condensation reactions.

c) Reaction of Urea and Formaldehyde at High Concentrations

Two typical reactions were carried out at pH 4 and
9 using urea and formaldehyde at 1M each at $30^{\circ}C$. The form-
ation of the products is shown graphically in figures 5 and 6.
The main products formed at pH 4 were MMU and MeDU. This is
in sharp contrast to the reaction at pH 9 where the main
products are MMU and DMU. This shows clearly that methylo-
lation is the preferred reaction in alkaline medium and
methylene bridge formation is the preferred reaction in
acidic conditions.

At pH 9 monomethylolurea was the initial product.
No dimethylolurea was detected in the TLC analysis upto 30
minutes. But from 40 minutes onwards small amounts of DMU
were found to be formed. By 100 minutes DMU became prominant.
MMU and DMU were estimated by the quantitative TLC method and
unreacted formaldehyde was determined by sulphite method.

Table 30

Analytical Data on Urea-Formaldehyde Reaction

Temp. (°C)	pH	k_1 $\times 10^4$ lit mol^{-1}sec^{-1}	k_2 $\times 10^6$ sec^{-1}	K_1 (calculated) $\times 10^2$ lit mol^{-1}	K_1 (experimental) $\times 10^2$ lit mol^{-1}
30	7	1.13	2.78	2.46	2.40
50	7	3.2	8.35	2.61	2.60
50	3.5	8.25	21.32	2.58	2.604
50	9.4	14.6	37.96	2.60	2.6
60	7	5.36	14.6	2.72	2.8

Fig.5 FORMATION OF MONOMETHYLOL UREA AND METHYLENEDIUREA
Urea : 1M, Formaldehyde : 1M, PH : 4, Temp. : 30 C

● MMU
○ MDU

Fig.6 FORMATION OF MONOMETHYLOL UREA AND DIMETHYLOL UREA.
Urea 1M, Formaldehyde : 1M, PH : 9, Temp. : 30°C
○ MMU
● DMU
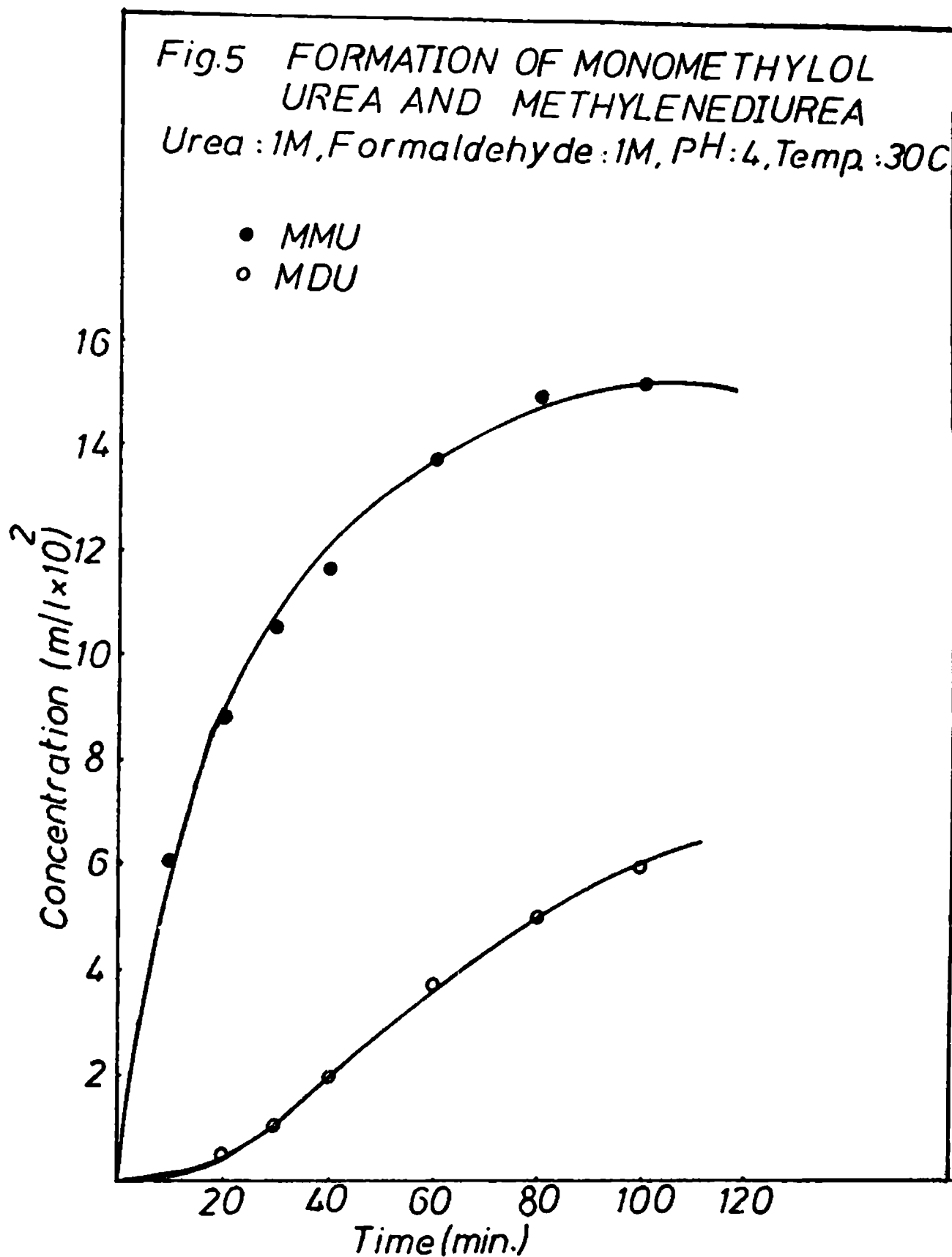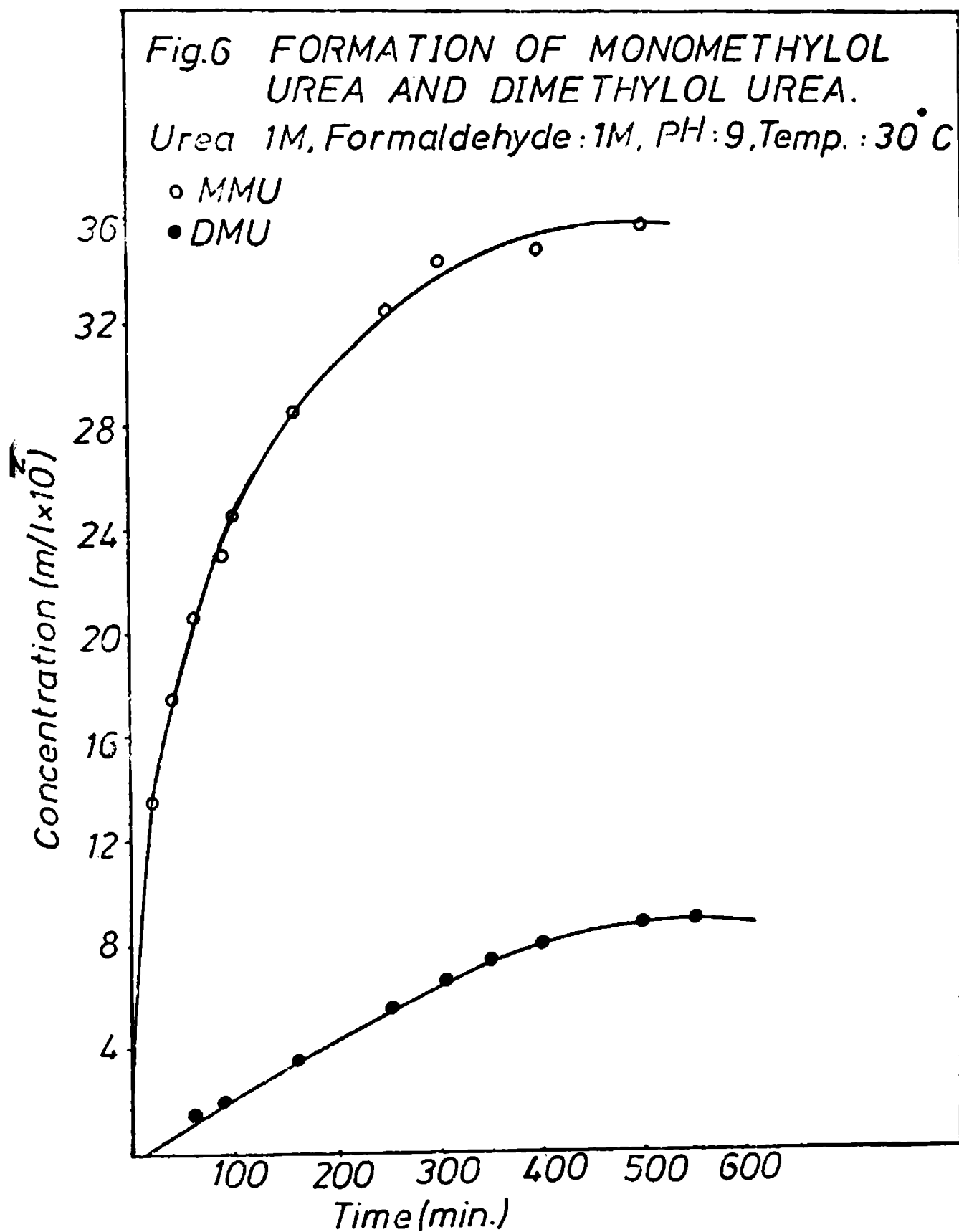
At 100 minutes the reaction mixture contained MMU (0.2453$\underline{M}$), DMU (0.025$\underline{M}$) and unreacted formaldehyde (0.6847$\underline{M}$). The other major product was trimethylolurea.

At pH 4 also MMU was the first product formed in the reaction. But within 30 minutes MeDU was seen to be formed. No DMU was formed during the reaction. The concentration of MMU reached a maximum in 90 minutes and then slowly decreased. During this time MeDU concentration was constantly increasing. At 90 minutes small amounts of DMeTU was also found and the reaction mixture got emulsified at 110 minutes. This is probably due to the formation of higher methyleneurea homologues by condensation reaction. These compounds were detected only after 80 minutes of reaction.

REACTION OF MONOMETHYLOLUREA WITH FORMALDEHYDE

a) Formation of Dimethylolurea from Monomethylolurea
   and Formaldehyde

The reaction of MMU and formaldehyde can be
represented as follows:

$$MMU \;+\; F \;\xrightleftharpoons[k_4]{k_3}\; DMU \qquad\qquad (12)$$

$$\big\uparrow k_1 \;\big\downarrow k_2$$

$$U \;+\; F$$
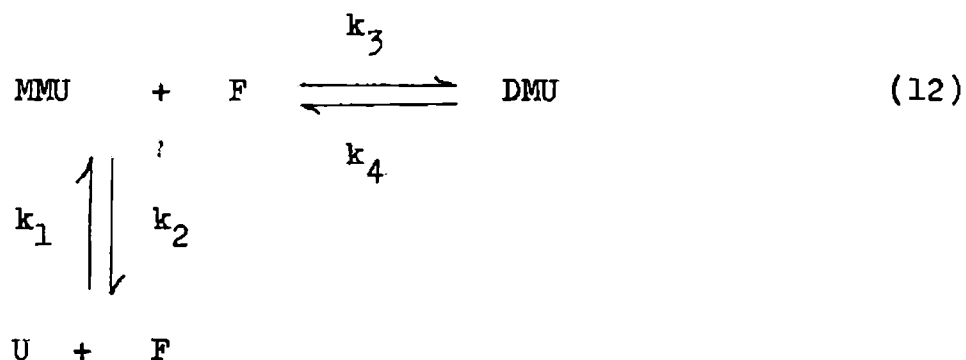
Formaldehyde reacts with MMU giving DMU. Simultaneously
MMU may dissociate giving urea and formaldehyde. Hence
the initial rate of disappearance of MMU can be represented
as

$$-\;\frac{d[MMU]}{dt} \;=\; k_3[MMU][F] \;-\; k_2[MMU] \qquad\qquad (13)$$

Here $k_4[DMU]$ and $k_1[U][F]$ have been neglected since in the
initial stages of the reaction DMU and U concentrations are
very small. In the presence of excess of formaldehyde the

88

dissociation of MMU may be neglected. Hence second order kinetics may be expected in the early stages of the reaction.

Formation of DMU was studied using 0.25$\underline{M}$ MMU and 0.25$\underline{M}$ formaldehyde at pH 7 and 40°C. The results are listed in Table 31. Free formaldehyde was determined by the sulphite method and sum of the free formaldehyde and methylols were determined by the iodimetric method. The latter method showed that no methylene linkages were formed during the reaction upto 250 minutes. Unreacted MMU and DMU formed by the reaction were estimated using the TLC method (Chapter III). During the initial stages of the reaction, only spots corresponding to MMU and DMU were present.

Effect of Temperature

Reactions of MMU and formaldehyde were also conducted at equimolar concentrations (0.25$\underline{M}$) and neutral pH at temperatures 50 and 60°C. The results are given in Tables 32 and 33. The activation energy was found to be 14.3 k cals/mole (Fig.7). At temperatures studied the amount of MMU disappeared and DMU formed agreed with the concentration of the formaldehyde reacted during the early stages of the reaction. During the later stages of

Table 31

Analytical Data on MMU and Formaldehyde Reaction

MMU: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 7, Temperature: $40^{\circ}C$

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMU m/1x10^2	DMU m/1x10^2	k_3(second order) x10^5 lit mol^{-1}sec^{-1}
0	25.00				
30	24.80	0.2	24.8	0.2	1.792
60	24.61	0.39	24.55	0.385	1.761
90	24.42	0.58	24.37	0.530	1.759
120	24.24	0.758	24.12	0.70	1.737
150	24.07	0.93	23.87	0.87	1.717
180	23.89	1.11	23.57	0.91	1.722
210	23.72	1.28	23.45	0.99	1.713
240	23.55	1.45	23.15	1.21	1.710
				Av:	1.738

Table 32

Effect of Temperature on MMU and Formaldehyde Reaction

MMU: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH:7, Temperature: $50^{\circ}C$.

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMU m/1x10^2	DMU m/1x10^2	k_3(second order) x10^5 lit mol^{-1}sec^{-1}
0	25.00				
15	24.79	0.21	24.80	0.2	3.764
30	24.60	0.40	24.50	0.35	3.613
60	24.20	0.80	24.10	0.76	3.673
90	23.83	1.17	23.70	1.10	3.632
120	23.45	1.55	23.20	1.47	3.672
150	23.12	1.88	22.90	1.70	3.613
180	22.82	2.18	22.40	2.06	3.538
				Av:	3.628

Table 33

Effect of Temperature on MMU and Formaldehyde Reaction
MMU: 0.25$\underline{M}$, CH$_2$O: 0.25$\underline{M}$, pH: 7, Temperature: 60°C

Time (min.)	CH$_2$O m/1x10^2	Decrease in CH$_2$O m/1x10^2	MMU m/1x10^2	DMU m/1x10^2	k$_3$(second order) x10^{5}lit mol^{-1}sec^{-1}
0	25.00				
15	24.62	0.38	24.6	0.36	6.859
30	24.25	0.75	24.11	0.73	6.87
45	23.90	1.10	23.80	1.00	6.818
60	23.57	1.43	23.20	1.24	6.741
90	22.90	2.10	22.50	2.00	6.700
				Av:	6.798

Fig.7 ACTIVATION ENERGY FOR THE REACT-
ION OF MONOMETHYLOLUREA AND
FORMALDEHYDE AT PH:7.

Monomethylolurea : 0.25$\underline{M}$.
Formaldehyde : 0.25$\underline{M}$.
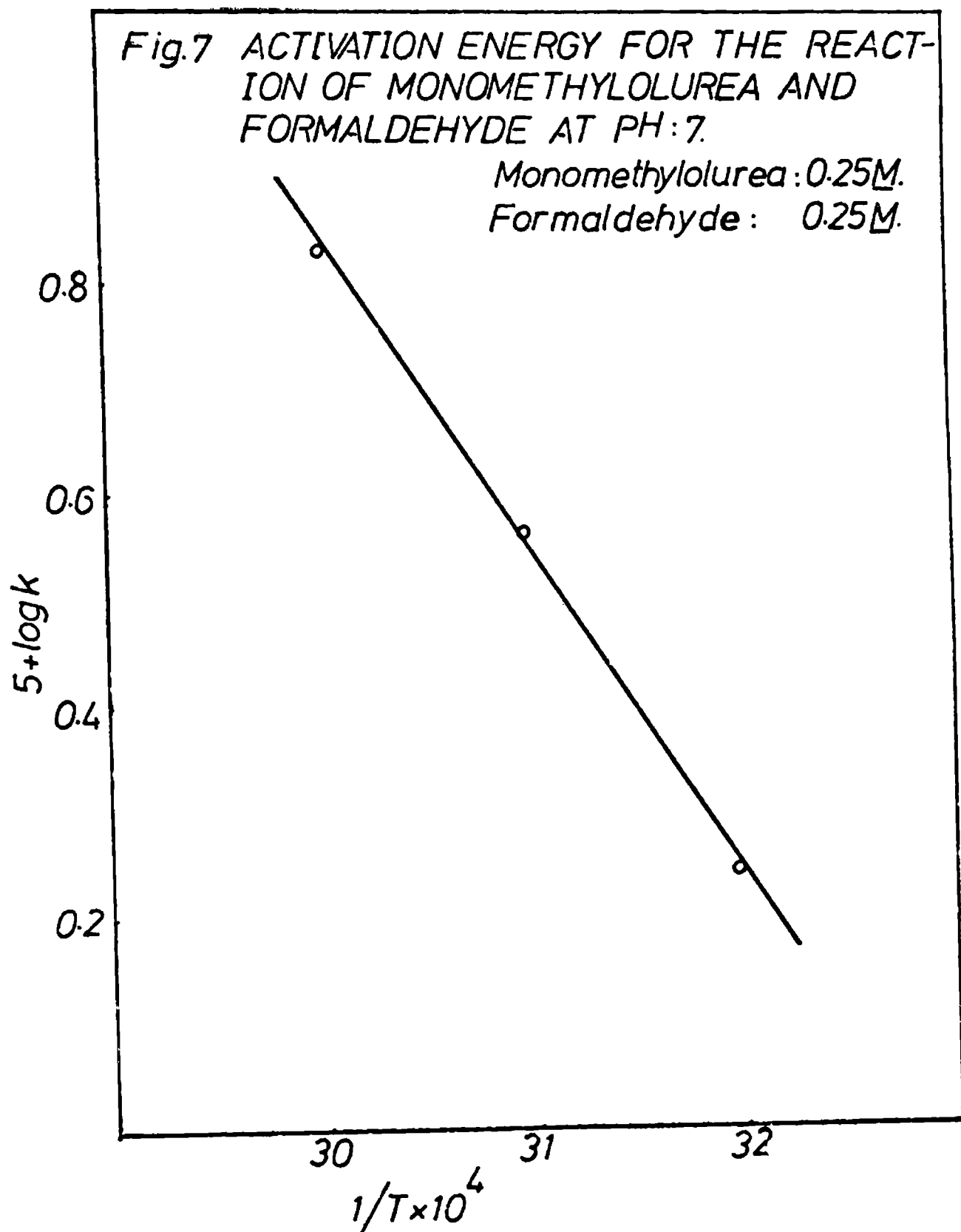
the reaction, TLC and iodimetric determination showed the
formation of methylene linkages to a small extent especially
in reactions at 60°C. This may be due to the intercondensa-
tion of MMU or condensation between MMU and free urea formed
by dissociation of MMU. Since the concentration of DMU
formed during the course of the reaction was more in agree-
ment with formaldehyde consumed than MMU reacted, it may be
assumed that the rate of condensation between DMU and MMU
was very small. At 40 and 50°C, the equilibrium was reached
at 400 and 250 minutes respectively. At later stages many
side products like MeDU, MMMeDU, DMMeDU, DMeTU etc. were
detected in the TLC plate.

