

Faculty of Science

(Applied Chemistry)

S.a.c. 1. RAVEENDRAN NAIR, B.—Kinetics and Mechanism of Urea-Formaldehyde and related reactions—1988—Dr. D. Joseph Francis.

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 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., MMeU, 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, methylation 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) methylation 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 containing 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 methylolated 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.