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Kinetics of Reaction of Methylene Iodide with Alkoxide Ion in Binary Solvent Mixtures

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Methylene iodide-alkoxide reactions in the respective alcohol-DMSO/DMF mixtures are bimolecular two-step consecutive processes, the first step being slower than the second step. The reactivity increases with increase in dipolar aprotic component of the solvent mixture. The results have been rationalised in the light of solvent polarity parameters.

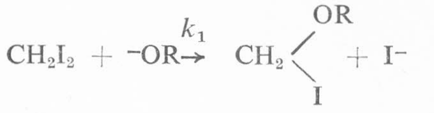
HINE and coworkers[1] studied the reaction between methylene halides and methoxide ion in methanol and found it to be a S_N2 process whereas an elimination process was observed[2] when methylene halides reacted with potassium *t*-butoxide in benzene. Later Hine and coworkers[3] studied the reaction of methylene halides with metal alkoxides in respective alcohols in detail in order to detect the change of mechanism from elimination to nucleophilic substitution. They pointed out that displacement of both the halogen atoms leading to the formation of the respective dialkyl formal, is either a one-step process or involves displacement of the first halogen atom in a rate-determining step followed by displacement of the second halogen atom in a fast step. Recently, we have reported the reaction of methylene iodide with amines[4] wherein the reactions have been shown to involve a two-step consecutive process in a number of binary solvent mixtures following nucleophilic substitution. In the background of this information, it was thought worthwhile to study the reaction of methylene iodide with alkoxide ions with a view to examining the nature of halogen displacement as well as the effect of dipolar aprotic solvents on the displacement process.

Materials and Methods

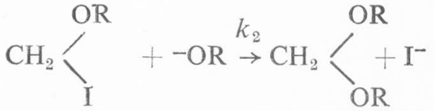
Methylene iodide (K. Light), DMSO and DMF were of extra pure grade. Absolute alcohols were used as such. Stock solutions of the alkoxides were prepared by dissolving carbonate-free conc. sodium hydroxide solution[5] in the respective alcohols. The strength of the solution was determined by acidimetry using screened indicator (mixture of methylene blue and neutral red 1% in alcohol). The reaction was followed beyond 60% by Volhard's method.

Results and Discussion

Methylene iodide reacted smoothly with alkoxide ion in binary solvent mixtures consisting of the respective alcohol and dimethyl sulphoxide or dimethylformamide at 50°C. The reaction followed total second order kinetics till about 20% of the reaction. An examination of the stoichiometry of the reaction showed that both the iodine atoms of methylene iodide are being substituted in the presence of alkoxide ions and application of Frost-Schwemer (F. S.) treatment[6], meant for a competitive and consecutive two-step process, resulted in the separation of rate constants for both the steps. The second order rate constants for the first step obtained by the F. S. treatment agreed well except a few deviations, with the calculated rate constants (obtained with second order integrated rate expression) assuming no incursion of the second step in the early phases of the reaction (Table 1). The deviations might be due to early incursion of the second step. Thus it is evident from the data that the reaction is a two-step competitive and consecutive process (Eqs 1 and 2) and not a one step one as envisaged by some of the earier workers[3].



$$CH_2I_2 + {}^-OR \xrightarrow{k_1} CH_2\left\langle \begin{matrix} OR \\ I \end{matrix} \right. + I^- \qquad ..(1)$$



$$CH_2\left\langle \begin{matrix} OR \\ I \end{matrix} \right. + {}^-OR \xrightarrow{k_2} CH_2\left\langle \begin{matrix} OR \\ OR \end{matrix} \right. + I^- \qquad ..(2)$$

Whereever it has been possible to separate k_1 and k_2 by F. S. treatment, $k_1 < k_2$ $(k_1/k_2 < 1)$ in agreement with the assumptions made by the earlier workers that second halogen atom is removed in a fast step.

The activation parameters for the first step of the reaction in various solvent mixtures have been evaluated from Arrhenius plots involving atleast four temperatures in each case (Table 2). The activation parameters are presented in Table 3.

