

Second Order Fit for Mercuric Chloride Catalysed Solvolysis of Alkyl Chlorides in Aqueous DMSO Solvents

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Kinetics of mercuric chloride catalysed solvolysis of *t*-butyl chloride, benzyl chloride, *p*-methylbenzyl chloride, 1-phenylethyl chloride and triethylcarbinyl chloride have been studied in aq. DMSO, aq. acetonitrile and aq. ethanol. The kinetic data fit a second order rate equation in aq. DMSO. The calculated values of the second order rate coefficients increase in the case of aq. acetonitrile and aq. ethanol. The order in catalyst in 95% (v/v) aq. DMSO is less than unity.

It was suggested earlier that the observed drift¹ in the first order rate coefficients in the solvolysis of alkyl chlorides in aq. acetone and aq. ethanol could be eliminated by considering a second order interaction between the alkyl chloride and the catalyst². In the present note we report the results of the title investigation in order to assess the applicability of second order rate equation to the kinetic data in aq. DMSO and aq. acetonitrile.

The order in catalyst is unity in 80% DMSO-20% water and 90% DMSO-10% water. It is independent of the nature of the alkyl chloride. On the other hand in 95% DMSO-5% water the order is less than unity, the value being dependent on the structure of the alkyl chloride (Table 1). The results are tentatively explained as follows.

It is known that mercuric chloride forms solvates with DMSO³. In aquo-organic solvent media containing 80% and 90% DMSO, the water present prevents the formation of solvates. 5% (v/v) Water is insufficient to prevent the formation of mercuric chloride DMSO solvates. DMSO-water mixtures are extensively H-bonded systems like water⁴. Further the dielectric constant of DMSO is 48.9 and aq. DMSO solvents are sufficiently polar. Hence the participation of mercuric chloride as a solvating agent for the transition state is quite unlikely. One molecule of mercuric chloride is involved as an electrophilic catalyst provided there is sufficient water concentration ($\geq 10\%$) to prevent the mercuric chloride from forming solvates with DMSO. Hence the order in catalyst of unity in 80% and 90% (v/v) aq. DMSO.

The order in catalyst for various substrates decreases in the order *t*-butyl chloride > triethylcarbinyl chloride = 1-phenylethyl chloride > *p*-methylbenzyl chloride > benzyl chloride. Such an order in catalyst may be explained as follows:

In aq. DMSO solvents there is not much of selective solvation of the transition state upto 80% (v/v) aq. DMSO⁵. However, kinetic data on the salt effect in the solvolysis of alkyl chloride in 90% (v/v) aq. DMSO do appear to indicate some amount of selective solvation⁶. Hence alkyl chloride and mercuric chloride may undergo selective solvation in 95% aq. DMSO. The different alkyl chlorides undergo selective solvation to different extents. Such difference in selective solvation might get reflected in the transition state resulting in the above order in catalyst in 95% (v/v) aq. DMSO. The fact that the order in catalyst appears to be larger with the three substrates which solvolyse by S_N1 mechanism (*t*-butyl chloride, triethylcarbinyl chloride and 1-phenylethyl chloride) than with the substrates which are hydrolysed by a S_N2 mechanism (benzyl chloride and *p*-methylbenzyl

Table 1—Order in Catalyst and Catalytic Coefficient for Mercuric Chloride Catalysed Solvolysis of Alkyl Chlorides in aq. DMSO Solvents

% DMSO (v/v)	Temp. °C	Order in catalyst <i>m</i>	Catalytic coeff. $c \times 10^3$ (dm ³ mol ⁻¹ s ⁻¹)	c/k_0^* (dm ³ mol ⁻¹)	Corr. Coeff.
<i>Substrate: t-Butyl chloride</i>					
95	45	0.94	5.075	2030	1.000
90	35	1.02	3.794	1818	1.000
80	25	1.00	4.782	819	1.000
80	35	0.99	12.75	647	1.000
<i>Benzyl chloride</i>					
95	75	0.61	0.360	37	0.995
80	47	0.99	0.192	29	0.997
<i>p-Methylbenzyl chloride</i>					
95	45	0.79	0.17	136	0.999
<i>Triethylcarbinyl chloride</i>					
95	45	0.92	10.22	1392	0.993
<i>1-Phenylethyl chloride</i>					
95	45	0.92	3.579	1238	1.000

* k_0 is the first order rate coefficient for the solvolysis of alkyl chloride in the absence of catalyst and k_{obs} is that for the catalysed reaction (total rate in the presence of catalyst minus the rate of normal reaction). The initial value of the first order rate coefficient is obtained by the extrapolation method.

chloride)⁷ supports the interpretation. The decrease in catalytic coefficient is in the same order as the order in catalyst is in agreement with earlier work in the field that catalytic activity is a function of the inherent tendency of the substrate to solvolyse by a S_N1 mechanism.