Effect of pH on the Reaction

Reactions of MMU with formaldehyde at equimolar
concentrations (0.25M) have been tried in the pH range
3.5 to 10 at 30°C. Results are presented in Tables 34-36.
At neutral and acid solutions formation of DMU was favoured
over dissociation of MMU. But at alkaline pH dissociation
of MMU was comparatively greater, reducing the concentration
of MMU, and the rate-constants started decreasing after 20
minutes. At acid pH condensation occurred as a side reaction.
Here also the decrease in concentration of MMU and DMU formed

Table 34

Effect of pH on MMU and Formaldehyde Reaction

MMU: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 3.5, Temperature: 30°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMU m/1x10^2	DMU 1m/1x10^2	k_3(second order) x10^{5}lit mol^{-1}sec^{-1}
0	25.00				
10	24.83	0.17	24.8	0.20	4.564
20	24.67	0.33	25.5	0.30	4.458
30	24.50	0.55	24.2	0.51	4.535
40	24.36	0.64	24.1	0.60	4.378
50	24.12	0.82	24.0	0.80	4.521
60	24.05	0.95	23.87	0.91	4.389
70	23.92	1.08	23.69	0.919	4.279
				Av:	4.446

Table 35

Effect of pH on MMU and Formaldehyde Reaction

MMU: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 4.7 ,Temperature: 30°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMU m/1x10^2	DMU m/1x10^2	k_3(second order) x10^{5}lit mol^{-1}sec^{-1}
0	25.00				
30	24.64	0.36	24.8	0.40	3.155
60	24.34	0.66	24.2	0.65	3.012
90	24.02	0.98	23.9	0.89	3.022
120	23.68	1.32	23.5	1.28	3.097
150	23.40	1.60	23.2	1.50	3.038
180	23.09	1.91	22.6	1.86	3.064
210	22.85	2.72	22.38	2.59	2.987
				Av:	3.054

Table 36

Effect of pH on MMU and Formaldehyde Reaction
MMU: 0.25$\underline{M}$, CH$_2$O: 0.25$\underline{M}$, pH: 10, Temperature: 30°C

Time (min.)	CH$_2$O m/1x10^2	Decrease in CH$_2$O m/1x10^2	MMU m/1x10^2	DMU m/1x10^2	k$_3$(second order) x10^{4}lit mol^{-1}sec^{-1}
0	25.00				
5	24.35	0.68	24.4	0.70	3.559
10	23.74	1.36	23.5	1.40	3.538
15	23.20	1.80	22.8	1.70	3.448
20	22.65	2.35	22.18	2.10	3.458
25	22.35	2.65	21.50	2.45	3.162
				Av:	3.433

were not in agreement with the formaldehyde consumed after
the very early stages of the reaction. Due to the constant
decrease of methylols as methylenes, the rate of consumption
of formaldehyde was reduced, decreasing the rate. Since
spots corresponding to MeDU, MMMeDU and DMeTU were obtained
only after early stages, it may be assumed that the methylene
linkages were formed by (i) inter-condensation of MMU, and
(ii) condensation of MMU with DMU.

In all the experiments described above equimolar
concentrations of urea and formaldehyde were used. If the
concentration of formaldehyde was increased, trimethylol-
urea was also formed and if the concentration of MMU was
increased, intercondensation and dissociation predominated
over the DMU formation. At pH 7, the rate of formation of
DMU increased 4 times for 20° rise of temperature while the
rate increased 11.3 times for a change of pH from 4.7 to
10 at 30°C (Fig.6).

b) Dissociation of DMU

Dissociation of DMU was studied at 30°C using
0.25M DMU at neutral pH. The results are listed in Table 37.
Rate of dissociation was found to be almost the same as that
of MMU. Since the MMU formed also underwent dissociation to

Table 37

Effect of Temperature on the Dissociation of DMU

DMU: 0.25$\underline{M}$, pH: 7, Temperature   30°C

Time (min.)	CH_2O formed m/1 x 10^2	DMU m/1x10^2	Estimated DMU m/1 x 10^2	Estimated MMU m/1x10^2	k_4(first order) x $10^6 sec^{-1}$
0		25.00			
300	1.25	23.75	23.8	1.30	2.814
600	2.50	22.50	22.45	2.30	2.899
900	3.58	21.42	21.40	3.42	2.861
1200	4.73	20.27	20.00	4.45	2.906
1500	5.87	19.13	19.00	5.47	2.928
1800	7.01	17.99	16.9	6.90	3.04
				Av:	2.858

a small extent, the rate increased slightly with time.
But since the concentration of MMU is very small its disso-
ciation can be neglected. Iodimetric determination and
TLC analysis showed that no methylene linkages were produced
during the reaction. Only spots corresponding to MMU and
DMU were present in the TLC plates.

Dissociation of DMU was also studied at 40 and
$50^{o}C$ keeping the pH and reactant concentration same. Results
are tabulated in Tables 38 and 39. The activation energy
for the reaction was found to be 21.8 k cals/mole (Fig.8).
The rate increased 3 times for 10° rise of temperature. With
increase of temperature, rate of dissociation of MMU also
increased.

The effect of pH on the reaction was studied at
pH 3.5 and 10.5 at $30^{o}C$. Results are listed in Tables 40
and 41. The reaction was catalysed by both acid and base
and first order kinetics was observed. At pH 3.5 methylene
linkages were found to be formed after 30 minutes, thus
reducing the rate. The rate of dissociation of DMU increased
3.7 times for a change of pH from 7 to 3.5 at $30^{o}C$. But
for a change of pH from 7 to 10.5 the rate increased 4.8
times. This shows that the rate does not increase much in
alkaline pH as compared to the dissociation of MMU.

Table 38

Effect of Temperature on the Dissociation of DMU

DMU: 0.25$\underline{M}$, pH: 7, Temperature: 40°C.

Time (min.)	CH$_2$O formed m/l x 10^2	DMU m/1x10^2	Estimated DMU m/1x10^2	Estimated MMU m/1x10^2	k$_4$(first order) x 10^{6}sec^{-1}
0		25.00			
50	0.65	24.35	24.4	0.60	8.90
100	1.32	23.68	23.5	1.28	8.90
200	2.53	22.47	22.4	2.40	8.82
300	3.73	21.27	21.19	3.50	8.90
400	4.75	20.25	20.00	4.50	8.89
500	5.91	19.09	18.60	5.20	8.96
				Av:	8.867

Table 39

Effect of Temperature on the Dissociation of DMU

DMU: 0.25$\underline{M}$, pH: 7, Temperature: 50°C

Time (min.)	CH$_2$O formed m/l x 10^2	DMU m/1x10^2	Estimated DMU m/1x10^2	Estimated MMU m/1x10^2	k$_4$(first order) x 10^5 sec^{-1}
0		25.00			
25	0.93	24.07	24.00	1.00	2.487
50	1.85	23.15	23.00	1.80	2.560
100	3.60	21.40	21.30	3.40	2.58
150	5.04	19.96	19.86	4.85	2.48
200	6.40	18.60	17.90	6.00	2.46
250	7.95	17.05	16.66	6.50	2.52
				Av:	2.515

Fig.8 ACTIVATION ENERGY FOR THE DISSOCIATION OF DIMETHYLOL-UREA AT P^H:7   DMU:0.25$\underline{M}$.
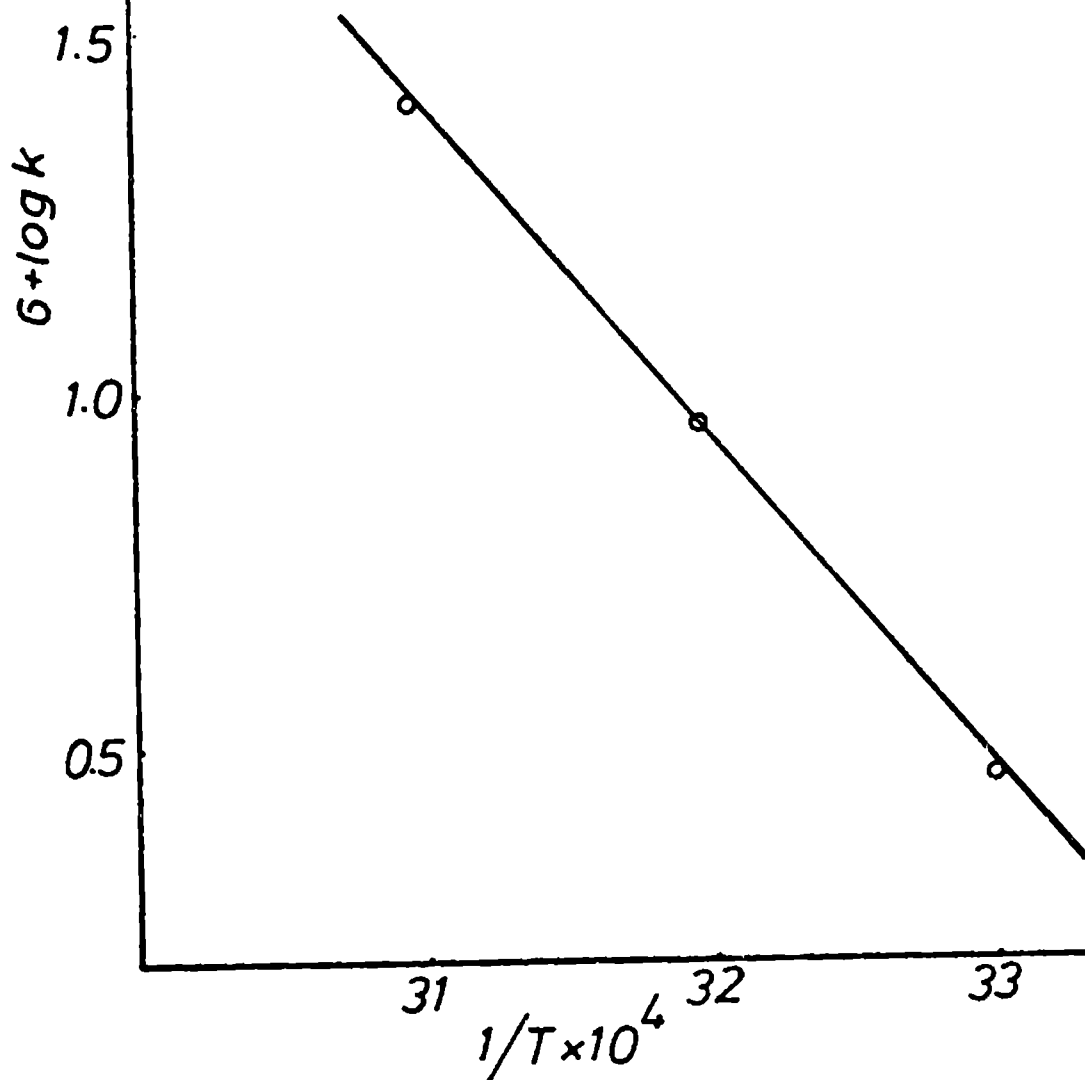
Table 40

Effect of pH on Dissociation of DMU

DMU: 0.25$\underline{M}$, pH: 3.5, Temperature: 30°C

Time (min.)	CH_2O formed m/l x 10^2	DMU m/1x10^2	Estimated DMU m/1x10^2	Estimated MMU m/1x10^2	k_4(first order) x 10^5 sec^{-1}
0		25.00			
15	0.20	24.75	24.80	0.25	1.1
30	0.50	24.50	24.47	0.47	1.1
60	0.98	24.01	23.90	0.84	1.087
90	1.35	23.65	23.30	1.25	1.023
120	1.82	23.18	23.00	1.65	1.043
150	2.25	22.75	22.50	1.98	1.040
				Av:	1.067

Table 41

Effect of pH on Dissociation of DMU

DMU: 0.25$\underline{M}$, pH: 10.5, Temperature: 30°C

Time (min.)	CH_2O formed m/1 x 10^2	DMU m/1x10^2	Estimated DMU m/1x10^2	Estimated MMU m/1 x 10^2	k_4(first order)x 10^4sec^{-1}
0		25.00			
5	1.06	23.94	23.9	1.00	1.435
10	2.06	22.94	22.8	2.00	1.424
15	2.89	22.11	22.0	2.70	1.358
20	3.90	21.10	20.1	3.50	1.38
25	4.54	20.46	19.6	4.0	1.326
				Av:	1.385

The equilibrium constant $K_2 = \dfrac{[DMU]}{[MMU]\,[F]}$

calculated from the equilibrium concentrations of reactants and products as described earlier, agreed with those obtained from the ratio k_4/k_3. Details are given in Table 42.

Table 42

Analytical Data on MMU-F Reaction

Temperature (°C)	pH	k_3 x10⁵lit.mol⁻¹sec⁻¹	k_4 x10⁶sec⁻¹	K_2 (exp)	$K_2 = k_4/k_3$ cal
30	7		2.86		
40	7	1.74	8.87	0.52	0.51
50	7	3.64	25.15	0.71	0.69
30	3.5	4.45	10.67	0.28	0.24
30	4.7	3.05			
30	10.5		138.50		

METHYLENE BRIDGED COMPOUNDS

Methylol derivatives of urea can undergo intermolecular condensation among themselves, or with urea resulting in compounds in which urea fragments are in one way or other interlinked by methylene groups. These compounds may additionally have a certain number of methylol groups distributed over the structure. The possible reactions are:

i) Condensation of MMU with urea,

ii) Condensation of DMU with urea,

iii) Intercondensation of MMU and DMU, and

iv) Self condensation of MMU and DMU.

These reactions were investigated in detail and the results are presented in this chapter.

a) Formation of MeDU from MMU and urea

The reaction between urea and MMU may be represented as follows:

$$H_2NCONH_2 \ + \ HOCH_2NHCONH_2 \ \xrightarrow{\ H+\ }$$

$$H_2NCONHCH_2NHCONH_2 \qquad\qquad (14)$$
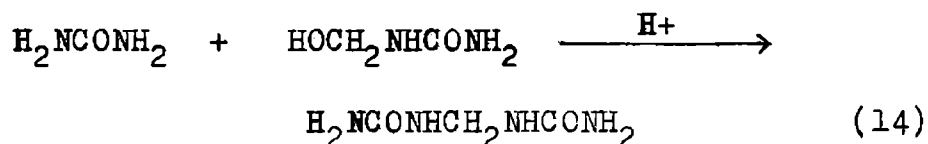
Under equimolar concentration of reactants the reaction was found to exhibit second order kinetics and to be catalysed by acid. Results obtained when 0.25$\underline{M}$ each of the reactants were reacted together at pH 4.8 and 20°C are tabulated in Table 43. It was possible to follow the reaction by determining the rate of disappearance of the methylolurea iodimetrically. Side products were seen to be formed in the later stages. The concentrations of MeDU formed and concentration of the unreacted MMU present were estimated and second order rate constants were calculated. During the initial stages MeDU alone was present in the reaction mixture. From 20 minutes of the reaction very small amounts of MMMeDU and after 45 minutes traces of higher methylene homologues were also obtained.

Reaction of MMU with urea was also studied at 30 and 10°C at pH values 4.2 and 3.8. Results obtained are tabulated in Tables 44-48. The activation energy for the reaction calculated at pH 4.2 was found to be 18.3 k cals/mole (Fig.9). At low temperatures and pH 4.8 the reaction was quite in agreement with second order kinetics even upto more than one hour. But at higher temperature and low pH values, deviation from second order kinetics was observed. Decrease of pH beyond 3.5 increased the rate of formation of higher

Table 43

Effect of Temperature on MMU-U Reaction
Urea: 0.25$\underline{M}$, MMU: 0.25$\underline{M}$, pH: 4.8, Temperature: 20°C

Time (min.)	MMU m/1x10^2	Decrease in MMU m/1x10^2	DMU m/1x10^2	k_5(second order) x 10^5 lit mol^{-1}sec^{-1}
0	25.00			
5	24.90	0.10	0.12	5.354
10	24.80	0.20	0.18	5.376
15	24.75	0.30	0.30	5.307
20	24.61	0.39	0.40	5.282
25	24.51	0.49	0.50	5.33
30	24.42	0.58	0.55	5.278
35	24.37	0.63	0.55	5.165
			Av:	5.299

Table 44

Effect of Temperature on MMU-U Reaction
Urea: 0.25$\underline{M}$, MMU: 0.25$\underline{M}$, pH: 4.2, Temperature: 10°C

Time (min.)	MMU m/1x10^2	Decrease in MMU m/1x10^2	DMU m/1x10^2	k_5(second order) x 10^5 lit mol^{-1}sec^{-1}
0	25.00			
20	24.65	3.5	3.00	4.732
40	24.3	7.0	6.50	4.801
60	23.98	1.02	1.00	4.726
80	23.65	1.35	1.20	4.756
100	23.3	1.70	1.60	4.864
			Av:	4.776

Table 45

Effect of Temperature on MMU-U Reaction

Urea: 0.25$\underline{M}$, MMU: 0.25$\underline{M}$, pH: 4.2, Temperature: 20°C

Time (min.)	MMU m/1x10^2	Decrease in MMU m/1x10^2	DMU m/1x10^2	k_5(second order) x 10^{4}lit mol^{-1}sec^{-1}
0	25.00			
10	24.48	0.52	0.50	1.416
25	23.72	1.28	1.20	1.439
50	22.67	2.33	2.40	1.409
75	21.51	3.49	3.40	1.442
100	20.46	4.54	4.20	1.479
			Av:	1.435

Table 46

Effect of Temperature on MMU-U Reaction

Urea: 0.25$\underline{M}$, MMU: 0.25$\underline{M}$, pH: 4.2, Temperature: 30°C

Time (min.)	MMU m/1x10^2	Decrease in MMU m/1x10^2	DMU m/1x10^2	k_5(second order) x 10^{4}lit mol^{-1}sec^{-1}
0	25.00			
5	24.70	0.30	0.30	3.841
10	23.57	1.43	1.30	4.045
15	22.95	2.05	2.00	3.970
20	22.27	2.73	2.40	4.086
25	21.65	3.35	3.20	4.126
30	21.20	3.80	3.50	3.980
35	20.45	4.55	4.00	4.238
			Av:	4.04

Table 47

Effect of pH on MMU-U Reaction

Urea: 0.25$\underline{M}$, MMU: 0.25$\underline{M}$, pH: 3.8, Temperature: 20°C

Time (min.)	MMU m/1x10^2	Decrease in MMU m/1x10^2	DMU m/1x10^2	k_5(second order) x 10^{4}lit mol^{-1}sec^{-1}
0	25.00			
5	24.25	0.75	0.80	4.124
10	23.50	1.50	1.50	4.215
15	22.85	2.15	2.10	4.182
20	22.01	2.99	2.78	4.204
25	21.61	3.59	3.40	4.183
30	21.07	3.93	3.60	4.144
35	20.48	4.52	4.10	4.204
			Av:	4.181

Table 48

Effect of pH on MMU-U Reaction

Urea: 0.25$\underline{M}$, MMU: 0.25$\underline{M}$, pH: 3.8, Temperature: 30°C

Time (min.)	MMU m/1x10^2	Decrease in MMU m/1x10^2	DMU m/1x10^2	k_5(second order) x 10^{3}lit mol^{-1}sec^{-1}
0	25.00			
5	23.19	1.81	1.60	1.041
10	21.61	3.39	3.20	1.045
15	20.36	4.64	4.10	1.013
20	18.87	6.13	5.60	1.083
25	17.39	7.61	6.10	1.167
			Av:	1.069

Fig. 9 ACTIVATION ENERGY FOR THE REACTION OF MONOMETHYLOLUREA AND UREA. P^H:4.2, MMU:0.25$\underline{M}$, U:0.25$\underline{M}$
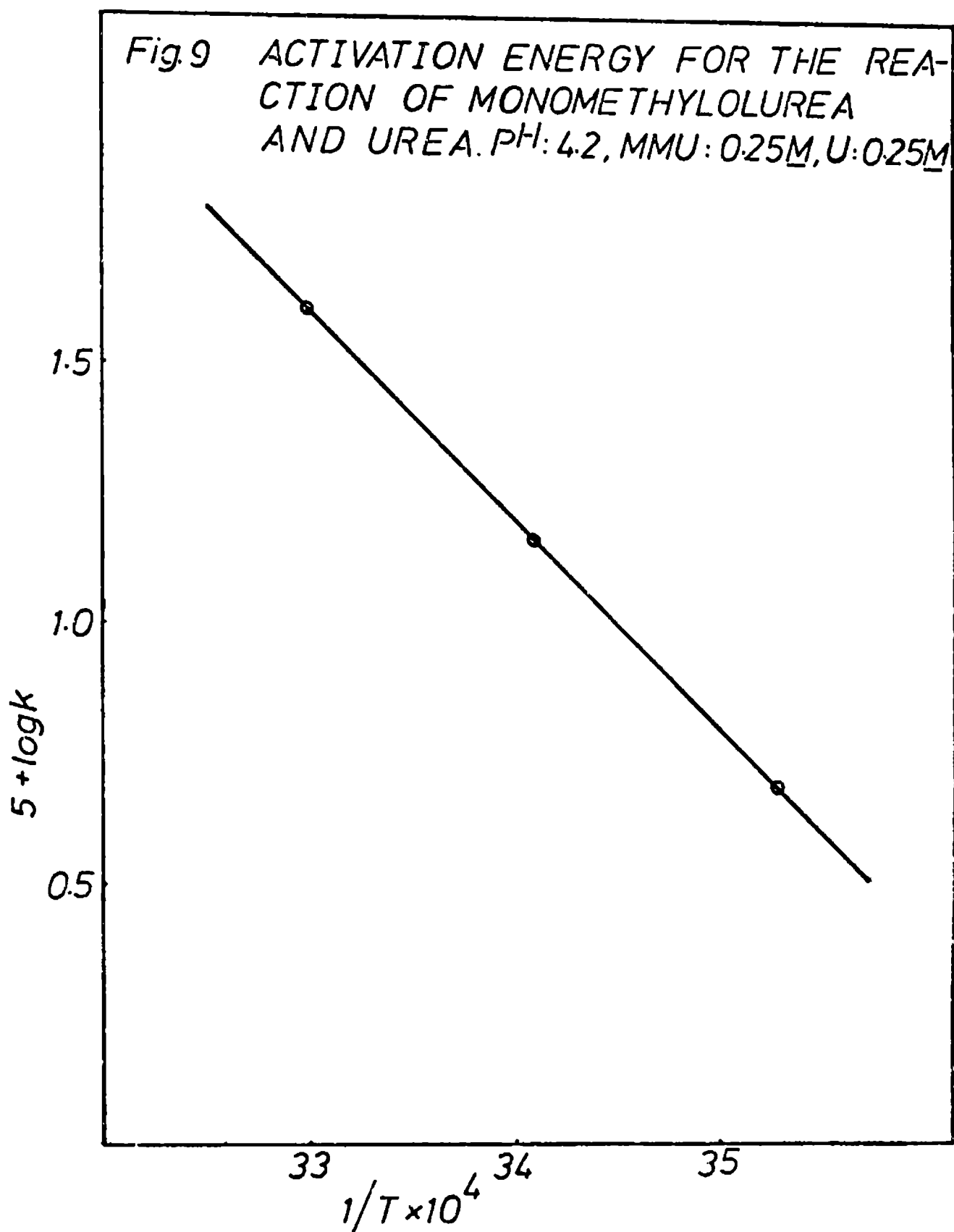
methylene homologues and increase of pH above 5 increased the dissociation of the methylols. Hence pH values between 5 and 3.5 and temperatures 10-40°C was selected as suitable conditions for the study of the reaction.