Analysis of the data of Tables 1 and 2 reveals the following points :

(i) Increasing proportion of dipolar aprotic component in a given pair of solvents increases the rate almost linearly in the region of higher proportions of dipolar aprotic component but exponentially in regions of lower proportions. Reverse trend has

TABLE 1 — SECOND ORDER RATE CONSTANTS FOR THE TWO STEPS IN THE REACTION OF METHYLENE IODIDE WITH ALKOXIDES IN BINARY SOLVENT MIXTURES AT 50°C

Solvent	k_1(litre mol^{-1} min^{-1})		k_2(litre mol^{-1} min^{-1})
	Obs.	Calc.	Calc.
Ethyl alcohol : DMSO(v/v)			
80:20	0.034	0.030	0.059
70:30	0.084	—	—
70:30(c)	0.213	0.184	0.367
60:40	0.238	0.208	0.260
60:40(d)	1.27	1.08	3.60
50:50	0.337	—	—
40:60. .	0.713	0.630	2.09
30:70	2.36	2.14	3.40
20:80	3.88	—	—
20:80(a)	1.07	0.870	5.79
DMSO(100%)	17.28	—	—
Isopropyl alcohol : DMSO(v/v)			
80:20	0.059	0.048	0.221
70:30	0.156	0.133	0.381
70:30(d)	1.10	0.876	8.76
60:40	0.250	0.201	0.543
60:40(b)	0.196	0.155	0.360
50:50	0.888	0.757	2.29
50:50(a)	0.327	0.289	0.483
40:60	2.74	—	—
30:70	2.97	—	—
20:80	8.35	—	—
t-Butyl alcohol : DMSO(v/v)			
50:50	0.419	—	—
40:60	0.460	—	—
30:70	1.80	—	—
20:80	3.33	—	—
Ethyl alcohol : DMF(v/v)			
80:20	0.013	—	—
70:30	0.020	0.019	0.052
60:40	0.033	0.028	0.077
50:50	0.044	0.038	0.142
50:50(d)	0.323	0.265	1.06
30:70	0.112	0.099	0.211
30:70(d)	0.448	0.349	3.49
30:70(b)	0.071	0.054	0.218
20:80	0.168	0.169	0.174
20:80(d)	1.15	1.01	1.56
20:80(c)	0.495	0.383	1.09
Isopropyl alcohol : DMF(v/v)			
50:50	0.068	0.056	0.208
40:60	0.072	—	—
30:70	0.192	—	—
20:80	0.257	—	—
DMF(100%)	0.480	—	—

a = 35°C; b = 40°C; c = 60°C; d = 70°C.

$k_{1\mathrm{obs}}$ = Calculated upto 20% of the reaction using second order rate expression.

$k_{1\mathrm{calc}}$ = Rate constant obtained by F. S. treatment for the first step.

$k_{2\mathrm{calc}}$ = Rate constant obtained by F. S. treatment for the second step.

TABLE 2 — RATE CONSTANTS FOR THE FIRST STEP IN THE REACTION OF METHYLENE IODIDE WITH ALKOXIDE AT VARIOUS TEMPERATURES*

Solvent	$k_{1\mathrm{obs}}$ (litre mol^{-1} min^{-1}) at					
	35°	40°	45°	60°	70°	80°
Ethyl alcohol : DMSO(v/v)						
80:20	—	0.015	—	0.077	0.268	—
70:30	—	0.032	—	0.213	0.541	—
60:40	0.030	—	0.060	0.344	1.27	—
50:50	0.078	0.141	0.223	—	—	—
40:60	0.185	0.240	0.317	—	—	—
DMSO (100%)	3.44	5.61	—	—	—	—
Isopropyl alcohol : DMSO(v/v)						
70:30	—	0.069	—	0.317	1.10	—
60:40	—	0.196	—	0.901	2.31	—
50:50	0.327	0.529	—	2.11	—	—
40:60	1.07	1.60	—	3.95	—	—
Ethyl alcohol : DMF(v/v)						
50:50	—	—	—	0.103	0.323	0.647
30:70	—	0.071	—	0.234	0.448	—
20:80	—	0.103	—	0.495	1.15	—

*Values at 50°C are presented in Table 1.

