

Mercuric Chloride Catalysed Solvolysis of Benzyl Chloride in Water & Highly Aqueous Organic Solvent Systems

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Kinetics of mercuric chloride catalysed solvolysis of benzyl chloride have been studied in water, 10% aq. ethanol, 10, 20 and 30% aq. acetone and 20% aq. DMSO. The results confirm the operation of a mass law effect.

Previous work^{1,2} on the mercuric chloride catalysed solvolysis of alkyl chlorides has shown that (i) the order in catalyst is non-integral and more than unity, (ii) the order appears to reach limiting value of unity with increase in water content of the organic solvent and (iii) the catalytic activity decreases with increase in water content of the solvent. In order to verify if these observations hold good in pure aqueous medium also, we have presently investigated the solvolysis of benzyl chloride in water, water-ethanol, water-acetone and water-DMSO mixtures containing 10% (v/v) ethanol, 10, 20 and 30% (v/v) acetone and 20% (v/v) DMSO, respectively, in the presence and absence of catalyst.

Materials and Methods

The kinetics of the reaction was followed by equilibrating benzyl chloride to start the reaction, pipetting out aliquots at regular time intervals, mixing with acetone (100 ml) containing enough KI so as to destroy mercuric chloride and titrating the contents against standard alkali. In a preliminary investigation it was ascertained that titrimetric method³ was quite suitable for the present investigation.

Results and Discussion

The kinetic data presented in Table I reveal that the order in mercuric chloride is higher than one, non-integral in aquo-organic solvent containing lesser water content and decreases to a limiting value of unity as the water content of the aquo-organic solvent increases. The catalytic coefficient decreases to a minimum as described earlier¹ and then increases again with increase in water content of the solvent.

The reason for the change in catalyst order may be due to the dual role played by mercuric chloride as an electrophilic catalyst and as a polar solvating agent of the transition state in a highly nonpolar environment. In a polar environment alkyl chloride may form a

complex⁴ with mercuric chloride, thereby decreasing the enthalpy of activation for the hydrophobic process⁵. Further the inclusion of the large polarizable mercuric chloride molecule in the transition state will make it notably hydrophobic so that preferential solvation of the transition state of the mercuric chloride will become energetically favourable. The justification for the view that the presence of mercuric chloride in the transition state enhances in hydrophobicity lies in the observation reported earlier that the *m* value⁶ of the Grunwald-Winstein equation is very much less for mercuric chloride catalysed reaction than for the normal reaction. When the environment becomes sufficiently polar the capacity of

Table I—The Order in Catalyst and Catalytic Coefficient* for the Solvolysis of Benzyl Chloride

Solvent	Order in catalyst <i>m</i>	[Temp. = 40°C]	
		Catalytic coeff. c/k_0 ($\text{dm}^3 \text{mol}^{-1}$)	Corr. coeff.
Acetone (% v/v) in water			
70†	1.21	29.32	0.999
60†	1.15	21.26	0.999
50†	1.10	17.34	0.998
30	—	11.03	—
20	—	14.42	—
10	—	15.42	—
Ethanol (% v/v) in water			
80†	1.10	18.11	0.998
60†	—	17.64	—
50†	1.06	12.88	0.999
40	—	17.90	—
10	1.00	21.31	1.000
Water	1.01	25.99	0.998
Water‡	1.00	29.25	0.999

*Calculated using the Mangaly Saramma equation¹.

† Calculated from kinetic data from references 9 and 13.

‡ At 32°C

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mercuric chloride to solvate the transition state should necessarily decrease with the result that when water content of the solvent is high mercuric chloride acts only as an electrophilic catalyst.

The decrease in the value of catalytic coefficient from relatively less aqueous to more aqueous organic solvents is ascribed to the interplay of two factors, viz. (i) the capacity of mercuric chloride to solvate the transition state progressively decreases with increase in water content of the aquo-organic solvent thereby resulting in decreased catalytic activity; and (ii) although the catalysed reaction is assumed to be S_N1 (see ref. 7), the presence in the transition state of the large and polarizable mercuric chloride molecules would confer on it many of the characteristics of S_N2 transition state, i.e. the expected increase in rate with increase in polarity of the environment on the assumption that the reaction follows the S_N1 mechanism does not occur. The observation that the catalytic coefficient reaches a minimum value with increase in water content of the organic solvent and then increases can be explained as follows: In water the catalyst shifts the mechanism from the S_N2 - S_N1 borderline to the S_N1 side. In aqueous organic solvent systems the transition state of the normal reaction will lie further to the S_N2 side so that it will be more difficult for the catalyst to bring out mechanistic transition.

The first order rate constants[†] decrease with the progress of reaction in water and water-rich organic solvents employed here. This is also observed in less aq. organic solvents but the extent of decrease in rate is quite small⁹.