It has been suggested earlier that the observed drift⁸ in the first order rate coefficients for the mercuric chloride catalysed solvolysis of alkyl chlorides in aqueous acetone mixtures of varying compositions can be eliminated by considering a second order interaction between the alkyl chloride and the catalyst². The corresponding studies are carried out in aq. DMSO, aq. acetonitrile and aq. ethanol. The results are as follows.

The second order treatment employed by Winstein and co-workers²

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

fits well in aq. DMSO irrespective of the composition of the solvent (60%, 80%, 90% and 95% v/v aq. DMSO) and the nature of the substrate. In aq. ethanolic solvents (70%, 80% and 90% v/v) the second order rate coefficients increase with the progress of reaction whereas the first order rate coefficients are fairly constant (Table 3). In the case of aq. acetonitrile (90% v/v) the second order rate coefficients increase and first order rate coefficients decrease during the progress of the reaction (Table 2).

A second order fit for the kinetic data implies that the complex ion $HgCl_3^-$ is formed by the second order interaction viz., $RCl + HgCl_2 \rightleftharpoons R^+ + HgCl_3^-$ in the solvent system. An increase in the second order rate coefficient with the progress of reaction indicates that the amount of mercuric chloride actually used up may be less than that calculated according to the second order rate law. This could arise due to the dissociation of $HgCl_3^-$ to $HgCl_2$ & Cl^- and hence an increase in concentration of mercuric chloride which may be the case with aq. ethanolic and acetonitrilic solvents. The kinetic data which fit a first order rate equation in aq. ethanolic solvents give rise to two possibilities: (i) instantaneous dissociation of the complex ion $HgCl_3^-$ and (ii) no complex formation. Earlier Foote has shown that mercuric chloride does not complex with chloride ions in ethanolic solvents⁹. In other words in aq. ethanolic solvents the equilibrium between mercuric chloride and its complex ions with chloride ions lies well in favour of mercuric chloride. On the other hand in aq. DMSO and aq. acetone the equilibrium is well in favour of the complex ion $HgCl_3^-$

Table 2—Mercuric Chloride Catalysed Solvolysis of *t*-Butyl Chloride

(Solvent = 90% (v/v) aq. DMSO; temp. = 35°C; $[RCl] = 0.025 M$; $[HgCl_2] = 0.035 M$)

Time (s)	$10^4 k_1$ (s^{-1})	$10^3 k_2$ ($dm^3 mol^{-1} s^{-1}$)
2700	1.14	3.63
3660	1.10	3.65
4640	1.07	3.65
5760	1.04	3.63
6900	1.01	3.69
7500	0.99	3.65

Table 3—Mercuric Chloride Catalysed Solvolysis of *t*-Butyl Chloride

($[RCl] = 0.05 M$; $[HgCl_2] = 0.05 M$)

Time (sec.) $10^4 k_1$ (s^{-1}) $10^3 k_2$ ($dm^3 mol^{-1} s^{-1}$)

Solvent: 90% (v/v) aq. acetonitrile; temp.: 32°C

1800	1.25	3.16
2940	1.22	3.21
3960	1.19	3.29
5160	1.16	3.40
7410	1.10	3.62
8280	1.08	3.71

Solvent: 70% (v/v) aq. ethanol; temp.: 25°C

1200	1.68	4.27
2100	1.67	4.41
2670	1.67	4.57
3180	1.67	4.77
3450	1.68	4.91
4710	1.68	5.46

and it is stabilized by these solvents. Aqueous acetonitrile shows an intermediate behaviour. The complex ion $HgCl_3^-$ progressively dissociates during the course of the reaction.

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