Rate of formation of MeDU from urea and MMU at pH 4.2 increased three-fold for a rise of 10°C. But the rate of the reaction increased 8 times when the pH was changed from 4.8 to 3.8.

The formation of MeDU from MMU and urea was also studied at pH values 3.5 and 4, and in the temperature range 20 to 40°C using 0.4M urea and 0.1M MMU. Experimental results are tabulated in Tables 49-54. When the concentration of urea was increased 4 times, the rate-constant for the reaction increased more than five times. Even at 40°C the reaction followed second order kinetics. This may be due to the fact that the presence of large amounts of urea reduced several side reactions. Monomethylolmethylenediurea formed in the equimolar reactants by the intercondensation of MMU, was not observed in these reactions, even after one hour at pH 3.5 and 30°C. Increase of urea concentration also reduced the rate of dissociation of MMU. Free formaldehyde was not at all detected during the reaction. The concentration of MeDU determined, was in good agreement with the decrease in MMU concentration.

Table 49

Effect of Concentration on MMU-U Reaction

U: 0.40$\underline{M}$, MMU: 0.1$\underline{M}$, pH: 4, Temperature: 20°C

Time (min.)	MMU m/1x10^2	Decrease in MMU m/1x10^2	DMU m/1x10^2	k_5(second order) x 10^4 lit mol^{-1}sec^{-1}
0	10.00			
10	7.99	2.01	1.95	9.583
20	6.52	3.48	3.40	9.346
35	4.88	5.12	4.50	9.208
45	3.99	6.01	5.80	9.328
61	2.93	7.07	6.66	9.403
76	2.26	7.74	7.00	9.311
			Av:	9.362

Table 50

Effect of Concentration on MMU-U Reaction

Urea: 0.4$\underline{M}$, MMU: 0.1$\underline{M}$, pH: 4, Temperature: 30°C

Time (min.)	MMU m/1x10^2	Decrease in MMU m/1x10^2	DMU m/1x10^2	k_5(second order) x 10^3 lit mol^{-1}sec^{-1}
0	10.00			
10	7.004	2.996	3.00	1.543
20	4.983	5.017	5.00	1.562
30	3.710	6.290	6.20	1.519
45	2.307	7.691	7.10	1.547
60	1.638	8.362	7.90	1.477
			Av:	1.542

Table 51

Effect of Concentration on MMU-U Reaction

Urea: $0.4\underline{M}$, MMU: $0.1\underline{M}$, pH: 4, Temperature: $40^{\circ}C$

Time (min.)	MMU $m/lx10^2$	Decrease in MMU $m/lx10^2$	DMU $m/lx10^2$	k_5(second order) $x\ 10^3$lit mol^{-1}sec^{-1}
0	10.00			
10	4.701	5.299	5.00	3.403
15	3.295	6.705	6.50	3.432
21.5	2.290	7.710	7.40	3.2557
25	1.970	8.030	7.70	3.113
30	1.63	8.370	8.01	2.925
			Av:	3.141

Table 52

Effect of Concentration on MMU-U Reaction

Urea: $0.4\underline{M}$, MMU: $0.1\underline{M}$, pH: 3.5, Temperature: $20^{\circ}C$

Time (min.)	MMU $m/lx10^2$	Decrease in MMU $m/lx10^2$	DMU $m/lx10^2$	k_5(second order) $x\ 10^3$lit mol^{-1}sec^{-1}
0	10.00			
11	7.49	2.51	2.45	1.130
20	6.18	3.82	3.75	1.040
30	5.04	4.96	4.80	1.023
40	4.14	5.86	5.50	1.005
50	3.40	6.60	6.10	0.998
			Av:	1.016

Table 53

Effect of Concentration on MMU-U Reaction

Urea: 0.4$\underline{M}$, MMU: 0.1$\underline{M}$, pH: 3.5, Temperature: 30°C

Time (min.)	MMU $m/1x10^2$	Decrease in MMU $m/1x10^2$	DMU $m/1x10^2$	k_5(second order) x 10^3 lit $mol^{-1}sec^{-1}$
0	10.00			
5	7.49	2.51	2.5	2.48
10	5.68	4.32	4.2	2.506
15	4.501	5.499	5.2	2.408
20	3.5	6.500	6.3	2.423
30	2.28	7.720	7.5	2.340
			Av:	2.428

Table 54

Effect of Concentration on MMU-U Reaction

Urea: 0.4$\underline{M}$, MMU: 0.1$\underline{M}$, pH: 3.5, Temperature: 40°C

Time (min.)	MMU $m/1x10^2$	Decrease in MMU $m/1x10^2$	DMU $m/1x10^2$	k_5(second order) x 10^3 lit $mol^{-1}sec^{-1}$
0	10.00			
5	5.66	4.34	4.2	5.09
10	3.38	6.62	6.5	5.02
15	2.05	7.95	7.5	5.05
20	1.285	8.715	8.01	5.02
			Av:	5.045

Under alkaline conditions, the dissociation of MMU was favoured. The formaldehyde formed methylolated urea and MMU. Small amounts of methylenediurea could also be detected after several hours.

b) Dissociation of MeDU

Decomposition of MeDU was studied in aqueous acid solutions at $0.1\underline{M}$ concentration. The reaction was followed by determining the sum of the concentrations of methylols and formaldehyde by the iodimetric method and the undissociated methylenediurea by quantitative TLC method. Results obtained for the reaction at pH 4, 3.5 and 2.9 at temperatures 30 and $40^{\circ}C$ are tabulated in Tables 55-60. The reaction followed first order kinetics and was catalysed by hydronium ions.

At higher temperatures and low pH side reactions were observed. During the early stages of the reaction the only product was MMU. But at later stages small amounts of MMMeDU were detected. Since free formaldehyde was not found in the reaction mixture it may be assumed that MMMeDU was formed by the intercondensation of MMU.

Rate of dissociation of MeDU increased three times for a change of pH from 4 to 3.5 at $30^{\circ}C$. Similarly the

Table 55

Analytical Data on Dissociation of MeDU

MeDU: 0.1$\underline{M}$, pH: 4, Temperature: 30°C

Time (min.)	Free CH_2O + MMU $m/1 \times 10^2$	Decrease in $MeDU$ $m/1 \times 10^2$	Estimated $MeDU$ $m/1 \times 10^2$	k_6(first order) $\times 10^5 sec^{-1}$
0		10.00		
25	0.230	9.770	9.80	1.505
50	0.454	9.546	9.52	1.528
100	0.870	9.130	9.08	1.513
140	1.153	8.847	8.72	1.456
165	1.327	8.673	8.50	1.438
200	1.550	8.450	8.20	1.401
265	2.060	7.940	7.57	1.448
			Av:	1.4698

Table 56

Analytical Data on Dissociation of MeDU

MeDU: 0.1$\underline{M}$, pH: 4, Temperature: 40°C

Time (min.)	Free CH_2O + MMU $m/1 \times 10^2$	Decrease in $MeDU$ $m/1 \times 10^2$	Estimated $MeDU$ $m/1 \times 10^2$	k_6(first order) $\times 10^5 sec^{-1}$
0		10.00		
20	0.52	9.48	9.52	4.376
40	1.00	9.00	9.00	4.385
60	1.45	8.55	8.14	4.401
100	2.36	7.64	7.52	4.480
140	3.143	6.857	6.73	4.491
165	3.56	6.44	6.38	4.441
			Av:	4.428

Table 57

Analytical Data on Dissociation of MeDU

MeDU: 0.1$\underline{M}$, pH: 3.5, Temperature: 30°C

Time (min.)	Free CH_2O + MMU $m/1 \times 10^2$	Decrease in MeDU $m/1 \times 10^2$	Estimated MeDU $m/1 \times 10^2$	k_6(first order) x 10^5 sec^{-1}
0		10.00		
20	0.524	9.476	9.50	4.472
40	1.048	8.952	8.64	4.596
65	1.624	8.376	8.26	4.523
80	1.840	8.160	8.12	4.279
100	2.220	7.780	7.52	4.180
120	2.549	7.451	7.32	4.085
150	3.200	6.800	6.69	4.281
170	3.527	6.473	6.24	4.265
			Av:	4.335

Table 58

Analytical Data on Dissociation of MeDU·

MeDU: 0.1$\underline{M}$, pH: 3.5, Temperature: 40°C

Time (min.)	Free CH_2O + MMU $m/1 \times 10^2$	Decrease in MeDU $m/1 \times 10^2$	Estimated MeDU $m/1 \times 10^2$	k_6(first order) x 10^4 sec^{-1}
0		10.00		
20	1.223	8.78	8.75	1.0843
40	2.113	7.887	7.89	0.9903
65	3.070	6.930	6.50	0.9407
80	3.800	6.200	6.06	0.9960
100	4.300	5.700	5.69	0.9365
120	4.785	5.220	5.05	0.9039
			Av:	0.9039

Table 59

Analytical Data on Dissociation of MeDU

MeDU: 0.1$\underline{M}$, pH: 2.9, Temperature: 30°C

Time (min.)	Free CH_2O + MMU m/1x10^2	Decrease in MeDU m/1x10^2	Estimated MeDU m/1x10^2	k_6(first order) x 10^4 sec^{-1}
0		10.00		
15	1.130	8.870	8.82	1.328
35	2.409	7.591	7.46	1.312
60	3.877	6.123	6.08	1.363
75	4.550	5.450	5.20	1.349
90	4.831	5.169	4.58	1.348
			Av:	1.339

Table 60

Analytical Data on Dissociation of MeDU

MeDU: 0.1$\underline{M}$, pH: 2.9, Temperature: 40°C

Time (min.)	Free CH_2O + MMU m/1x10^2	Decrease in MeDU m/1x10^2	Estimated MeDU m/1x10^2	k_6(first order) x 10^4 sec^{-1}
0		10.00		
15	3.350	6.650	6.60	4.534
30	5.490	4.510	4.52	4.424
45	6.900	3.100	3.02	4.338
60	8.137	1.863	1.50	4.668
75	8.500	1.500	1.09	4.214
90	8.900	1.094	0.80	4.096
			Av:	4.379

rate increased three times for a 10° rise of temperature at
pH 4. At pH 2.9 and 40^oC side products were seen to be formed
after 80 minutes. Hence high temperatures and high acid
concentrations were not tried. The dissociation of MeDU
was very slow at pH 6 at temperatures 30 and 40^oC.

Activation energy for the dissociation of MeDU
was found to be 25.6 k cals/mole at pH 4 (Fig.10).

c) Condensation of Urea with DMU

Dimethylolurea reacts with urea in aqueous acid
solutions giving monomethylolmethylenediurea. Second order
kinetics was observed and the rate constant for the reaction
was found to increase proportional to hydronium ion concen-
tration. Results obtained for the reaction at pH 4.2 and
30^oC for 0.25$\underline{M}$ each of the reactants are given in Table 61.
The reaction was followed by determining unreacted dimethylol-
urea by the iodimetric method. MMMeDU formed was estimated
by colorimetric method. Results obtained from these two
methods agreed well. Here the free amino groups of urea
can react with either of the two methylol group of DMU.
Therefore a higher rate may be expected for the reaction,
when compared with the reaction between urea and MMU. But
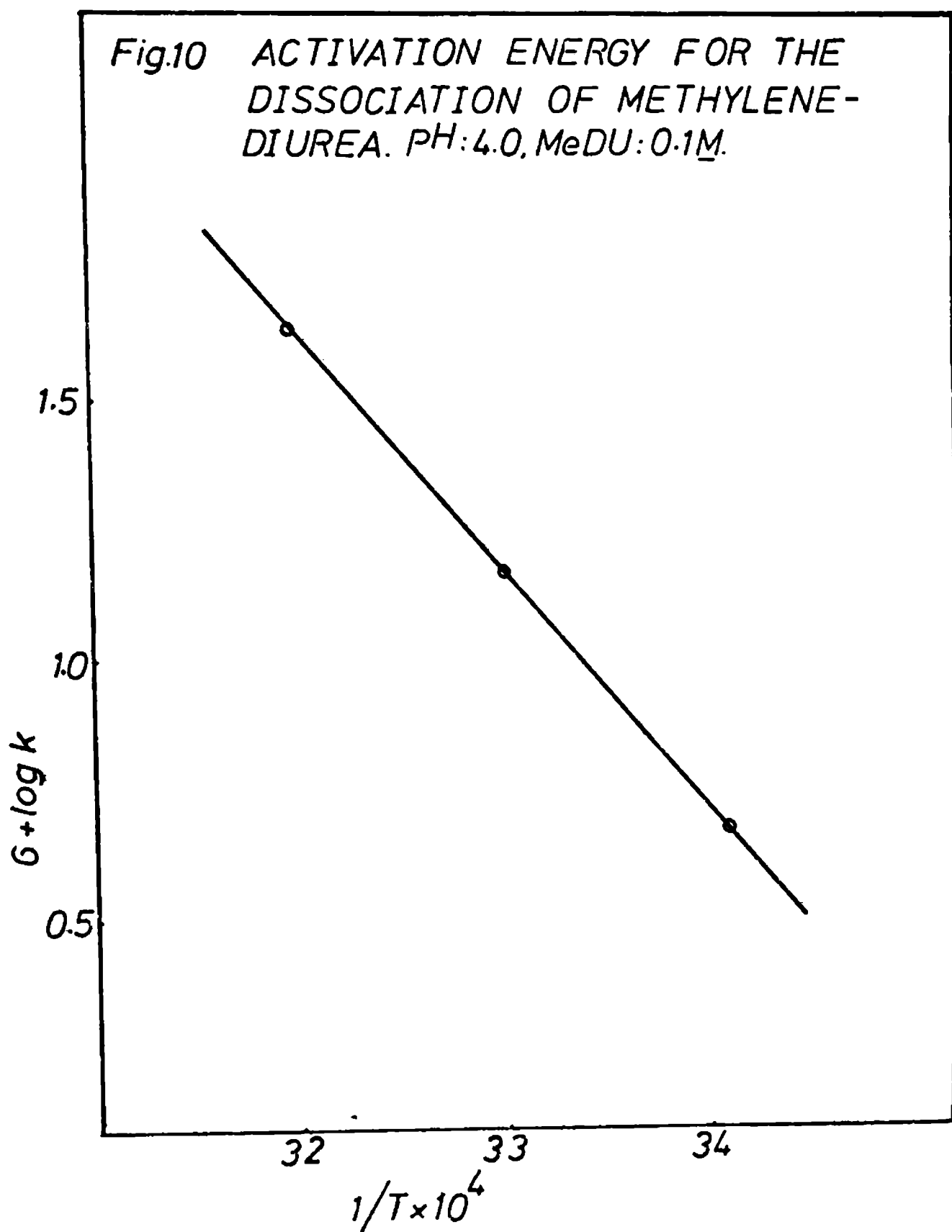it was found that the rate of the reaction of DMU with urea

Fig.10 ACTIVATION ENERGY FOR THE DISSOCIATION OF METHYLENE-DIUREA. PH:4.0, MeDU:0.1$\underline{M}$.

Table 61

Analytical Data on DMU-Urea Reaction
DMU: 0.25$\underline{M}$, U: 0.25$\underline{M}$, pH: 4.2, Temperature: 30°C

Time (min.)	DMU m/1x10^2	Decrease in DMU m/1x10^2	MMMeDU$_2$ m/1x10^2	k_7(second order) x 10^4 lit mol^{-1}sec^{-1}
0	25.00			
10	24.38	0.62	0.52	1.6953
20	23.75	1.25	1.30	1.7543
30	23.22	1.78	1.70	1.7035
40	22.67	2.33	2.10	1.7129
50	22.17	2.83	2.52	1.7019
60	21.68	3.32	3.40	1.7015
			Av:	1.72

was less than half of the rate of the reaction of MMU with urea. This proves that in MMU reactivity of the methylol group is increased by the free amino group, while in DMU, the methylol substituent reduces the reactivity of the second one. Increase of temperature and acid concentration favoured side reactions like dissociation of DMU. Only MMMeDU was detected on the TLC plate as product during the early stages of the reaction. But later, small amounts of MMU and traces of MeDU were found in the TLC plate. Raising the pH above 5 increased the dissociation of the DMU and decreased the methylene bridge formation.

d) Self Condensation of MMU

Methylene linkage can also be produced by the self-condensation of MMU under acid conditions. Formation of MMMeDU by the self-condensation of MMU was studied using $0.25\underline{M}$ solution under acid pH and $30^{\circ}C$. Data collected at pH 4.2 is recorded in Table 62. The reaction was found to obey second order kinetics. The rate of self-condensation was less than that of formation of MMMeDU by the reaction between DMU and urea. The rate of methylene bridge formation was followed by determining the unreacted methylol group using iodimetric method. The products formed was estimated

Table 62

Analytical Data on MMU-MMU Reaction

MMU: 0.25, pH: 4.2, Temperature: $30^{\circ}C$

Time (min.)	MMU $m/1 \times 10^2$	Decrease in MMU $m/1 \times 10^2$	MMMeDU $m/1 \times 10^2$	k_8(second order) $\times 10^4$ lit mol^{-1}sec^{-1}
0	25.00			
10	24.45	0.55	0.50	1.4995
20	23.92	1.18	1.21	1.505
30	23.42	1.58	1.52	1.499
40	22.95	2.05	1.80	1.488
50	22.50	2.50	2.32	1.484
60	22.02	2.98	2.78	1.5036
			Av:	1.5

by the colorimetric method. Formaldehyde was not formed during the early stages of reaction. Only spots corresponding to MMMeDU and MMU were found to be present at the initial stages. But later, traces of both MeDU and DMeTU were seen to be formed.

e) Condensation of MMU with DMU

Rate of formation of DMMeDU was studied from MMU and DMU at pH 4.2 and $30^{\circ}C$. The second order rate constants calculated showed wide deviation due to side reactions even from the early stages of the reaction. This may be due to the self-condensation of MMU. Here also the reaction was followed by determining the consumed methylol iodimetrically and the reactants and products by the colorimetric method. Spots corresponding to MMU, DMU, DMMeDU and MMMeDU were present in the TLC plate even from the very beginning of the reaction. The product of self condensation of MMU viz., MMMeDU was the major product showing thereby that the self condensation of MMU is faster than its condensation with DMU.

f) Self Condensation of DMU

Self-condensation of DMU was carried out at pH 4.2 and $30^{\circ}C$ using 0.25$\underline{M}$ solution of the substance. The reaction

was followed by determining the unreacted methylol groups, Using iodimetric method. Results obtained are listed in Table 63. The reaction followed second order kinetics. TLC analysis showed that no methylene bridged compounds were formed since spots corresponding to DMMeDU were not present on the TLC plate. The decrease in DMU concentration may be due to the ether bridge formation. TLC analysis showed that besides the spot corresponding DMU, a little of the material was found to be retained at the bottom of the plate where the samples were spotted. The intensity of this spot was found to increase with time. This spot which did not move with the solvent used, may be the ether fromed from DMU. Further the amount of methylol groups estimated iodimetrically agreed well with the unreacted DMU estimated by TLC. Thus it is seen that no free formaldehyde is present and hence the decrease in DMU concentration is solely due to formation of ether linkage.