When the second-order treatment employed by Winstein¹⁰

$$k_2 = \frac{2.303}{t(b-a)} \log \frac{a}{b} \left(\frac{b-x}{a-x} \right)$$

is applied to the data in water and in water containing 10% ethanol (v/v) at [catalyst]=0.01 M, the drift observed in the first order rate coefficients is eliminated as can be seen from data in Table 2 showing a good second order fit.

Similar results were obtained by Winstein in acetone rich aq. acetone mixtures¹⁰ and he attributed the good second order fit to the formation of highly associated and effectively inactive $HgCl_3^-$ ion instead of the more stable $HgCl_4^{2-}$ ion. The same conclusion applies here also.

The situation in respect of the reactions in water and 10% aq. ethanol at higher [catalyst] and in aq. acetone is different. Unlike in the former case, the second order treatment does not eliminate the downward drift of the

†The initial value of the rate coefficient was obtained by the extrapolation method⁸.

Table 2—Mercuric Chloride Catalysed Solvolysis of Benzyl Chloride

[RCl] = 0.0033 M; [HgCl ₂] = 0.01 M		
Time (s)	10 ³ k ₁ (s ⁻¹)	10 ³ k ₂ (dm ³ mol ⁻¹ s ⁻¹)
Solvent: water; temp. = 32°C		
5280	3.85	4.01
10140	3.67	3.92
13980	3.59	3.91
18010	3.52	3.90
19440	3.49	3.88
Solvent: 10% (v/v) aq. ethanol; temp. = 40°C.		
3600	6.76	7.11
5550	6.50	7.08
7800	6.51	7.19
9600	6.44	7.19
10520	6.43	7.24

rate coefficients in the latter. As the [catalyst] is increased, the magnitude of decrease in rate due to complexation must necessarily become smaller, e.g. at [benzyl chloride]=0.0033 M and [catalyst]=0.01 M, even in the most favourable case of only $HgCl_3^-$ being formed, the extent of rate-reduction of 100% reaction will only be 3%. However, it is observed that the extent of reduction, as judged by the decrease in values of the first order rate coefficients, is actually much larger than when the [catalyst]=0.01 M. This implies that complexation cannot account for the decrease in rate.

The results can be explained by assuming that the catalyst is able to induce a mass-law effect. The objections to this proposal are: (i) no mass-law effect is observed at [catalyst]=0.01 M; (ii) in aquo-organic solvent poor in water content the second-order equation gives a good fit so that a mass-law effect will not be operative and (iii) a mass law effect is postulated in the reactions of a primary alkyl chloride, while such an effect is absent in the hydrolysis of a tertiary alkyl chloride such as *t*-butyl chloride.

We consider first, objections (ii) and (iii) together since the same type of argument is used to meet these objections. It has been seen that in aq. acetone solvents having a relatively small proportion of water, the stability constant of the complex ion is larger than that in water. Therefore, unless the carbonium ion possesses exceptional stability, no mass-law effect will be seen. This is obviously not true of the benzyl cation, and therefore in solvents such as 60-80% aq. acetone no mass-law effect has been noted. By the same token, the *t*-butyl cation, though more stable than the benzyl cation, also does not possess the required stability, as has been demonstrated by Bunton and Nayak using sensitive tracer method¹¹. It can be concluded that the occurrence of a mass-law effect will become more difficult in less aq. organic solvents. As the solvent is made more aqueous, the stability of the complex ions

decreases and the equilibrium shifts more in favour of mercuric chloride. Under these conditions, it will be easier for a mass-law effect to occur. In water, 10% aq. ethanol and 10% and 20% aq. acetone, the per cent decrease in rate at 50% reaction is 31.8, 19.8, 18.0 and 22.0 respectively in the presence of 0.1 M HgCl_2 ; the rate-decrease being maximum in water. On the other hand, the per cent rate decrease in 30% aq. acetone is less (only 8.3%). Further, Saramma¹² has shown that in 45% aq. acetone, the first order rate coefficients are constant even at a catalyst concentration as high as 0.3 M. Thus it can be surmised that the rate-decrease is characteristic of only water-rich solvent systems. With this background information it will be easy to comprehend as to why mass-law effect is not seen at [catalyst] = 0.01 M. At [catalyst] = 0.01 M, one of the factors affecting the mass-law effect is [carbonium ion] and the [complex ion]. Since a constant concentration of benzyl chloride has been used, the first factor is constant. The case of the complex ion will, in turn, depend on the [mercuric chloride] and [chloride ion]. Since the latter is constant, only the former is decisive. As [mercuric chloride] is increased, [complex ion] increases. Therefore, a certain minimum concentration of 0.02 M or above of the catalyst is required to

produce sufficient complex ions to bring about a significant reversal of the rate-determining stage.

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