TABLE 3 — ACTIVATION PARAMETERS FOR THE FIRST STEP OF METHYLENE IODIDE—ALKOXIDE REACTION IN BINARY SOLVENT MIXTURES AT 50°C

Solvent	$\Delta E\ddagger$ kJ mol^{-1}	$\Delta H\ddagger$ kJ mol^{-1}	$\Delta S\ddagger$ J mol^{-1} K^{-1}
Ethyl alcohol : DMSO(v/v)			
80:20	83.93	81.25	— 8.32
70:30	83.17	80.50	—10.92
60:40	93.26	90.60	— 2.17
50:50	79.74	77.06	—10.75
40:60	70.75	68.07	—15.48
Isopropyl alcohol : DMSO(v/v)			
70:30	79.74	77.06	—12.13
60:40	76.69	74.01	—13.38
50:50	60.66	57.99	—21.92
40:60	53.38	50.71	—24.80
Ethyl alcahol :			
50:50	86.02	83.34	—10.16
30:70	55.31	52.63	—29.32
20:80	73.43	70.75	—16.27

been noticed with increasing proportion of the protic component.

(ii) Higher reactivity is observed in solvent mixtures containing DMSO than that containing DMF.

(iii) The order of reactivities of alkoxides is isopropoxide > ethoxide > *t*-butoxide. This order of reactivity is very similar to that reported by Hine in so far as reactivities of isopropoxide and *t*-butoxide are concerned. The higher rate observed with sodium ethoxide over sodium *t*-butoxide compares well with methoxide and *t*-butoxide rates of Hine

TABLE 4 — ESTIMATED SOLVENT POLARITY/POLARIZABILITY PARAMETERS FOR THE MIXED SOLVENTS

Solvent	D	E_T	Z
Ethyl alcohol : DMSO(v/v)			
80:20	28.10	50.71	78.14
70:30	30.11	50.09	77.37
60:40	32.20	49.44	76.57
50:50	34.36	48.77	75.75
40:60	36.61	48.08	74.89
30:70	38.96	47.36	74.01
20:80	41.40	46.60	73.07
DMSO (100%)	46.60	45.00	71.10
Isopropyl alcohol : DMSO(v/v)			
80:20	24.25	47.80	75.14
70:30	27.02	47.44	74.62
60:40	29.85	47.12	74.16
50:50	32.64	46.76	73.65
40:60	35.43	46.41	73.14
30:70	38.22	46.06	72.63
20:80	41.01	45.70	72.11
t-Butyl alcohol : DMSO(v/v)			
50:50	31.82	44.48	—
40:60	35.09	44.58	—
30:70	38.20	44.68	—
20:80	41.13	44.78	—
Ethyl alcohol : DMF(v/v)			
80:20	27.28	49.98	76.98
70:30	28.68	49.09	75.75
60:40	30.02	48.24	74.58
50:50	31.30	47.42	73.46
30:70	33.71	45.88	71.35
20:80	34.85	45.16	70.36
DMF(100%)	37.00	43.80	68.50
Isopropyl alcohol : DMF(v/v)			
50:50	27.59	46.20	72.41
40:60	29.46	45.72	71.63
30:70	31.34	45.24	70.84
20:80	33.22	44.76	70.06

et al.[3] A decrease in rate with comparatively a more basic ion like *t*-butoxide ion rules out the possibility of an α-elimination mechanism, where one could expect large acceleration in rate with increased basicity. The higher rate in isopropoxide as compared to ethoxide is due to the higher basicity of the isopropoxide. Steric hindrance does not seem to influence the isopropoxide ion reaction with methylene iodide for isopropoxide ion can orient itself with its α-hydrogen atom towards the plane of the three non-reacting substituents of the carbon atom at which displacement is occurring, thus resulting in a planar S$_N$2 transition state[3]. On the other hand in *t*-butoxide reaction, formation of a planar transition state is difficult due to steric hindrance and basicity of the ion is therefore less significant than steric hindrance which causes lower reactivity.