g) Formation of Higher Homologues

Reactions of MeDU with MMU

Reactions of MeDU with MMU in aqueous acid solution may be represented as follows:-

$$\text{MeDU} \quad + \quad \text{MMU} \quad \rightleftharpoons \quad \text{DMeTU} \qquad (15)$$
$$\updownarrow \qquad\qquad\qquad \updownarrow$$
$$\text{MMU + U} \qquad\quad \text{U + F}$$
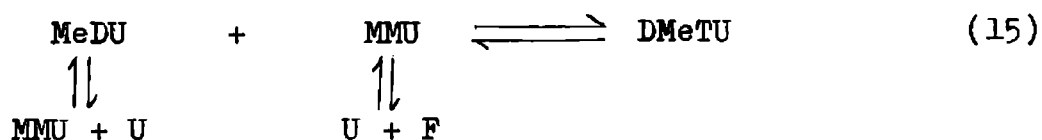
Table 63

Analytical Data on DMU-DMU Reaction

DMU: 0.25$\underline{M}$, pH: 4.2, Temperature: 30°C

Time (min.)	DMU m/1x10^2	Decrease in DMU m/1x10^2	Estimated DMU m/1x10^2	k (second order) x 10^6 lit mol^{-1}sec^{-1}
0	25.00			
120	24.92	0.08	0.248	1.78
300	24.80	0.20	0.2452	1.79
600	24.60	0.40	0.241	1.80
900	24.42	0.58	0.2384	1.75
1200	24.23	0.77	0.2326	1.76
			Av:	1.78

Rate of formation of DMeTU has been studied from MeDU and
MMU using 0.1M solutions of the reactants at pH 4.2 and
30°C. The reaction was followed by determining the un-
reacted methylol, using iodimetric method and products by
the quantitative TLC method. It was found that the total
concentration of methylol increased with time due to the
dissociation of methylenediurea. Eventhough a spot
corresponding to DMeTU was obtained, since the dissociation
of MeDU and MMU were the predominant reactions, formation
of DMeTU could not be investigated.

h) Reactions of DMeTU with MMU

Reactions of DMeTU with MMU may also be repre-
sented as follows:

$$\begin{array}{cccc}
\text{DMeTU} & + & \text{MMU} & \rightleftharpoons \text{TMeTeU} \\
\updownarrow & & \updownarrow & \\
\text{MeDU} + \text{MMU} & & \text{U} + \text{F} &
\end{array} \qquad (16)$$
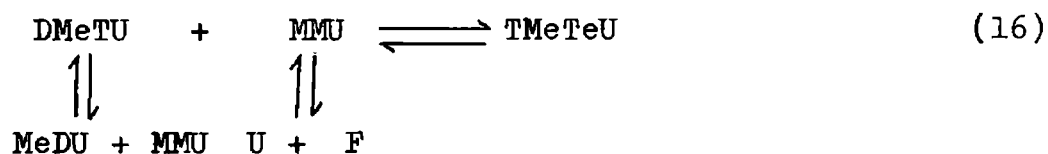
Rate of formation of TMeTeU from DMeTU and MMU was also
studied using 0.1M solutions of the reactants at pH 4.2
and 30°C. As in the case of the formation of DMeTU from
MMU and MeDU, here also the net formaldehyde equivalent due
to methylols and free formaldehyde was found to increase
with time. Traces of TMeTeU was found to be seen on the

TLC plate. But since the dissociation of the reactants was predominant in kinetics of formation of TMeTU could not be studied.

i) Reaction of MeDU with Formaldehyde

Formation of monomethylolmethylenediurea was studied using 0.1$\underline{M}$ solutions each of MeDU and formaldehyde at 7.75 pH and 30°C.

$$H_2N \; CO \; NH \; CH_2NH \; CO \; NH_2 \; + \; CH_2O \; \rightleftharpoons$$

$$H_2N \; CO \; NH \; CH_2 \; NH \; CO \; NH \; CH_2OH \qquad (17)$$
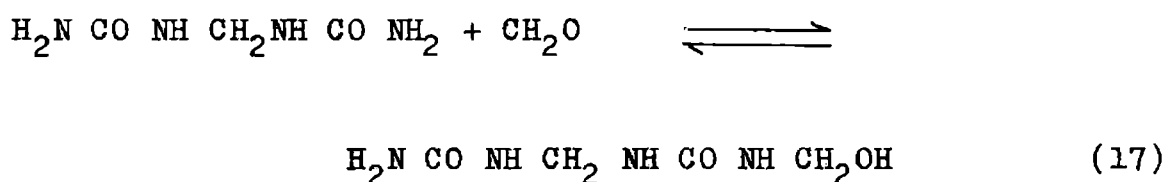
The results are tabulated in Table 64. The reaction was in good agreement with second order kinetics. The reaction was followed by determining unreacted formaldehyde using sulphite method and the unreacted MeDU and the product MMMeDU formed by the colorimetric method after separation. Traces of DMMeDU were found on the TLC plates after early stages of the reaction.

Effect of temperature on the reaction was studied by conducting the reaction at 40 and 50°C keeping the pH

Table 64

Analytical Data on MeDU-Formaldehyde Reaction

MeDU: $0.1\underline{M}$, CH_2O: $0.1\underline{M}$, pH: 7.75, Temperature: $30^\circ C$

Time (min.)	CH_2O $m/lx10^2$	Decrease in CH_2O $m/lx10^2$	MeDU $m/lx10^2$	k_9(second order) $x\ 10^5 lit\ mol^{-1}sec^{-1}$
0	10.00			
60	9.78	0.22	9,71	6.249
120	9.58	0.42	9.53	6.089
180	9.37	0.63	9.40	6.226
240	9.18	0.82	9.22	6.203
360	8.81	1.19	8.71	6.253
420	8.65	1.35	8.50	6.193
480	8.47	1.53	8.20	6.272
			Av:	6.213

and concentration same as those at $30^{o}C$. Data obtained are given in Tables 65 and 66. Activation energy for the reaction was found to be 13.7 k cals/mole (Fig.11). The rate increased 4 times for 20° rise of temperature.

Reactions were also conducted at pH 5, 9, 10.5 at $30^{o}C$. It was catalysed by both acid and alkali. Under alkaline conditions the reaction was more favoured. The results are tabulated in Tables 67-69. Change of pH for the reaction from 7.75 to 10.5 caused the rate to increase one hundred and twenty times at $30^{o}C$. Under acid conditions the increase was only slight (2.5×10^{-4} to 2.3×10^{-4} l $mole^{-1}sec^{-1}$) for a change of pH from 7.75 to 5.

Table 65

Effect of Temperature on MeDU-F Reaction

MeDU: 0.1$\underline{M}$, CH_2O: 0.1$\underline{M}$, pH: 7.75, Temperature: 40°C

Time (min.)	CH_2O m/lx10^2	Decrease in CH_2O m/lx10^2	MeDU m/lx10^2	k_9(second order) x 10^4 lit mol^{-1}sec^{-1}
0	10.00	0		
30	9.775	0.225	9.66	1.278
60	9.550	0.450	9.49	1.309
90	9.335	0.665	9.2	1.319
120	9.135	0.865	9.02	1.315
150	8.939	1.061	8.82	1.318
180	8.759	1.241	8.58	1.311
210	8.585	1.415	8.20	1.308
			Av:	1.308

Table 66

Effect of Temperature on MeDU-F Reaction

MeDU: 0.1$\underline{M}$, F: 0.1$\underline{M}$, pH: 7.75, Temperature: 50°C

Time (min.)	CH_2O m/lx10^2	Decrease in CH_2O m/lx10^2	MeDU m/lx10^2	k_9(second order) x 10^4 lit mol^{-1}sec^{-1}
0	10.00			
15	9.77	1.23	9.70	2.615
30	9.55	1.45	9.55	2.617
60	9.09	1.91	9.04	2.688
90	8.75	1.25	8.50	2.645
120	8.39	1.61	8.11	2.665
150	8.105	1.895	8.03	2.598
180	7.750	2.250	7.4	2.688
			Av:	2.6454

Fig.11 ACTIVATION ENERGY FOR THE REACTION OF METHYLENEDIUREA AND FORMALDEHYDE AT PH 7.75
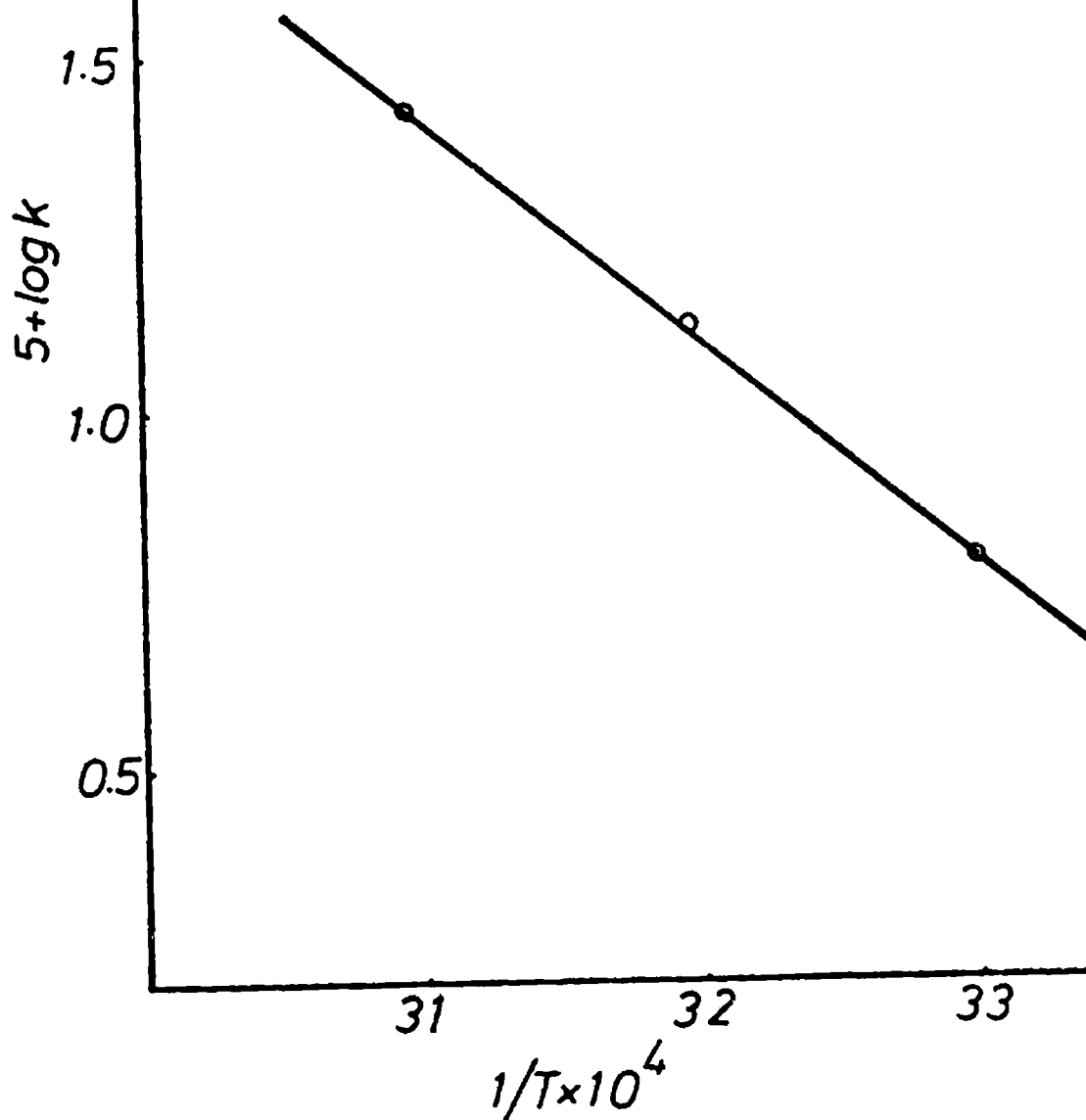
MeDU : 0.1M
F   0.1M

Table 67

Effect of Concentration on MeDU-F Reaction

MeDU: 0.1$\underline{M}$, F: 0.1$\underline{M}$, pH: 9, Temperature: 30°C

Time (min.)	CH_2O m/lx10^2	Decrease in CH_2O m/lx10^2	MeDU m/lx10^2	k_9(second order) x 10^{4}lit mol^{-1}sec^{-1}
0	10.00			
15	9.79	0.21	9.52	2.383
30	9.57	0.43	9.47	2.496
45	9.39	0.61	9.20	2.406
60	9.23	0.77	9.15	2.317
75	9.03	0.97	9.02	2.387
90	8.88	1.12	8.52	2.336
105	8.75	1.25	8.60	2.280
120	8.59	1.41	8.40	2.267
			Av:	2.3465

Table 68

Effect of Concentration on MeDU-F Reaction

MeDU: 0.1$\underline{M}$, F: 0.1$\underline{M}$, pH: 10.5, Temperature: 30°C

Time (min.)	CH_2O m/lx10^2	Decrease in CH_2O m/lx10^2	MeDU m/lx10^2	k_9(second order) x 10^3 lit mol^{-1}sec^{-1}
0	10.00			
5	8.15	1.85	8.25	7.566
10	6.98	3.02	6.52	7.211
15	5.93	4.07	5.70	7.63
20	5.24	4.76	5.02	7.57
25	4.795	5.205	4.52	7.236
			Av:	7.443

Table 69

Effect of pH on MeDU-F Reaction

MeDU: 0.1$\underline{M}$, F: 0.1$\underline{M}$, pH: 5, Temperature: 50°C

| Time (min.)	CH_2O m/lx10^2	Decrease in CH_2O m/lx10^2	MeDU m/lx10^2	k_9(second order) x 10^{4}lit mol^{-1}sec^{-1}
0	10.00			
15	9.78	0.22	9.80	2.499
30	9.60	0.40	9.60	2.315
60	9.19	0.81	9.21	2.448
90	8.89	1.11	8.54	2.312
120	8.59	1.41	8.45	2.28
150	8.34	1.66	8.00	2.212
			Av:	2.344

CHAPTER VIII

REACTIONS OF METHYL AND PHENYLUREA WITH FORMALDEHYDE

The reaction of substituted ureas like methylurea and phenylurea with formaldehyde was studied to find the effect of substituents on the urea-formaldehyde reaction.

Reactions of Methylurea with Formaldehyde

The reaction of methylurea with formaldehyde gives monomethylolmethylurea (MMMeU) as the product.

$$CH_3NHCONH_2 \ + \ CH_2O \ \rightleftharpoons CH_3NHCONHCH_2OH \qquad (18)$$
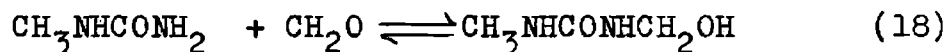
The reaction was studied at pH 7 and $30^{\circ}C$ using $0.25\underline{M}$ solutions of the reactants. Results obtained are listed in Table 70. The reaction followed second order kinetics. Rates were determined by following the reaction using sulphite method for the determination of the concentration of unreacted formaldehyde. The product of the reaction, MMMeU, was estimated by the quantitative thin layer chromatographic technique. No dimethylols or methylene bridged compounds were found during the initial stages of the reaction. This was checked by TLC analysis and

134

Table 70

Analytical Data on MeU-F Reaction

MeU: $0.25\underline{M}$, CH_2O: $0.25\underline{M}$, pH: 7, Temperature: $30^{\circ}C$

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMMeU m/1x10^2	k_{10}(second order) x 10^{4}lit mol^{-1}sec^{-1}
0	25.00			
5	24.00	1.00	1.00	5.267
15	22.40	2.60	2.50	5.1586
30	20.18	4.82	4.75	5.307
40	19.06	5.94	5.57	5.194
50	17.93	7.07	6.89	5.257
60	17.19	7.81	7.46	5.0482
			Av:	5.205

136

iodimetric determination. But after 100 minutes small amounts of dimethylol was found to be formed on the TLC plate.

To study the effect of pH on the reaction, it was also conducted at pH 2.5 and 9 at $30^{\circ}C$. Results are tabulated in Tables 71-73. Even at pH 2.5 methylenebis-methylurea was not formed during the initial stages of the reaction. At later stages small amounts of methylene-bismethylurea were formed. At alkaline pH also small amounts of dimethylol of MeU were formed at later stages. The reaction was catalysed by both acid and base. The rate increased nearly 5 times for a change of pH from 7 to 9 at $30^{\circ}C$. But at acid pH the rate increased only 2.5 times for a change of pH from 7 to 2.5. This showed that as in the case of urea formaldehyde reaction, form-ation of MMMeU was more favoured in alkaline medium than in the acid medium.

Rate of dissociation of MMMeU was also studied at pH 9 and $30^{\circ}C$ using 0.25$\underline{M}$ solution. The results are tabulated in Table 74. As compared to the dissociation of MMU, MMMeU dissociated very slowly. This showed the increased stability of the latter in aqueous medium.

Table 71

Analytical Data on MeU-F Reaction

MeU: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 9, Temperature: 20°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMMeU m/1x10^2	k_{10}(second order) x 10^{3}lit mol^{-1}sec^{-1}
0	25.00			
5	23.02	1.98	2.00	1.1468
10	21.34	3.66	3.54	1.1434
15	19.76	5.24	5.20	1.1786
20	18.77	6.27	6.10	1.1064
25	17.68	7.32	7.22	1.1041
30	16.60	8.40	8.04	1.1245
			Av:	1.134

Table 72

Analytical Data on MeU-F Reaction

MeU: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 9, Temperature: 30°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMMeU m/1x10^2	k_{10}(second order) x 10^{3}lit mol^{-1}sec^{-1}
0	25.00			
5	21.04	3.96	4.02	2.4346
10	18.38	6.62	6.39	2.4011
15	16.20	8.80	8.69	2.4143
20	14.62	10.38	10.20	2.3666
25	13.63	11.37	11.07	2.2245
			Av:	2.368

Table 73

Analytical Data on MeU-F Reaction

MeU: $0.25\underline{M}$, CH_2O: $0.25\underline{M}$, pH: 2.5, Temperature: $30^\circ C$

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMMeU m/1x10^2	k_{10}(second order) x 10^3 limt mol^{-1}sec^{-1}
0	25.00			
6	22.34	2.66	2.50	1.323
10	20.70	4.30	4.30	1.384
15	19.18	5.82	5.78	1.3486
21	17.40	7.60	7.48	1.3866
25	16.61	8.39	8.24	1.3469
30	15.62	9.38	9.08	1.3345
			Av:	1.354

Table 74

Analytical Data on Dissociation of MMMeU

MMMeU: $0.25\underline{M}$, pH: 9, Temperature: $30^\circ C$

Time (min.)	MMMeU m/1x10^2	Decrease in MMMeU m/1x10^2	Estimated MMMeU m/1x10^2	k_{10}(first order) x 10^7 sec^{-1}
0	25.00			
300	24.15	0.85	0.80	8.2
600	23.36	1.64	1.60	8.1
900	22.55	2.45	2.30	8.2
1200	21.75	3.25	3.00	8.3
1500	21.01	3.99	3.40	8.3
			Av:	8.22

Reaction of Phenylurea with Formaldehyde

Reaction between phenylurea and formaldehyde
was studied at pH 3 and 40°C using 0.25$\underline{M}$ solutions of the
reactants.

$$C_6H_5NHCONH_2 \quad + \quad CH_2O \rightleftharpoons C_6H_5NHCONHCH_2OH \qquad (19)$$
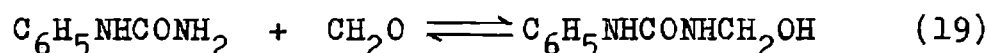
The results are listed in Table 75. MeBPhU was obtained
as the major product of the reaction. The reaction followed
first order kinetics with respect to formaldehyde. The
reaction was followed by iodimetric and sulphite methods.
The product obtained was analysed by the quantitative TLC
method which agreed well with the amount of formaldehyde
consumed. Traces of MMU was found to be present in the
TLC plate. But its concentration remained constant without
any further increase. This may be due to the fact that the
rate of formation of MeBPhU from PhU and MMPhU were much
faster than the reaction of PhU with formaldehyde.

To study the effect of temperature on the rate of
the reaction, it was also conducted at temperatures 50 and
65°C. The results are given in Tables 76 and 77. The
activation energy for the reaction is found to be 14.15
k cals/mole at pH 3 (Fig.12). With increase of temperature

Table 75

Analytical Data on PhU-F Reaction

PhU: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 3, Temperature: 40°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MeBPhU$_2$ m/1x10^2	k_{11}(first order) x 10^{4}sec^{-1}
0	25.00			
15	24.28	0.72	--	1.318
30	23.58	1.42	1.34	1.338
45	22.89	2.11	2.08	1.365
60	22.24	2.76	2.58	1.379
75	21.72	3.28	3.32	1.342
90	21.05	3.95	3.85	1.388
			Av:	1.346

Table 76

Effect of Temperature on PhU-F Reaction

PhU: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 3, Temperature: 50°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MeBPhU$_2$ m/1x10^2	k_{11}(first order) x 10^4 sec^{-1}
0	25.00			
5	24.52	0.48	--	2.6101
15	23.62	1.38	1.42	2.6365
22	23.00	2.00	2.02	2.635
30	22.34	2.66	2.54	2.646
45	21.26	3.74	3.50	2.647
60	20.19	4.81	4.76	2.647
			Av:	2.637

Table 77

Effect of Temperature on PhU-F Reaction

PhU: $0.25\underline{M}$, CH_2O: $0.25\underline{M}$, pH: 3, Temperature: $65^\circ C$

Time (min.)	CH_2O m/lx10^2	Decrease in CH_2O m/lx10^2	MeBPhU$_2$ m/lx10^2	k_{11}(first order) x 10^4 sec^{-1}
0	25.00			
5	23.7	1.3	1.2	7.313
10	22.55	2.45	2.4	7.2431
15	21.45	3.55	3.46	7.3552
20	20.46	4.54	4.25	7.3955
25	19.57	5.43	5.24	7.399
			Av:	7.341

Fig.12 ACTIVATION ENERGY FOR THE REACTIONS OF METHYLUREA AND PHENYLUREA WITH FORMALDEHYDE

o MU 0.25$\underline{M}$
F 0.25$\underline{M}$
pH:9

• p^hU 0.25$\underline{M}$
F:0.25$\underline{M}$
pH:3
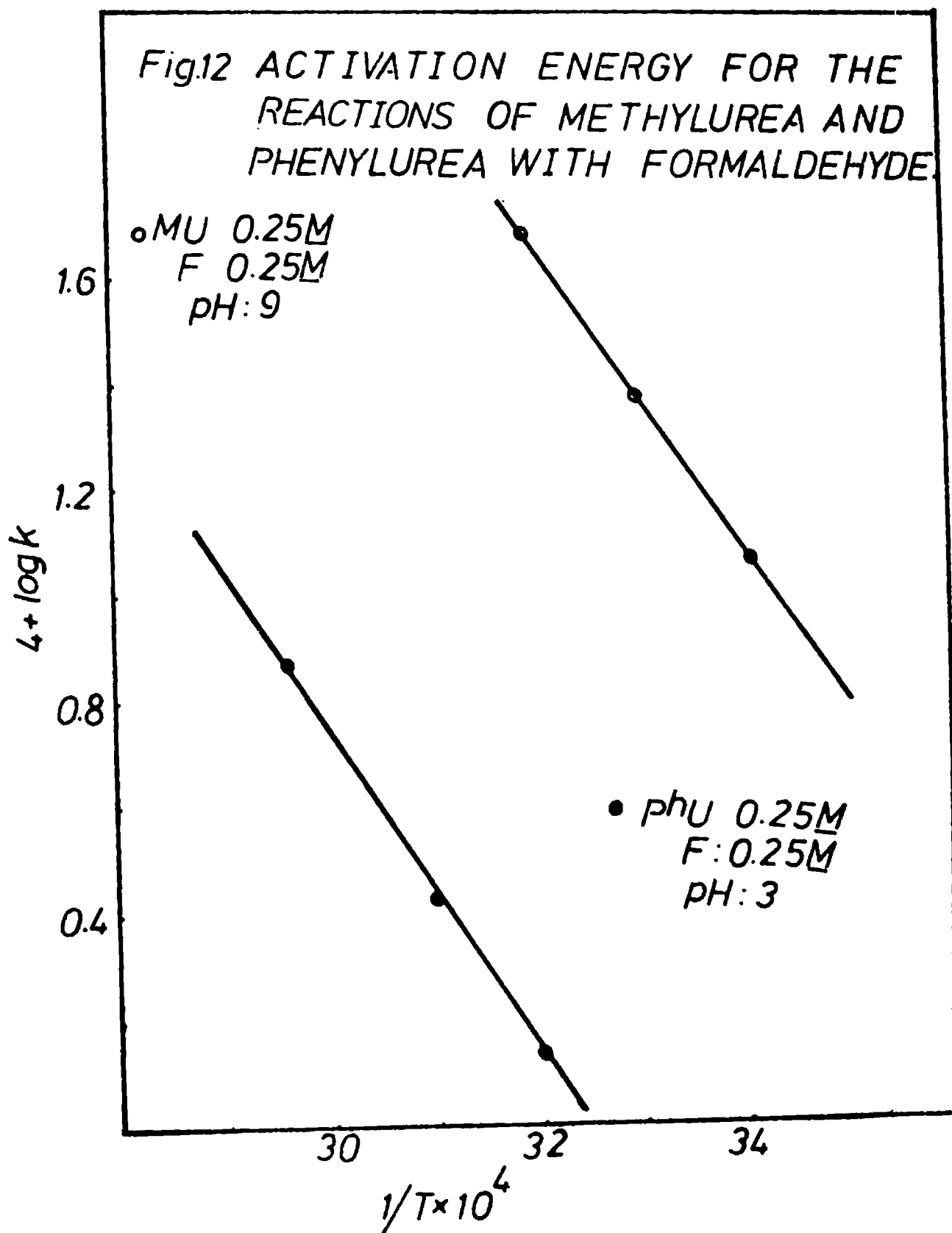
in rate of formation of MeBPhU also increased. For a 10° rise of temperature the rate doubled.

The reaction was also conducted at pH 4.7 to study the effect of acid concentration. Values obtained at 50^oC are listed in Table 78. The rate was found to be reduced more than four times at 50^oC for a change of pH from 3 to 4.7.

Reactions between PhU and F were also conducted at alkali pH. But since the pH was found to vary with time, only qualitative study has been done. Under alkaline conditions only MMPhU was formed at the very initial stages. Under strongly alkaline conditions after 24 hours, in addition to MMPhU and MeBPhU, three other additional spots were observed. In acid medium the rate of formation of the methylenebisphenylurea was reduced when the formaldehyde concentration was increased.

The above experimental details show that the condensation of MMPhU with phenylurea is exceedingly fast in acid medium and takes place to some extent also in alkaline medium. This is in contrast to the U-F reaction where no methylene linkage is produced under alkaline

Table 78

Effect of pH on PhU-F Reaction

PhU: 0.25$\underline{M}$, CH$_2$O: 0.25$\underline{M}$, pH: 4.7, Temperature: 50°C

Time (min.)	CH$_2$O m/1x10^2	Decrease in CH$_2$O m/1x10^2	MeBPhU m/1x10^2	k_{11}(first order) x 10^4 sec^{-1}
0	25.00			
30	24.40	0.60	--	5.464
60	23.83	1.17	1.4	5.455
120	22.75	2.25	2.15	5.494
180	21.75	3.25	3.26	5.534
240	20.84	4.16	4.09	5.544
300	19.95	5.05	5.00	5.625
			Av:	5.519

conditions. Therefore the reaction between PhU and F may be represented as

$$PhU + F \xrightarrow[\text{slow}]{} MMPhU \xrightarrow[\text{fast}]{PhU} MeBPhU \qquad (20)$$
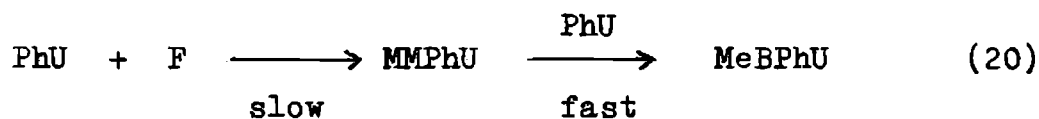
MeBPhU undergoes no dissociation under the above conditions. Since the reaction of phenylurea with formaldehyde directly gives MeBPhU the rate constants cannot be directly compared with those of urea. The first order rate constants for the disappearance of formaldehyde were calculated at $50^\circ C$ and pH 4.7 at equimolar ($0.25\underline{M}$) concentrations for urea and PhU. The values were 9.2×10^{-5} and $1.3 \times 10^{-5} sec^{-1}$ respectively. This clearly shows that the phenyl group deactivates urea towards formaldehyde addition.

CHAPTER IX

REACTIONS OF ACETAMIDE AND BENZAMIDE WITH FORMALDEHYDE

Formaldehyde reacts with amides to give methylol-amides. The reactions are reversible:

$$R\ CONH_2 \ +\ CH_2O \rightleftharpoons R\ CONHCH_2OH \qquad (21)$$
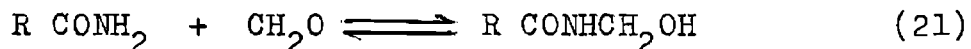
Rate of these reactions depended on the substituent R attached to the amide. Hence reactions were conducted with acetamide ($R = CH_3$) and benzamide ($R = C_6H_5$) with a view to compare the results with that of urea-formaldehyde reactions.

Reactions of formaldehyde with acetamide and benzamide were conducted only under acid conditions. In alkaline aqueous solutions the amides undergo hydrolysis. For maintaining acid pH dilute hydrochloric acid was used and no change in pH was noted during the progress of the reaction.

Reactions of Acetamide with Formaldehyde

Acetamide reacts with formaldehyde giving monomethylol-acetamide under acidic conditions. Results obtained for the formation of MMA at pH 2 and $30^\circ C$ using $0.25\underline{M}$ solutions

146

*of the reactants are given in Table 79. The reaction exhibited second order kinetics and was followed by deter-*mining the unreacted formaldehyde using hydroxylaminehydrochloride method. The results were further checked by determining the MMA formed using quantitative TLC method. Iodimetric estimation proved that methylene linkages were not formed during the reaction studied. No side products could be detected by the TLC analysis.

To study the effect of temperature on the reaction, it was also conducted at temperatures 40, 50 and $60^{\circ}C$. Results are listed in Tables 80-82. The activation energy for the reaction calculated from the plot of log k versus 1/T (at pH 2) is 15.386 k cal/mole (Fig.13). The rate constant of the reaction was found to increase 2.3 times for a rise of 10° from 50 to $60^{\circ}C$.

Effect of acid concentration on the reaction was also studied by conducting the reaction at pH values 1.2 and 3.5 at various temperatures. Data obtained at temperatures 30, 40, 50 and $60^{\circ}C$ are listed in Tables 83-87. The rate-constant was proportional to the hydrogen ion concentration. The rate increased 45 times for a change of pH from 3.5 to 1.2 at $60^{\circ}C$. At high acid concentration small amounts of methylene bisbenzamide was formed and its concentration was found to

Table 79

Analytical Data on A-F Reaction

A: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 2, Temperature: 30°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMA m/1x10^2	k_{12}(second order) x 10^6 lit mol^{-1}sec^{-1}
0	25.00			
120	24.83	0.17	--	3.80
300	24.60	0.40	--	3.61
600	24.22	0.78	0.80	3.57
900	23.81	1.19	1.10	3.70
1200	23.44	1.56	1.48	3.69
1500	23.12	1.88	1.78	3.61
1800	22.73	2.27	2.25	3.69
			Av:	3.67

Table 80

Effect of Temperature on A-F Reaction

A: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 2, Temperature: 40°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMA m/1x10^2	k_{12}(second order) x 10^6 lit mol^{-1}sec^{-1}
0	25.00			
50	24.84	0.16	--	8.58
100	24.68	0.32	--	8.39
200	24.39	0.61	0.50	8.33
300	24.10	0.90	0.95	8.29
400	23.81	1.19	1.10	8.32
500	23.52	1.48	1.38	8.39
600	23.25	1.75	1.58	8.36
			Av:	8.38

Table 81

Effect of Temperature on A-F Reaction

A: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 2, Temperature: 50°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMA m/1x10^2	k_{12}(second order) x 10^5 lit mol^{-1}sec^{-1}
0	25.00			
60	24.63	0.37	--	1.669
120	24.25	0.75	0.65	1.718
180	23.93	1.07	1.00	1.656
240	23.61	1.39	1.25	1.647
300	23.25	1.75	1.68	1.672
360	22.95	2.05	2.00	1.654
420	22.65	2.35	2.20	1.646
			Av:	1.663

Table 82

Effect of Temperature on A-F Reaction

A: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 2, Temperature: 60°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMA m/1x10^2	k_{12}(second order) x 10^5 lit mol^{-1}sec^{-1}
0	25.00			
30	24.58	0.42	0.50	3.797
60	24.19	0.81	0.80	3.721
120	23.40	1.60	1.58	3.798
180	22.65	2.35	2.20	3.842
240	21.98	3.02	2.88	3.816
300	21.42	3.58	3.44	3.738
			Av:	3.81

Table 83

Effect of pH on A-F Reaction

A: $0.25\underline{M}$, CH_2O: $0.25\underline{M}$, pH: 1.2, Temperature: $30^{\circ}C$

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMA m/1x10^2	k_{12}(second order) x 10^{5}lit mol^{-1}sec^{-1}
0	25.00			
120	24.51	0.49	--	1.133
240	24.02	0.98	0.90	1.133
360	23.53	1.47	1.37	1.156
480	23.02	1.98	1.86	1.194
600	22.61	2.39	2.19	1.174
900	21.59	3.41	3.19	1.169
			Av:	1.16

Table 84

Effect of pH on A-F Reaction

A: $0.25\underline{M}$, CH_2O: $0.25\underline{M}$, pH: 1.2, Temperature: $40^{\circ}C$

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMA m/1x10^2	k_{12}(second order) x 10^{5}lit mol^{-1}sec^{-1}
0	25.00			
30	24.72	0.28	--	2.517
60	24.40	0.60	--	2.732
120	23.77	1.23	1.2	2.875
240	23.04	1.96	1.81	2.363
300	22.45	2.55	2.40	2.524
400	21.94	3.06	2.88	2.324
			Av:	2.556

Table 85

Effect of pH on A-F Reaction

A: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 1.2, Temperature: 50°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMA m/1x10^2	k_{12}(second order) x10^{5}lit mol^{-1}sec^{-1}
0	25.00			
30	24.25	0.75	0.80	6.872
60	23.47	1.53	1.50	7.243
120	22.14	2.86	2.55	7.176
180	21.04	3.96	3.89	6.970
240	20.20	4.80	4.72	6.691
300	19.20	5.80	5.61	6.713
400	17.61	6.49	6.30	7.083
			Av:	6.964

Table 86

Effect of pH on A-F Reaction

A: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 1.2, Temperature: 60°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMA m/1x10^2	k_{12}(second order) 10^{4}lit mol^{-1}sec^{-1}
0	25.00			
30	23.19	1.81	1.57	1.734
60	21.66	3.44	3.20	1.713
90	20.23	4.77	4.57	1.746
120	19.00	6.00	5.89	1.754
150	17.98	7.02	6.89	1.735
180	17.16	7.84	7.50	1.692
			Av:	1.729

Table 87

Effect of pH on A-F Reaction
A: 0.25$\underline{M}$, CH_2O: 0.25$\underline{M}$, pH: 3.5, Temperature: $60^{\circ}C$

Time (min.)	CH_2O m/l x 10^2	Decrease in CH_2O m/l x 10^2	MMA m/l x 10^2	k_{12} (second order) x 10^6 lit mol^{-1}sec^{-1}
0	25.00			
120	24.83	0.17	--	3.80
240	24.65	0.35	--	3.94
360	24.49	0.51	--	3.85
480	24.32	0.68	--	3.88
600	24.15	0.85	0.8	3.91
810	23.77	1.23	1.2	3.81
			Av:	3.865

Fig.13 ACTIVATION ENERGY FOR THE REACTION OF ACETAMIDE AND FORMALDEHYDE.

ACETAMIDE : 0.25M
FORMALDEHYDE : 0.25M

● pH : 2.0
○ pH : 1.2
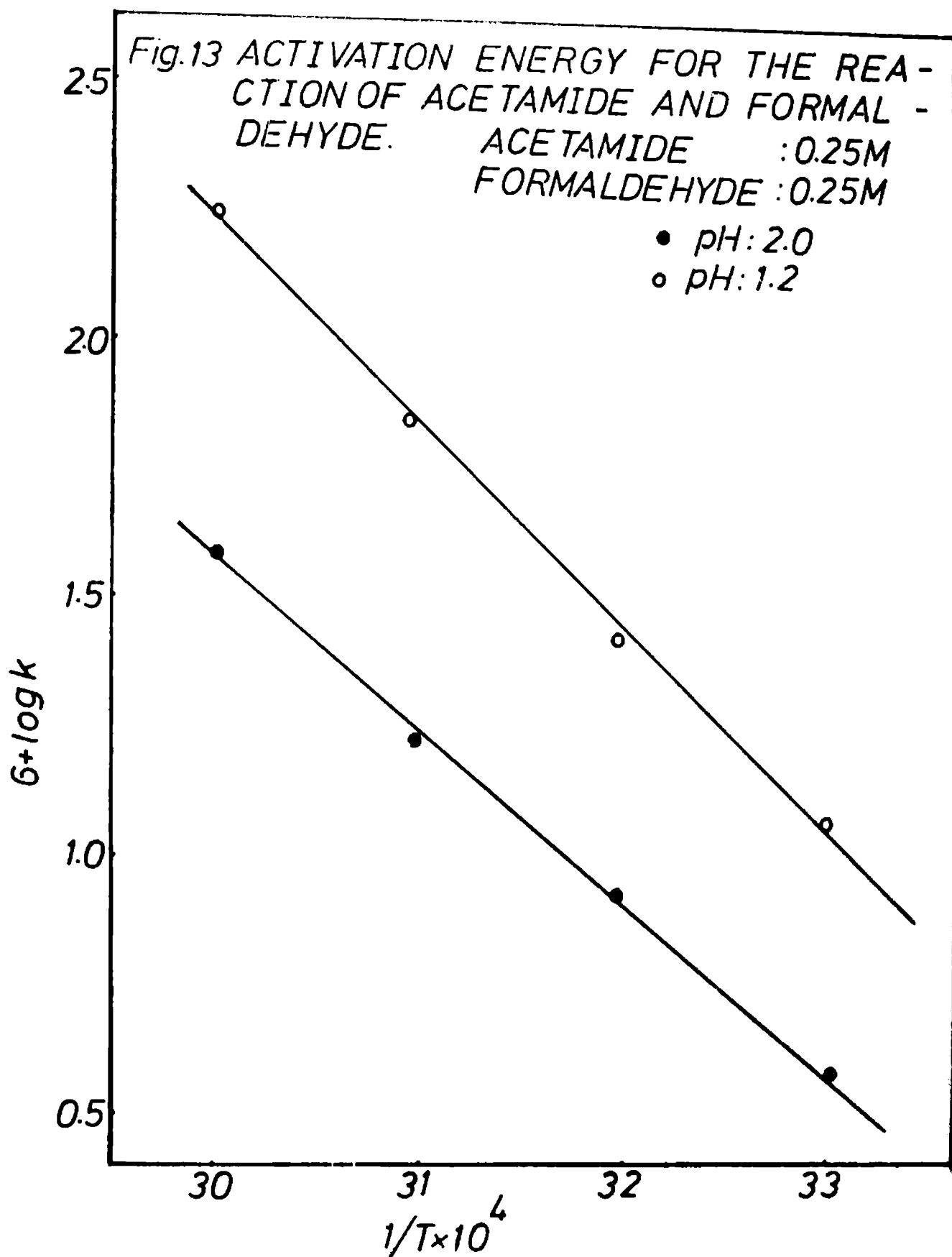
increase with increase of temperature during the later stages of the reaction.

The activation energy for the reaction at pH 1.2 was found to be 17.87 k cals/mole (Fig.13).

Reactions of benzamide with formaldehyde

Reactions of benzamide with formaldehyde was studied mainly at pH 3.5 using 0.25$\underline{M}$ solutions each of the reactants. Since the solubility of benzamide in water is poor, water and 1, 4 dioxane mixture in the ratio 1:10 was used as the medium. Monomethylolbenzamide was the only product formed during the initial stages of the reaction. Data collected for the reaction at 30°C are given in Table 88. The reaction followed second order kinetics and was catalysed by acid. Rates were determined by estimating the amount of unreacted formaldehyde using sulphite method. This was also checked by determining the amount of MMBA formed by the quantitative TLC method. Iodimetric method proved that no methylene linkages were produced during the progress of the reaction.

The effect of temperature on the reaction was studied by conducting it at 40, 50 and 60°C taking equal concentrations of the reactants (0.25$\underline{M}$) at pH 3.5. Results

Table 88

Analytical Data on BA-F Reaction

BA: 0.25$\underline{M}$, F: 0.25$\underline{M}$, pH: 3.5, Temperature: 30°C

Time (min.)	CH_2O m/lx10^2	Decrease in CH_2O m/lx10^2	MMBA m/lx10^2	k_{13}(second order) x 10^{5}lit mol^{-1}sec^{-1}
0	25.00			
60	24.75	0.25		1.122
120	24.55	0.45	0.45	1.018
180	24.31	0.69	0.70	1.051
240	24.10	0.90	0.85	1.037
300	23.89	1.19	1.15	1.031
360	23.70	1.30	1.20	1.015
			Av:	1.045

obtained are tabulated in Tables 89-91. The activation energy for the reaction was found to be 20 k cals/mole (Fig.14). The rate increased 3 times for a rise of 10° from 40 to 50^oC. Even at 60^oC no side products were found to be formed.

Reaction was also conducted at pH 4 to evaluate the effect of pH on the rate of the reaction. The rate was found to decrease. Results obtained at pH 4 and 60^oC for 0.25$\underline{M}$ concentrations each of the reactants are given in Table 92.

Increase of formaldehyde concentration did not affect the nature of the products under the above conditions. But at later stages of the reaction dimethylol benzamide was found to be present. On the other hand increase of benzamide concentration resulted in the formation methylenebisbenzamide at an earlier stage. This was also checked by iodimetric method.

Dissociation of MMBA was tried at 3.5 pH and 40-60^oC. No dissociation was observed upto 12 hours. At neutral and high acid medium the rate of dissociation was faster.

Table 89

Effect of Temperature on BA-F Reaction

BA: 0.25$\underline{M}$, F: 0.25$\underline{M}$, pH: 3.5, Temperature: 40°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMBA m/1x10^2	k_{13}(second order) x 10^{5}lit mol^{-1}sec^{-1}
0	25x00			
30	24.71	0.29	--	2.699
60	24.43	0.57	0.60	2.592
90	24.09	0.91	0.90	2.798
120	23.85	1.15	1.20	2.678
150	23.50	1.50	1.40	2.840
210	23.00	2.00	1.90	2.760
300	22.30	2.70	2.58	2.690
			Av:	2.723

Table 90

Effect of Temperature on BA-F Reaction

BA: 0.25$\underline{M}$, F 0.25$\underline{M}$, pH: 3.5, Temperature: 50°C

Time (min.)	CH_2O m/1x10^2	Decrease in CH_2O m/1x10^2	MMBA m/1x10^2	k_{13}(second order) x 10^{5}lit mol^{-1}sec^{-1}
0	25.00			
20	24.35	0.65	0.6	8.898
40	23.80	1.20	1.1	8.403
60	23.20	1.80	1.8	8.620
80	22.65	2.35	2.4	8.646
100	22.22	2.78	2.5	8.408
120	21.65	3.35	3.2	8.596
			Av:	8.595

Table 91

Effect of Temperature on BA-F Reaction

BA: 0.25$\underline{M}$, F: 0.25$\underline{M}$, pH: 3.5, Temperature: 60°C

Time (min.)	CH_2O m/lx10^2	Decrease in CH_2O m/lx10^2	MMBA m/lx10^2	k_{13} (second order) x 10^4 lit mol^{-1}sec^{-1}
0	25.00			
5	24.63	0.37	--	2.003
15	23.98	1.02	1.00	1.890
30	22.92	2.08	2.00	2.016
45	22.02	2.98	2.75	2.005
60	21.25	3.75	3.50	1.961
75	20.72	4.28	4.10	1.836
			Av:	1.952

Table 92

Effect of pH on BA-F Reaction

BA: 0.25$\underline{M}$, F: 0.25$\underline{M}$, pH: 4, Temperature: 60°C

Time (min.)	CH_2O m/lx10^2	Decrease in CH_2O m/lx10^2	MMBA m/lx10^2	k_{13} (second order) x 10^4 lit mol^{-1}sec^{-1}
0	25.00			
15	24.05	0.95	1.00	1.755
30	23.16	1.84	1.75	1.765
45	22.35	2.65	2.75	1.756
60	21.50	3.50	3.50	1.808
75	20.85	4.15	4.11	1.769
90	20.16	4.84	4.59	1.778
105	19.54	5.46	5.20	1.774
			Av:	1.771

Fig.14   ACTIVATION ENERGY FOR THE REACTION OF BENZAMIDE WITH FORMALDEHYDE.

BENZAMIDE   0.25ᴺ
FORMALDEHYDE   0.25ᴺ
pH 3.5
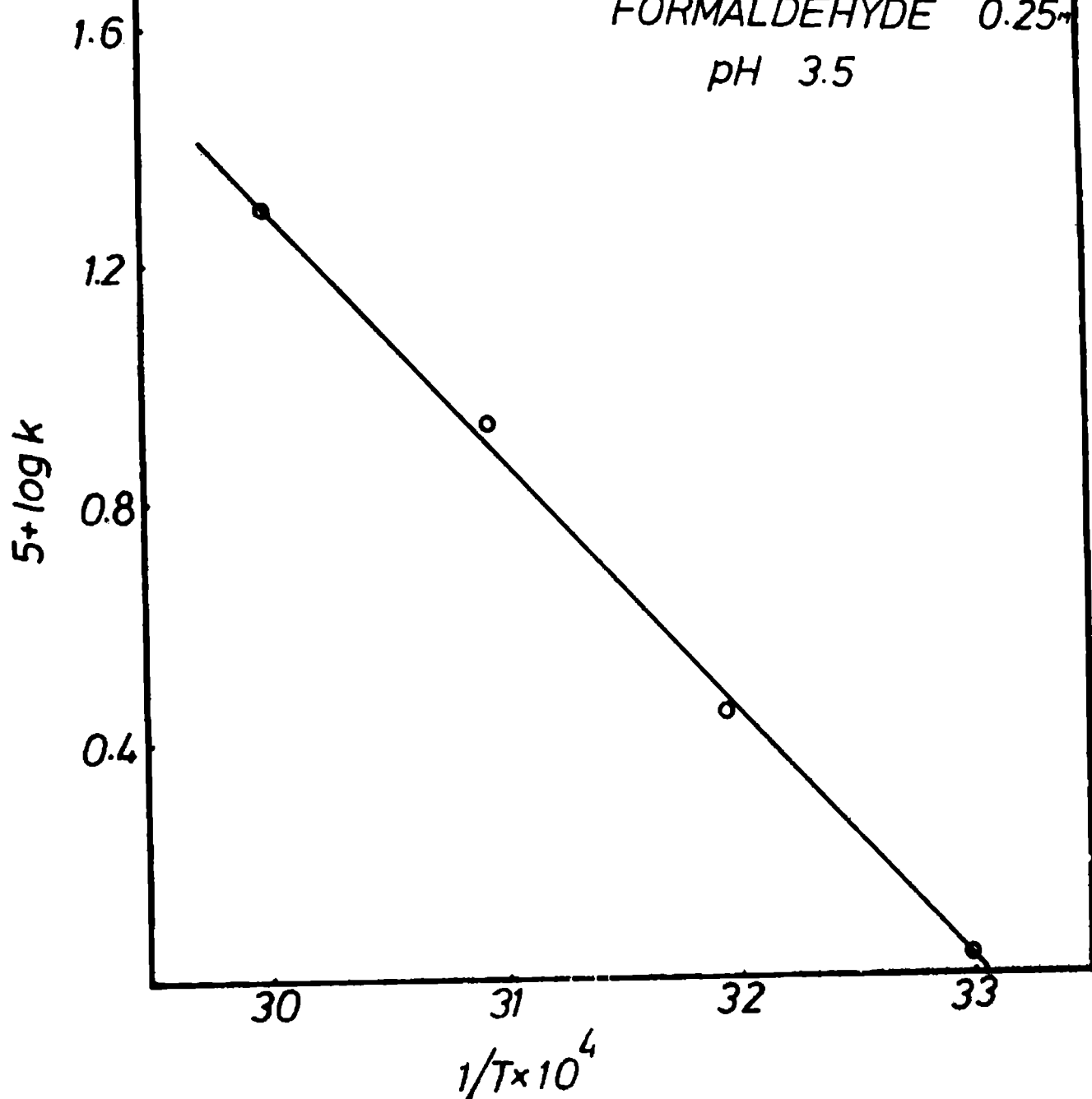
Formation of MeBBA from MMBA and Benzamide

Formation of methylene bridges by the reaction MMBA with benzamide was studied using $0.25\underline{M}$ solutions of the reactants at $40^{\circ}C$ and pH 2. Due to poor solubility of MeBBA and BA in water, water and 1, 4 dioxane in the ratio 1:1 was used as the solvent system. Results obtained are tabulated in Table 93. The reaction was followed by determining the unreacted methylol using iodimetric method. Product and unreacted methylol were estimated by the quantitative TLC method.

The methylenebisbenzamide showed no dissociation under the above pH and concentration in 1:1 dioxane-water mixture at $40^{\circ}C$ for 5 days.

Table 93

Analytical Data on MMBA - BA Reaction
MMBA: 0.25$\underline{M}$, BA: 0.25$\underline{M}$, pH: 2, Temperature: 40°C

Time (min.)	MMBA m/1x10^2	Decrease in MMBA m/1x10^2	MeBBA m/1x10^2	k'_{13}(second order) x 10^6 lit mol^{-1}sec^{-1}
0	25.00			
600	24.74	0.26	--	1.16
1800	24.23	0.77	0.65	1.17
3000	23.75	1.25	1.30	1.16
4200	23.29	1.71	1.80	1.16
5400	23.76	2.24	2.10	1.10
			Av:	1.15

DISCUSSION AND RESULTS

The main reaction steps involved in the urea formaldehyde reaction are summarised schematically in figure 15. The first and second order rate constants and activation energy values for the reactions of urea and its related compounds with formaldehyde and the dissociation of the products are summarised in Table 94. Experimental results are discussed under the following headings:-

1) Role of pH in the U-F reaction in (a) neutral, (b) alkaline, and (c) acid aqueous solutions.

2) Effect of methylol group on further additions of formaldehyde.

3) Formation of methylene bridged compounds and ether linkages.

4) Effect of substituents on the reaction of formaldehyde with amides.

Crystal structure studies and bond length measurements have shown that C-N bond in urea have some

Fig.15   COURSE OF UREA-FORMALDEHYDE REACTION

$$U + F \underset{k_2}{\overset{k_1}{\rightleftharpoons}} MMU \underset{k_6}{\overset{U\,k_5}{\rightleftharpoons}} MeDU$$
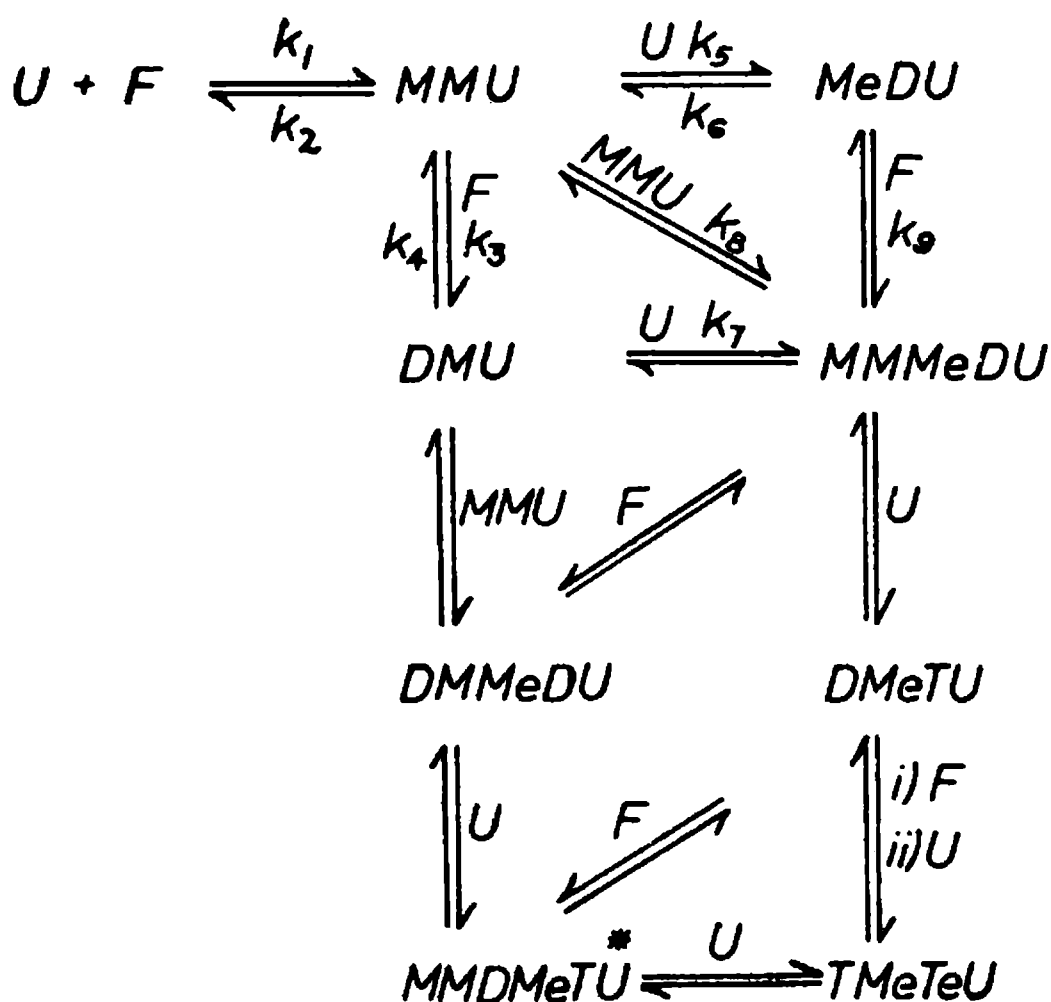
* Monomethylol dimethylene triurea

Table 94

Rate constants and activation energy values for the reactions of urea and its related compounds with formaldehyde --

Reactions of Urea with Formaldehyde

Urea m/l	CH_2O m/l	pH	Temperature $^\circ C$	Rate (second order) $\times 10^4$ lit $mol^{-1}sec^{-1}$	E k cals/ mole
0.25	0.25	7	30	1.13	
0.25	0.25	7	40	1.935	10.5
0.25	0.25	7	50	3.203	
0.25	0.25	7	60	5.365	
0.25	0.25	4.7	40	2.214	
0.25	0.25	4.7	50	3.793	11.44
0.25	0.25	4.7	60	6.708	
0.25	0.25	3.5	40	4.671	
0.25	0.25	3.5	50	8.253	13.07
0.25	0.25	3.5	60	15.954	
0.25	0.25	3	40	8.926	
0.25	0.25	3	50	22.149	17.16
0.25	0.25	3	60	40.640	
0.25	0.25	9.4	30	3.256	
0.25	0.25	9.4	40	6.612	16.7
0.25	0.25	9.4	50	14.613	
0.25	0.25	10.5	20	7.184	
0.25	0.25	10.5	30	19.546	18.3
0.25	0.25	10.5	40	54.764	
1.00	1.00	9.8	40	8.47	
0.25	0.25	9.8	40	8.25	
0.10	0.10	9.8	40	8.613	

Dissociation of MMU

MMU m/l	pH	Temperature ^oC	Rate (first order) x $10^5 sec^{-1}$	E k cals/mole
0.25	7	40	0.508	
0.25	7	50	0.835	12.0
0.25	7	60	1.460	
0.25	3.5	50	2.132	
0.25	10.5	50	13.570	

Reaction of MMU with Formaldehyde

MMU m/l	CH_2O m/l	pH	Temperature ^oC	Rate (second order) $x10^4 lit\ mol^{-1}sec^{-1}$	E k cals/mole
0.25	0.25	7	40	0.1738	
0.25	0.25	7	50	0.3628	14.29
0.25	0.25	7	60	0.6798	
0.25	0.25	4.7	30	0.3054	
0.25	0.25	3.5	30	0.4446	
0.25	0.25	10.5	30	3.4330	

Dissociation of DMU

DMU m/l	pH	Temperature ^oC	Rate (first order) x $10^5 sec^{-1}$	E k cals/mole
0.25	7	30	0.2858	
0.25	7	40	0.8867	21.8
0.25	7	50	2.5150	
0.25	3.5	30	1.067	
0.25	10.5	30	1.385	

Reactions of Urea with MMU

Urea m/l	MMU m/l	pH	Temperature °C	Rate (second order) $\times 10^4$ lit mol^{-1}sec^{-1}	E k cals/ mole
0.25	0.25	4.8	20	0.5299	
0.25	0.25	4.2	10	0.4776	
0.25	0.25	4.2	20	1.435	18.3
0.25	0.25	4.2	30	4.04	
0.25	0.25	3.8	20	4.181	
0.25	0.25	3.8	30	10.690	
0.40	0.10	4.0	20	9.362	
0.40	0.10	4.0	30	15.428	
0.40	0.10	4.0	40	31.141	
0.40	0.10	3.5	20	10.160	
0.40	0.10	3.5	30	24.28	
0.40	0.10	3.5	40	50.45	

Dissociation of MeDU

MeDU m/l	pH	Temperature °C	Rate (first order) $\times 10^5$ sec^{-1}	E k cals/mole
0.1	4.0	30	1.4698	
0.1	4.0	40	4.428	25.6
0.1	4.0	50		
0.1	3.5	30	4.335	
0.1	3.5	40	9.753	
0.1	2.9	30	13.39	
0.1	2.9	40	43.79	

Reaction of Urea with DMU

Urea m/l	DMU m/l	pH	Temperature $^{\circ}C$	Rate (second order) $\times 10^4$ lit $mol^{-1}sec^{-1}$
0.25	0.25	4.2	30	1.72

Intercondensation of MMU

MMU m/l	pH	Temperature $^{\circ}C$	Rate (second order) $\times 10^4$ lit $mol^{-1}sec^{-1}$
0.25	4.2	30	1.5

Intercondensation of DMU

DMU m/l	pH	Temperature $^{\circ}C$	Rate (second order) $\times 10^4$ lit $mol^{-1}sec^{-1}$
0.25	4.2	30	0.0178

Reactions of MeDU with Formaldehyde

MeDU m/l	CH_2O m/l	pH	Temperature $^{\circ}C$	Rate (second order) $\times 10^4$ lit mol^{-1}sec^{-1}	E k cals/ mole
0.1	0.1	7.75	30	0.6213	
0.1	0.1	7.75	40	1.308	13.73
0.1	0.1	7.75	50	2.645	
0.1	0.1	9.0	30	2.3465	
0.1	0.1	10.5	30	74.43	
0.1	0.1	5.0	50	2.344	

Reactions of MeU with Formaldehyde

MeU m/l	CH_2O m/l	pH	Temperature $^{\circ}C$	Rate (second order) $\times 10^4$ lit mol^{-1}sec^{-1}
0.25	0.25	7	30	5.205
0.25	0.25	9	20	11.34
0.25	0.25	9	30	23.68
0.25	0.25	2.5	30	13.54

Dissociation of MMMeU

MMMeU m/l	pH	Temperature $^{\circ}C$	Rate (first order) $\times 10^5$ sec^{-1}
0.25	9	30	0.0822

Reactions of PhU with Formaldehyde

PhU m/1	CH_2O m/1	pH	Temperature $^\circ C$	Rate (first order) $x\ 10^5\ sec^{-1}$	E k cals/mole
0.25	0.25	3	40	26.37	
0.25	0.25	3	50	73.41	14.5
0.25	0.25	3	65	55.19	
0.25	0.25	4.7	50	13.46	

Reactions of Acetamide with Formaldehyde

Acetamide m/1	CH_2O m/1	pH	Temperature $^\circ C$	Rate (second order) $x\ 10^4\ lit\ mol^{-1}sec^{-1}$	E k cals/mole
0.25	0.25	2	30	0.0367	
0.25	0.25	2	40	0.0838	15.386
0.25	0.25	2	50	0.1663	
0.25	0.25	2	60	0.3810	
0.25	0.25	1.2	30	0.116	
0.25	0.25	1.2	40	0.2556	
0.25	0.25	1.2	50	0.6964	17.87
0.25	0.25	1.2	60	1.729	
0.25	0.25	3.5	60	0.03865	

Reaction of Benzamide with Formaldehyde

Benzamide m/l	CH_2O m/l	pH	Temperature $^{\circ}C$	Rate (second order) $\times 10^4$ lit $mol^{-1}sec^{-1}$	E k cals/ mole
0.25	0.25	3.5	30	0.1045	
0.25	0.25	3.5	40	0.2723	20.0
0.25	0.25	3.5	50	0.8595	
0.25	0.25	3.5	60	1.952	
0.25	0.25	4.0	60	1.771	

Reaction of MMB with Benzamide

Benzamide m/l	MMB m/l	pH	Temperature $^{\circ}C$	Rate (second order) $\times 10^4$ lit $mol^{-1}sec^{-1}$
0.25	0.25	2	40	0.0115

double bond character (about 28 percent). This can be

explained by resonance.

H_2N \ / NH_2
     C
     ‖
     O

VI

$\overset{+}{H_2N}$ \ / NH_2
     C
     |
     O$-$

VII

H_2N \ / $\overset{+}{NH_2}$
     C
     |
     O$-$

VIII
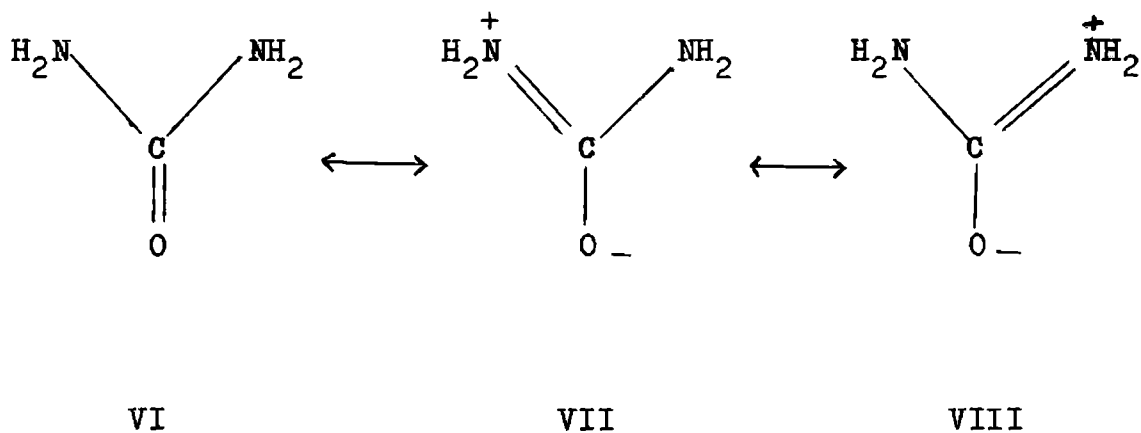
Both the N atoms are identical in the hybrid molecule.
U functions as a monoacidic base capable of protonating
with the oxygen atom. The protonated forms are

$\overset{+}{H_2N}$ \ / NH_2
     C
     |
     OH

IX

H_2N \ / $\overset{+}{NH_2}$
     C
     |
     OH

X

NH_2 \ / NH_2
     C
     ‖
     OH
     +

XI
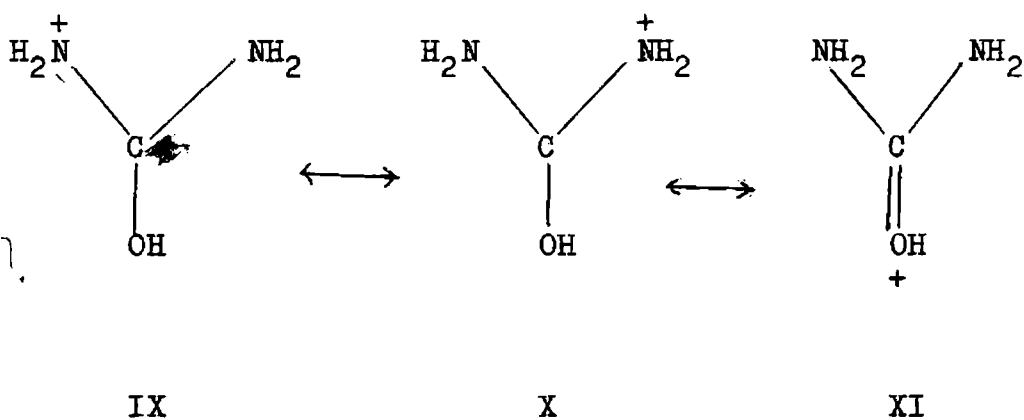
1) Role of pH in the Reaction of Urea with Formaldehyde

Reaction of urea with formaldehyde is reversible in acid, neutral and alkaline aqueous solutions. The equilibrium is independent of pH in the range 3 to 10.5. The formation of MMU follows second order kinetics while the dissociation is first order. There appears to be general acid and base catalysis.

(a) UF reaction in neutral medium

In neutral medium the formaldehyde molecule is polarised thus:

$$CH_2 = O \longleftrightarrow \overset{\delta+}{CH_2} - - - - \overset{\delta-}{O} \qquad (22)$$
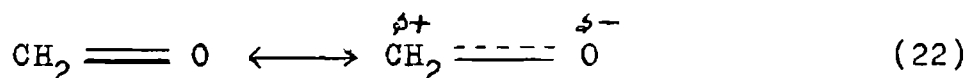
The polarised formaldehyde molecule attacks the nucleophilic amide nitrogen of urea by step (23) as follows:

$$NH_2 - \overset{\overset{\displaystyle O:}{\|}}{C} - \overset{\cdot\cdot}{NH_2} + \overset{\delta+}{CH_2} - - - - \overset{\delta-}{O}$$

$$\rightleftharpoons NH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - \overset{+}{NH_2} - CH_2 - O^-$$

$$\rightleftharpoons NH_2 - \overset{\overset{\displaystyle O}{\|}}{C} - NH - CH_2 - OH \qquad (23)$$
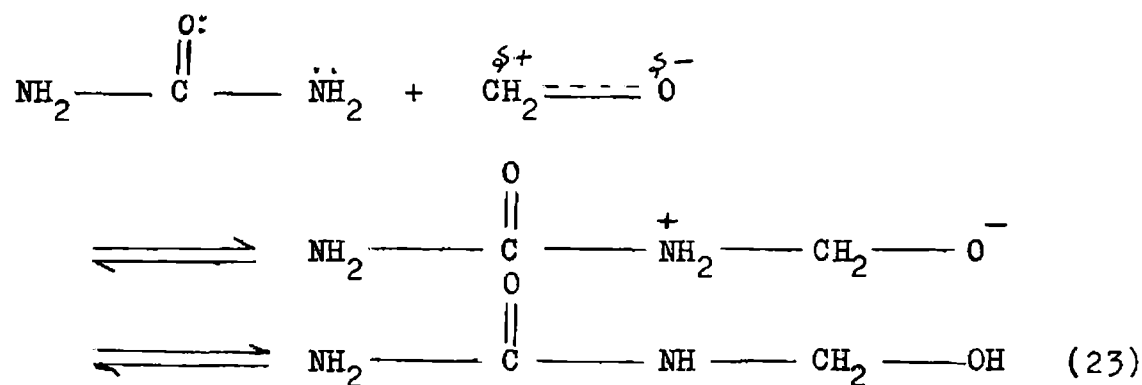
This is followed by a proton transfer giving MMU. The rate was found to be slow due to low activation of the amide nitrogen and the limited polarisation of formaldehyde molecule.

Urea formaldehyde reaction has the lowest rates in the pH range 4.5 to 8 (see Fig.1). This reaction is catalysed by acids and bases.

(b) UF reaction in acid medium

Formaldehyde is made more electrophilic by protonation.

$$CH_2 = O + H^+ \rightleftharpoons \overset{+}{C}H_2 - OH \qquad (24)$$
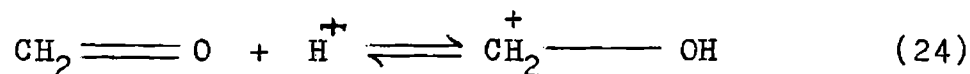
The carbonium ion so formed combines with urea molecule as follows:

$$NH_2 - \underset{\underset{O}{\|}}{C} - NH_2 + \overset{+}{C}H_2 - OH \rightleftharpoons$$

$$NH_2 - \underset{\underset{O}{\|}}{C} - \overset{+}{N}H_2 - CH_2 - OH \qquad (25)$$
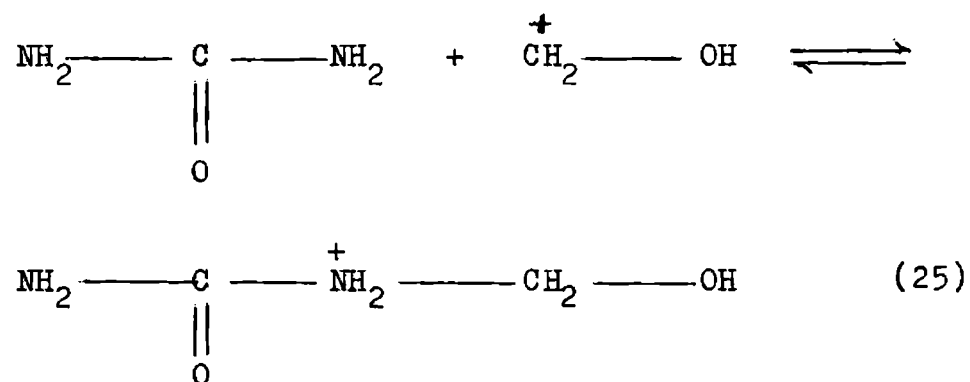
This is followed by the elimination of a proton resulting in the formation of MMU.

$$NH_2 \!-\! \overset{\displaystyle +}{\underset{\displaystyle O}{\overset{\|}{C}}} \!-\! NH_2 \!-\! CH_2 \!-\! OH \rightleftharpoons NH_2 \!-\! \underset{\displaystyle O}{\overset{\|}{C}} \!-\! NH \!-\! CH_2 \!-\! OH \quad (26)$$
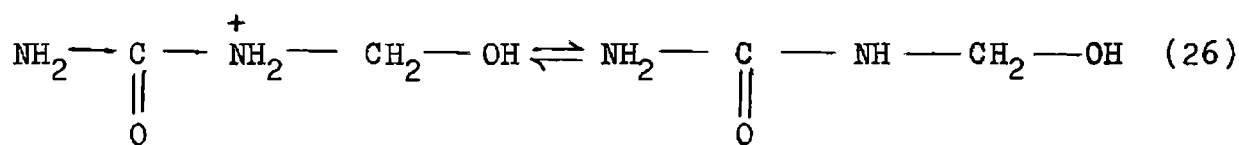
The increase of acid concentration increases the rate of the reaction by favouring the formation of methylol carbonium ion. The rate increases only 1.14 times for a change of pH from 7 to 4.7. But it increases 2.4 and 4.6 times for the pH change from 7 to 3.5 and 3 respectively. The activation energy also increases with increase of acid concentration.

(c) UF reaction in alkaline medium

Under alkaline conditions the basic catalyst may be favouring the reversible removal of a proton from urea

$$H_2N \!-\! \underset{\displaystyle O}{\overset{\|}{C}} \!-\! NH_2 + OH^- \rightleftharpoons H_2N \!-\! \underset{\displaystyle O}{\overset{\|}{C}} \!-\! NH^- + H_2O \quad (27)$$
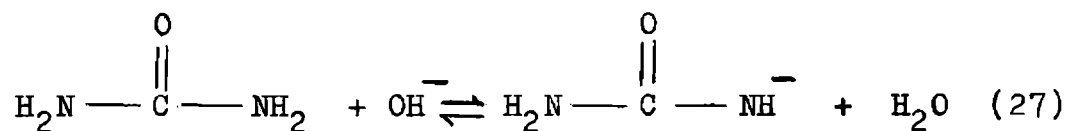
The anion thus formed may be combining with a polarised formaldehyde molecule

$$H_2N \!-\! \underset{\displaystyle O}{\overset{\|}{C}} \!-\! NH^- + \overset{\delta+}{CH_2} \!=\!\! \overset{\delta-}{O} \rightleftharpoons H_2N \!-\! \underset{\displaystyle O}{\overset{\|}{C}} \!-\! NH \!-\! CH_2 \!-\! O^-$$

$$(28)$$
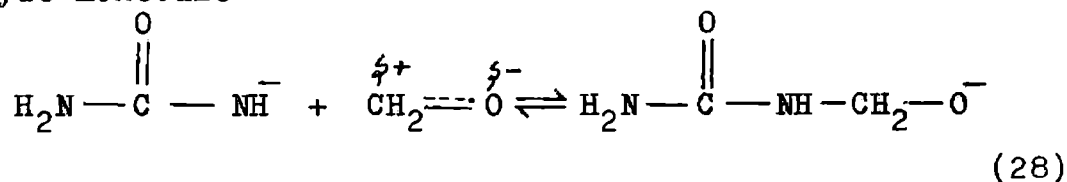
and leads to the formation of MMU by abstraction of a proton.

$$H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_2-O^- + H_2O \rightleftharpoons H_2N-\overset{\overset{\displaystyle O}{\|}}{C}-NH-CH_2-OH + OH^- \qquad (29)$$
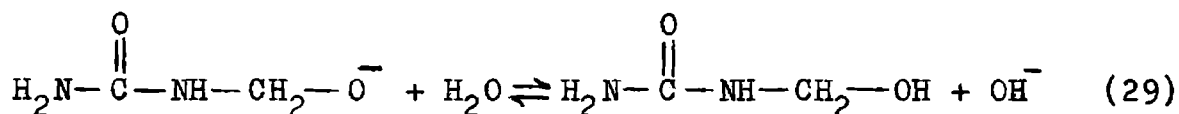
A steep increase in rate was observed in the alkaline medium which may be due to the facile formation of active amide anion. Eventhough the methylol carbonium ion favours the reaction in the acid medium a similar rapid increase of rate as in alkaline medium was not observed here. This may be due to the fact that the protonated form of urea is less reactive towards the carbonium ion.

The rate increased 28 times at $40^\circ C$ for a change of pH from 7 to 10.5.

The activation energy for the reaction increased with increase of alkali concentrations. But a steep increase was observed unlike in the case of acid pH. The entropy of activation $\Delta S^{\neq}$ (Table 24) decrease numerically with increase of acid or alkali concentration. The initial species in the U-F reaction ain acid and alkaline media are as shown below:

$$\overset{+}{N}H_2\diagdown_C\diagup NH_2 \qquad \overset{+}{C}H_2-OH \qquad NH_2^--CO-NH \qquad \overset{\delta+}{C}H_2 = \overset{\delta-}{O}$$

$$\underset{O-}{\big|}$$

XII	XIII	XIV	XV
Acid medium		Alkaline medium	
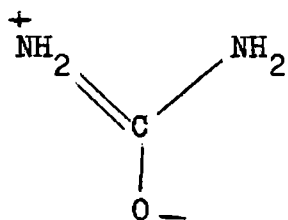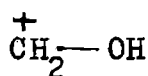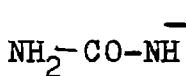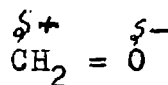
The transition states are

$$NH_2-C(=O)-\overset{+}{N}H_2-CH_2OH \qquad NH_2-C(=O)-NH-CH_2-\overset{-}{O}$$
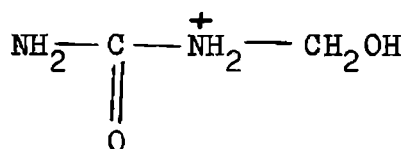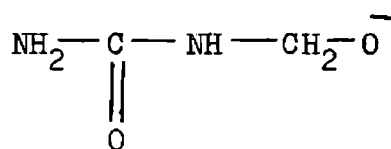
XVI   XVII

respectively in the acid and alkaline media. Increase of H^+

or OH^- increases the concentration of the initial species

and hence leads to a more order arrangement in the initial

state than in the corresponding transition states. This

explains the decreased numerical values of $\Delta S^{\neq}$ with

increase in H^+ or OH^-.

Rate of reaction of urea with formaldehyde calculated

at pH 7 and $40^{\circ}C$ for $0.25\underline{M}$ solutions (1.935×10^{-4}) was found to

be in agreement with the value of de Jong and de Jonge

(1.9×10^{-4}) collected at pH 7 and $42^{\circ}C$. But the rate was

found to be 19.546×10^{-4} lit. $mole^{-1} sec^{-1}$ at $30^{\circ}C$ and pH 10.5

and is not in agreement with the value of de Jong and de Jonge.

de Jong got only 16×10^{-4} for the reaction at pH 11.0 and $35^{\circ}C$.

Unlike phenol-formaldehyde reaction products, urea-

formaldehyde reaction products undergoes dissociation.

Monomethylolurea dissociates to urea and formaldehyde in aqueous solution due to hydrolysis. This may be due to the weak C-N bond present in urea derivatives. No change in pH was observed during the course of the reactions studied.

2) Effect of Methylol Group on Further Addition of Formaldehyde

Rate of addition of formaldehyde to MMU is lower compared to its reaction with free urea. At pH 7 and $40^{\circ}C$ the reactivity of monomethylolurea is only 1/22th of that of one amino nitrogen. The rate constants are 19.35×10^{-5} and 1.738×10^{-5} lit $mol^{-1} sec^{-1}$ for urea and MMU respectively. At pH 3.5, 4.7 and 10.5 at $30^{\circ}C$ the decrease in reactivity was constant (5-6 times). The rates lowered from 2.5×10^{-4} to 0.44×10^{-4}, 1.5×10^{-4} to 0.3×10^{-4} and 19.5×10^{-4} to 3.43×10^{-4} lit $mol^{-1} sec^{-1}$ respectively (Tables 94 and 95).

The main reason for the decreased reactivity is the statistical factor viz. methylolurea having only one reactive position compared to two in the case of urea. Further, the methylol group might be expected, on the basis of its apparent similarity with $-CH_2Cl$ group, to be electron withdrawing and hence deactivating in electrophilic

Table 95

Relative Reactivities and pK_a values for various Urea derivatives with Formaldehyde

Compound	pK_a	Overal rate constants $x10^4 lit\ mol^{-1} sec^{-1}$	Relative reactivity[*] with respect to Urea
Urea[a]		1.13	1.0
Urea[b]		1.18	1.0
Urea[c]		15.950	1.0
Urea[d]		19.546	1.0
MMU[a]		0.0794	0.140
MMU[d]		3.43	0.350
MeDU[b]		0.623	0.53
Acetamide[c]	+1.4	0.0386	0.0048
Benzamide[c]	-2.16	1.952	0.245
Methylurea[a]		23.68	41.91

[*] reactivity of one primary amino nitrogen taken as unity.

a U: 0.25M, F: 0.25M, pH: 7, Temperature: 30°C.
b U: 0.1M, F: 0.1M, pH: 7.75, Temperature: 30°C.
c U: 0.25M, F: 0.25M, pH: 3.5, Temperature: 60°C.
d U: 0.25M, F: 0.25M, pH: 10.5, Temperature: 30°C.

substitution.[109] Sprengling and Lewis[110](1953) found that
the methylol phenols have slightly higher dissociation
constants compared to phenol indicating that the $-CH_2$ OH
group is to a slight extent, electron withdrawing at
least in the ground state.

Eapen[111](1968) obtained conflicting observations
regarding the activity of a methylol group viz. a methylol
ortho to the $-OH$ of the benzene ring and a methylol group
at the para-position deactivating the ring for further
formaldehyde addition. This anomalous behaviour was
explained by him as due to hyperconjugative effect which
overtakes the inductive effect of $-OH$ group. But such an
effect is not possible in monomethylolurea. Hence the
reduced activity may be attributed to the $-I$ effect of the
methylol group.

3) Formation of Methylene Bridged Compounds and Ether
   Linkages

In the presence of acid the methylol species get
protonated resulting in the formation of a carbonium ion.
This readily combines with an amino group with the formation
of a methylene bridge.

$$> N - CH_2 - OH \overset{H^+}{\rightleftharpoons} > N - CH_2 - \overset{+}{O}H_2 \underset{-H_2O}{\rightleftharpoons}$$

$$> N - \overset{+}{C}H_2 \underset{-H^+}{\overset{:\overset{|}{N}-H}{\rightleftharpoons}} > N - CH_2 - N < \qquad (30)$$
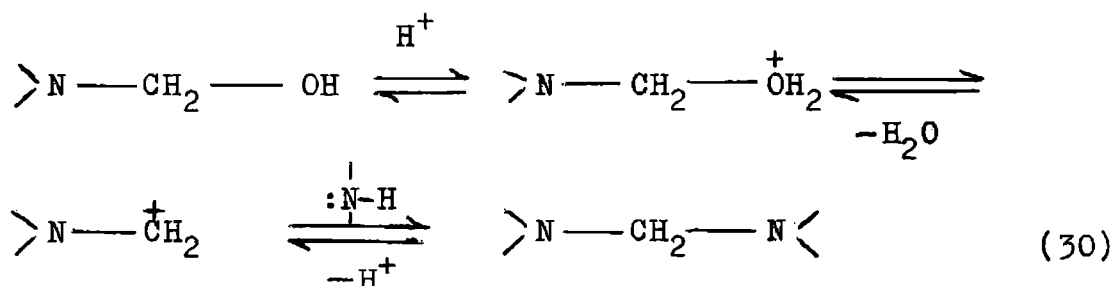
Methylene bridge formation can take place in three different ways: (i) condensation of the methylol compounds with urea, and (ii) self condensation and intercondensation of the methylol-ureas. These reactions were studied at low temperatures where the dissociation of the methylolureas are comparatively very slow. The results obtained are discussed below:-

(a) Condensation of the mono- and dimethylolureas with urea

Under similar conditions it is found that the rate of condensation of MMU with urea is greater than that of DMU with urea (Table 94). Since DMU has two reactive groups as compared to one in MMU, the former may be expected to be more reactive. The observed lower reactivity of DMU may be explained as due to the mutual deactivation of the methylol groups in DMU.

(b) Self condensation and intercondensation of MMU and DMU

These reactions were found to be slower than the reaction of MMU or DMU with urea. This is to be expected since on the one hand the methylolureas have lesser number of free reactive positions and on the other hand the methylol group has a deactivating effect on the amino group. The self condensation of DMU results probably in an ether, the

presence of which is not confirmed in the present investigation for lack of standard compounds. The intercondensation of MMU and DMU is complicated by their self condensation and hence the rates are not determined.

(c) Formation of higher homologues

There are two ways in which higher homologues can build in urea-formaldehyde reaction viz. (1) Reaction of MeDU with MMU, and (2) Formation of MMMeDU from MeDU and F, followed by its reaction with U.

In a typical reaction of MeDU and MMU it was observed that practically no trimer was obtained and the methylol and formaldehyde (as determined iodimetrically) actually increased with the time. Hence under these conditions dissociation was more favoured. On the other hand MeDU was found to react with formaldehyde readily[*], and the methylol so formed could condense easily with urea. The low reactivity of MeDU toward MMU could be attributed to the lower reactivity of the amide nitrogens as shown below:

---

[*]However the rate of formaldehyde addition to MeDU is much lower than that for the addition of F to U (Cf. p. 178)
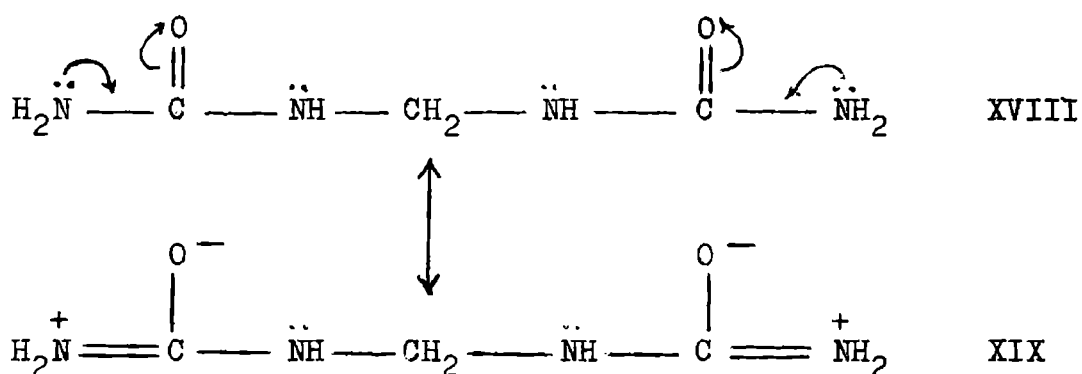
The higher reactivity of F as compared to MMU
compensates for this reduced activity of MeDU and hence
the methylols are formed. Thus the reaction of methylols
with free urea seems to be the main route for formation
of higher homologues in the UF reaction.

4) Effect of Substituents on the Reaction of Formaldehyde
   with Amides

When one of the amino group in urea was replaced
by CH_3 group (Acetamide) and C_6H_5 group (Benzamide) the
rate of the reaction of the respective amides was reduced
considerably. For acetamide the rate constant decreased
to 1/400th of that for urea at pH 3.5 and 60°C. But for
benzamide the decrease was only nearly to 1/8th under the
same conditions (Tables 94 and 95).

I.R. and NMR studies indicated that amides are
resonance hybrids and the C-N bond has a partial double

bond character.
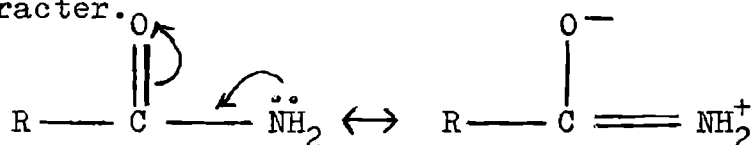
                XX   XXI

Amides are feebly basic and combine with acids (protons) to form salts of the following structure.
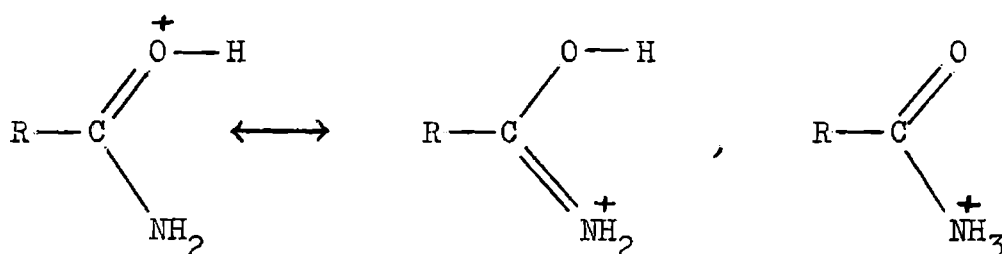
        XXII   XXIII   XXIV

NMR studies have provided evidence that the salts of acetamide is protonated on the oxygen atom. This would be in agreement with the fact that amides are resonance hybrids, the oxygen carrying a negative charge and the nitrogen a positive charge.

Unlike in the case of acetamide, in benzamide (XXVI) the ring resonates with the carbonyl group. Therefore the amino group is not deactivated to the same extent as in the

case of acetamide, eventhough protonation takes place on the oxygen atom.
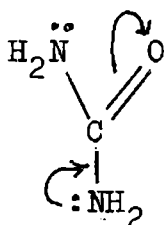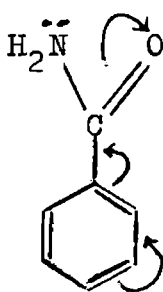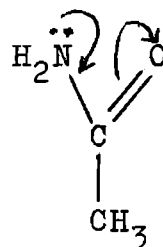
        XXV   XXVI   XXVII

In acetamide (XXVII) the amino group is deactivated since nitrogen is getting a positive charge and oxygen negative charge. In addition to that in acid medium the oxygen is protonated and nitrogen is permanently becoming positive eventhough CH_3 group is slightly electron donating. Hence the attack by the methylol carbonium ion at the amino group is inhibited and the rate of the reaction is reduced much. In benzamide (XXVI) the amino group is less deactivated since the strongly electron attracting carbonyl group which is in conjugation with the benzene ring cause electron displacement away from the nucleus and towards the carbonyl group (-R effect). In acid medium the negative oxygen will be protonated and amino group will be free for reaction. Therefore the rate of reaction with formaldehyde is not

much reduced as compared to U-F reaction. Small decrease in rate may also be explained due to the inductive effect of benzene ring eventhough it is very mild.

Introduction of a methyl group to one of the amino groups of urea increased its rate of reaction with formaldehyde 10 times at pH 7 and $30^{o}C$. But under alkaline conditions, pH 9 and $30^{o}C$, the increase was nearly 26 times (Tables 94 and 95).

The increased reactivity of methylurea towards formaldehyde is due to the fact that introduction of an electron releasing group ($-CH_3$group) is expected to increase reactivity towards formaldehyde by inductive effect.

Since the reaction of phenylurea with formaldehyde directly results in the formation of MeBPhU and not in MMPhU (chapter VIII) a direct comparison of the rate constants with those for urea or MeU cannot be made. But first-order rate constants calculated for the disappearance of formalde-hyde shows that reactivity of phenylurea towards formaldehyde is only approximately 0.3 times that of urea (Table 95). This reduced reactivity is explainable on the basis of the electron withdrawing nature of the phenyl group.

CHAPTER XI

SUMMARY AND CONCLUSION

Kinetic investigations of the reactions of urea and its related compounds with formaldehyde in aqueous acid, alkaline and neutral media have been carried out. A thin-layer chromatographic method was developed for the separation and estimation of the products of these reactions. Using this technique the various initial steps in the reactions were analysed and the rate constants have been determined.

A new method for preparing dimethylenetriurea and a modified method for the preparation of trimethylenetetraurea were reported. The products of the reactions of methylurea, phenylurea, acetamide and benzamide with formaldehyde viz., MMMeU, MeBPhU, MMA, MeBA, MMB and MeBB have been prepared by the newly developed methods.

A new spraying reagent viz., phenylhydrazine sulphate--Fe$^{(111)}$ chloride, has been used for identifying the reaction products and their colorimetric estimation.

The reaction of urea with formaldehyde is reversible in acid, alkaline and neutral aqueous solutions. The equilibrium was found to be independent of pH in the

range 3 to 10.5. The formation of monomethylolurea follows second order kinetics while the dissociation is first order. The urea-formaldehyde reaction is highly pH dependent. The rate constants being lowest in the pH range 4.5 to 8.0. Both below 4.5 and above 8.0 the rate increased rapidly with change in pH. Introduction of a methylol group was found to deactivate the urea molecule to further formaldehyde addition.

Under alkaline conditions, especially above pH 8, methylolation was the only preferred reaction and even trimethylolurea and tetramethylolurea were formed from urea and formaldehyde. In acid medium both methylols and methylene bridged compounds were formed. The formation of higher methylols were less favoured.

The various routes for methylene bridge formation were investigated and it was found that higher homologues can be formed mainly through the reaction of (i) methylenediurea with monomethylolurea (ii) methylolation of methylenediurea followed by its reaction with urea. The latter route seems to be the preferred one. The low reactivity of methylenediurea towards monomethylolurea could be attributed to the low reactivity of the amide nitrogens. Therefore the higher homologues

may be formed mainly by the reaction of methylols of
methyleneureas with urea and not by the reaction of
methylolurea with higher methyleneureas.

Hence in the alkaline media urea reacts with
formaldehyde giving low molecular weight resins contain-
ing only methylols of urea. These compounds may react
with free urea in the acid medium giving methylene
bridged compounds with or without methylol groups. The
methylene compounds thus formed may be further methylol-
ated in presence of excess formaldehyde and condense
further with free urea present. But after the trimer
stage rate of further reactions may be considerably
reduced due to less reactivity of the methylol and
primary amino groups of methyleneureas. The mechanism
of urea-formaldehyde reaction is discussed.

The reaction of acetamide and benzamide with
formaldehyde were found to be slower than that of urea
with formaldehyde. Introduction of a methyl group to
one of the amino groups (methylurea) increased its
reactivity whereas introduction of a phenyl group
(phenylurea) reduced the reactivity. The effect of
substituents on the reaction rate are explained on the
basis of the electron donating and electron withdrawing
property of the respective groups.

REFERENCES

1. B. Tollens, Ber. 17, 659 (1884).

2. Gold Schmidt, Encyclopedia of Polymer Science and
   Technology, Interscience Publishers, New York,
   Vol.2, p.13 (1965).

3. C. Ellis, Chemistry of Synthetic Resins, Reinhold,
   New York, Vol.1, p.564-723 (1935).

4. A. Einhorn, Ann. Chem., 343, 207 (1905).

5. A. Einhorn and A. Hamberger, Chem. Ber., 41, 24-28,
   (1908).

6. A. Einhorn, Ann. Chem., 361, 113 (1908).

7. H. John, U.S. Pat. 1,355,834 (1920).

8. F. Pollak, British Pat., 171, 094 (1920).

9. G. Walter, Trans. Faraday Soc., 32, 377-395 (1936).

10. A.E. Dixon, J. Chem. Soc. 113, 238-239 (1918).

11. Henkel and Cie, G.N.B.H., British Pat., 455,008 (1935).

12. F. Pollak, U.S. Pat., 1,458,543 (1923).

13. K. Ripper, U.S. Pat., 1,460,606 (1923).

14. Scheiber et al., Encyclopedia of Polymer Science and
    Technology, Interscience Publishers, New York,
    Vol.2, p.13 (1965).

15. H. Kadowaki, Bull. Chem. Soc. Japan, 11, 248 (1936).

16. G. Widmer and K. Frey in R. Houwink, Chemie und
    Technologie der Kunststoffe, Leipzig, p.276 (1939).

17. C.S. Mervel et al., J. Am. Chem. Soc. 68, 1681-1686 (1946).

18. J.I. de Jong and J. de Jonge, Rec. Trav. Chim., 72, 1027-36 (1953).

19. I. Gavat, O. Pascu-Butufei, G. Stoicescu and V. Kenyeres-Ursu, Rev. Roum. Chim., 13, 599 (1968).

20. I. Gavat, V. Kenyeres-Ursu and G. Stoicescu, Rev. Roum. Chim., 13, 809 (1968).

21. G. Valk, K. Schliefer, F. Klippel and Melliand; Textilber; 50, 335, 449, 569.

22. G. Zeppenfeld and S. Rommel, Holztechnologie, 9, 201 (1968).

23. Fundano and Shintaro, J. Am. Oil. Chem. Soc., 51 (11), 514-15 (1974).

24. J.C. Morath and J.T. Woods, Anal. Chem., 30, 1437 (1958).

25. E. Pfeil and G. Sehroth, Z. Anal. Chem., 34, 333 (1952).

26. H. Schliefer, F. Nassar and M. Kamel, Textilveredlung, 8, 207 (1973).

27. J.I. de Jong and J. de Jonge, Rec. Trav. Chim., 71, 890 (1952).

28. R. Bennewith and G. Toth, Faserforsch, Textiltech.
        19, 37 (1968).

29. S. Siggia and W. Maxcy, Ind. Eng. Chem. Anal. Ed.,
        19, 1023 (1947).

30. S.G. Denisova and T.V. Terscova, Listvennitsa,
        5, 115-19 (1974).

31. G. Coppa-Zucaria, Inds. Plastiques, 4, 183 (1948).

32. H. Levenson, Ind. Eng. Chem. Anal. Ed., 12, 332 (1940).

33. P.P. Grad and R.J. Dunn, Anal, Chem., 25, 1211 (1953).

34. Z. Ditrych, Synteticke Pryskyrice, 5, 240 (1955).

35. P.R. Avevell in "High Polymers", Vol.12, Analytical
        Chemistry of Polymers, G.M. Kline (Ed.),
        Part I, Analysis of Monomers and Polymeric
        Materials, Interscience, New York (1969).

36. C.E. Brieker and H.R. Johnson, Ind. Eng. Chem., Anal.
        Ed., 17, 400 (1945).

37. A. Petz, M. Cherubim and Holz Roh-u., Werkstoff,
        13, 70 (1955).

38. K. Dusek, J. Polym. Sci., 30, 431 (1958).

39. K. Probsthain, Z. Anal. Chem., 187, 104 (1962).

40. Haslam, J. Chem. Age, 71, 1301 (1954).

41. J. Haslam and H.S.A. Willis, Identification and
        Analysis of Plastics, Inst. Ed., Iliffe Books,
        London (1965).

42. M.L. Adams and M.H. Swann, Official Digest, 31, 1247 (1959).

43. W. Loos, Kunstoffe, 56, 222 (1966).

44. J.I. de Jong and J. de Jonge, Rec. Trav. Chim., 72, 653 (1953).

45. O. Blank and H. Finkenbeiner, Chem. Ber., 31, 2979 (1898).

46. L.M. Mobers, Plastica, 6, 392 (1953).

47. F. Kaesbauer, D. Merkel and O. Wittmann, Z. Anal. Chem., 281 (1), 17-21 (1976).

48. Richard, Brigitte., Gourdenne, Albert and C.R. Hebd. Seances, Acad. Soci. Ser. C, 281 (19), 761-3, (1975).

49. Richard, Brigitte and Gourdenne, Albert, FATIPEC Congr., 13, 550-553 (1976).

50. Richard, Brigitte and C.R. Hebd. Seances, Acad. Sci. Ser. C., 281 (20) 815-17 (1975).

51. Duclairorir, Christian and Brial, Jean C, J. Appl. Polymer. Sci., 20 (5), 1371-88 (1976).

52. J.H. Lady, R.E. Adams and I. Kesse, J. Appl. Polym. Sci. 3, 65 (1960).

53. H. Staudinger and G. Niessen, Makromole. Chemie, Sci.15, 75 (1960).

54. L.E. Smythe, J. Phys. Coll. Chem., 51, 369 (1947).

55. L.E. Smythe, J. Am. Chem. Soc., _73_, 2735 (1951).

56. L. Bettelheim and J. Cedwall, Svensk Kernisk Tidskrift, _60_, 208 (1948).

57. G.A. Crowe and C.L. Lynch, J. Am. Chem. Soc., _70_, 3796 (1948); _71_, 3791 (1949); _72_, 3622 (1950),

58. L. Donally, J. Phys. Coll. Chem., _54_, 741 (1950).

59. J.I. de Jong and J. de Jonge, Rec. Trav. Chim., _71_, 643-660 (1952).

60. J.I. de Jong and J. de Jonge, Rec. Trav. Chim., _71_, 661 (1952).

61. J.I. de Jong and J. de Jonge, Rec. Trav. Chim., _72_, 139 (1953).

62. N. Lanquist, Acta. Chem. Scand., _11_, 776-779 (1957).

63. N. Lanquist, Acta. Chem. Scand., _11_, 780-785 (1957).

64. N. Lanquist, Acta. Chem. Scand., _11_, 786-791 (1957).

65. N. Lanquist, Acta. Chem. Scand., _11_, 792-803 (1957).

66. V.A. Shenai and J.M. Manjeshwar, J. Appl. Poly. Sci. _18_, 1407-1410 (1974).

67. Y. Ito, Kogyo Kaguku Zasshi, _64_, 382-385 (1961).

68. Y. Ito, Kogyo Koguku Zasshi, _64_, 385-389 (1961).

69. S. Kambanis, R.C. Vasishth, J. Appl. Polym. Sci. _15_, 1911 (1971).

70. J.E. Armonas, For. Prod. J. _20_, 22 (1970).

71. P. Hope, B.P. Stark and S.A. Zahir, Br. Polym. J., _5_, 363 (1973).

72. D. Braun and F. Bayersdorf, Chem. Ztg., 96, 352 (1972).

73. W. Dankelman et al., Die Angewandte Makromoleculare
     Chemie, 54, 187-201 (1976).

74. D. Braun and F. Bayersdorf, Die Angewandte Makro-
     moleculare Chemie, 85, 1-13 (1980).

75. D. Braun and F. Bayersdorf, Die Angewandte Makro-
     moleculare Chemie 85, 1-13 (1980).

76. George A. Crowe, Jr. and Cecil C. Lynch, J. Am. Chem.
     Soc. 72, 3622 (1950).

77. Irma Tarvairen and Jouko Koskikallio, Acta. Chem.
     Scand, 24, 1129-1138 (1970).

78. Imoto, Minoru; Ouchi, Tatsuro; Ueno, Isamu and
     Isayama, Yasuyuki, Nippon Kagaku Kaishi (1) 155-8
     (1974)., Chemical Abstract, 81, 64393.

79. P.R. Ludlam, Analyst, 98,107-115 (1973); 98, 116-121
     (1973).

80. B. Raveendran Nair and Joseph D. Francis, J. Chrom.
     195, 158-161 (1980).

81. Y. Ogata, M. Okano and Sugawara, J. Am. Chem. Soc.,
     73, 1715 (1951).

82. Y. Ogata and M. Okano, J. Am. Chem. Soc., 72, 1459
     (1950).

83. L.E. Smythe, J. Am. Chem. Soc., 75, 574 (1953).

84. L.M. Mobers, Plastica, 7, 598 (1954).

85. G. Romijin, Z. Anal. Chem., 36, 19, 21 (1877).

86. J.F. Walker, 'Formaldehyde', (A.C.S. Monograph), Reinhold Publishing Corporation, New York, p.263 (1944).

87. W.Y. Lee, Anal. Chem., 44, 1284 (1972).

88. R. Williams, Biochem. Inst. Stud. IV, University of Texas, Publ., Austin/Texas. No.5 109, 205 (1951).

89. R.A. Fahmy, A. Niederwieser and G. Pataki u.M. Brenner., Helv. Chim. Acta. 44, 2022 (1961).

90. A.R. Patton and P. Chism., Anal. Chem., 23, 1683 (1951).

91. E. Kawerau and T. Wieland., Nature, 168, 77 (1951).

92. A. Mehlitz and K. Gierschner u.T. Minas, Chemiker-Ztg, 87, 573 (1963).

93. H. Ertel u.L. Horner., J. Chromatog., 7, 268 (1962).

94. J. Bertitti, Ann. Chim. (Rome), 44, 495 (1954).

95. R.A. Heacock and M.E. Mahon, J. Chromatog. 17, 338 (1965).

96. Blumenkrantz, Nelly and Asboe-Hansen, Gustav, Clin. Biochem., 8 (5), 293-7, (1975).

97. A. Constantinescu and C. Liteanu, Stud. Univ. Babes-Bolyai, Ser. Chem., 19 (2), 89-91 (1974).

98. M. Beroza., Agricult. and Food Chemistry, 11, 51 (1963).

99. J. Roche et al., Biochem. et. Biophys. Acta. 14, 17, (1954).

100. L. Fishbein and M.A. Cavanaugh, J. Chromatog. 20, 283 (1965).

101. L. Fishbein, Rec. Trav. Chim., 84, 465 (1965).

102. F. Reindel u.W. Hoppe., Chem. Ber. 87, 1103 (1954).

103. U. Pataki, J. Chromatog., 12, 541 (1963).

104. C.G. Grieg, and D.H. Leaback, Nature, 188, 310 (1960).

105. Lohnisky, Jan., Sverak, Vladimir and Hajik, Jiri., Krmivarstvi Sluzby, 10 (11-12), 218-22 (1974).

106. Taiwan Fertilizer Co. Hsinchu, Taiwan. Chemistry Taipei (2) 48-52 (1972).

107. Y. Ariyoshi, N. Sato, H. Zenda and K. Adachi, Bull. Chem. Soc. Jap., 44 (1971) 2558.

108. Arther A. Frost and Ralph G. Pearson, Kinetics and Mechanism, 2nd Edn., Wiley Eastern Pvt. Ltd., p.186-188 (1970).

109. L.N. Ferguson, Chem. Reviews, 50, 47 (1952).

110. G.R. Sprengling and C.W. Lewis, J. Am. Chem. Soc., 75, 5709 (1953).

111. K.C. Eapen and L.M. Yeddanapalli, Die Makromoleculare Chemie, 119, 4-16 (1968).