The observations (i) and (ii) can be rationalised on the basis of differential solvation of the reactant molecules and transition state by the solvent system used[7]. The alkoxide ions in the present reaction are better solvated by the protic solvents than by dipolar aprotic ones for the small anions with no electron withdrawing substituents attached to them, are strong hydrogen bond acceptors[8] and participate in hydrogen bonding with protic solvents. This type of hydrogen bonding between the reactant anion and dipolar aprotic solvents does not take place as the latter are also strong hydrogen bond acceptors and hence known to function as bases. Transition state solvation by DMSO or DMF is favoured due to greater polarizability of these solvents as well as of the transition state. Another explanation accorded by Kingsbury[9], to account for the rate enhancement in increasing dipolar aprotic media, is the catalysis by these solvents due to anion desolvation although this idea has been rejected subsequently by Parker[10]. The catalysis by DMSO is due to the ability of DMSO containing solvation shell to stabilise the transition state rather than due to anion desolvation[11]. It is thus clear that polarity, polarizability of solvent molecules and differential solvation of reactant and transition state (which, in turn, depends on polarizability) are the deciding factors for the observed order of reactivities in the solvent systems. That the reactivity is a function of physical parameters of the solvents, has been shown by correlating rate parameters with quantities measuring the polarity and the polarizability of the solvent systems. Dielectric constant (D) and solvent polarity parameters of Kosower (Z) and Dimroth (E_T)[12] have been calculated from those of the pure solvents by applying Eq. (3).

$$P_{\text{mix}} = P_{s_1}.\ X_{s_1} + P_{s_2}.X_{s_2} \qquad ..(3)$$

where P_{mix}, P_{s_1} and P_{s_2} are the solvent property for mixed solvent, solvent-1 and solvent-2 respectively. X_{s1} and X_{s2} are the mol fractions of the pure solvents in the mixture. A similar procedure has been adopted recently by Ballistreri *et al.*[13] The estimated values of D, Z and E_T for solvent mixtures are given in Table 4. The plots of log k_1 versus D, E_T and Z values (Figs 1, 2 and 3 respectively) are linear (correlation coefficient 0.985 ± 0.005), thus emphasising the importance of the solvent medium.

Thus, solvation of the transition state by the dipolar aprotic component or of the reactant anion by the protic component appears to be the major factor for the observed trend in the mixed solvents. This is well brought out by the magnitude of activation entropy values in different solvent mixtures. The activation entropy values are small and negative which may be explained by invoking complex formation between solvent molecules and the solute. Solute-solvent interactions leading to solvation of either reactant molecules or the transition state is also seen from the fair linearity of activation enthalpy and entropy plots[14] (correlation coefficient .98±.01).

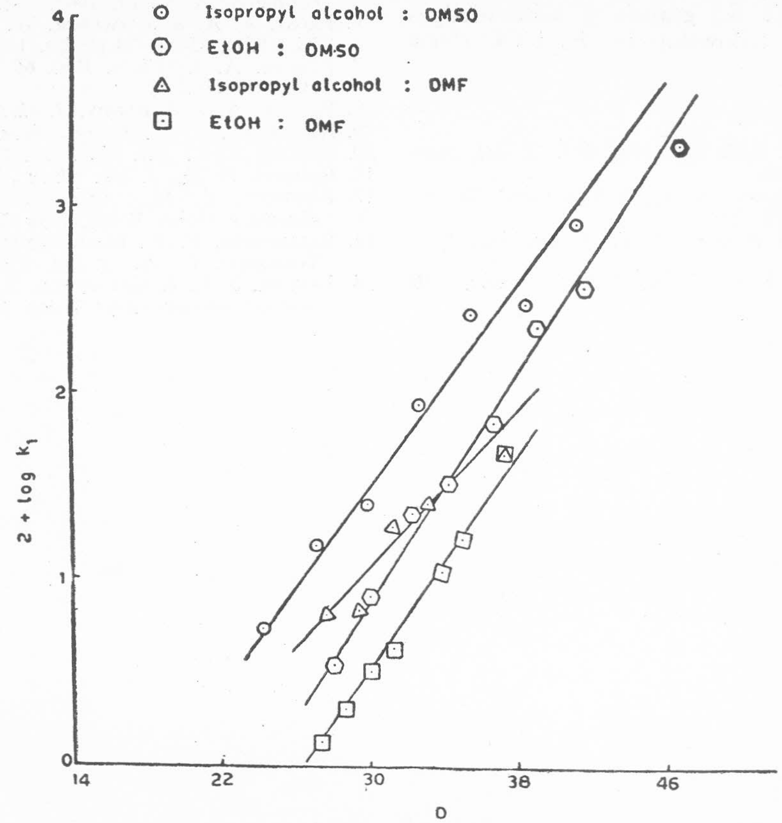


Fig. 1 — Plot of log k_1 (second order rate constant for the first step in the reaction of methylene iodide with alkoxide ion in different solvent mixtures) versus dielectric constant.

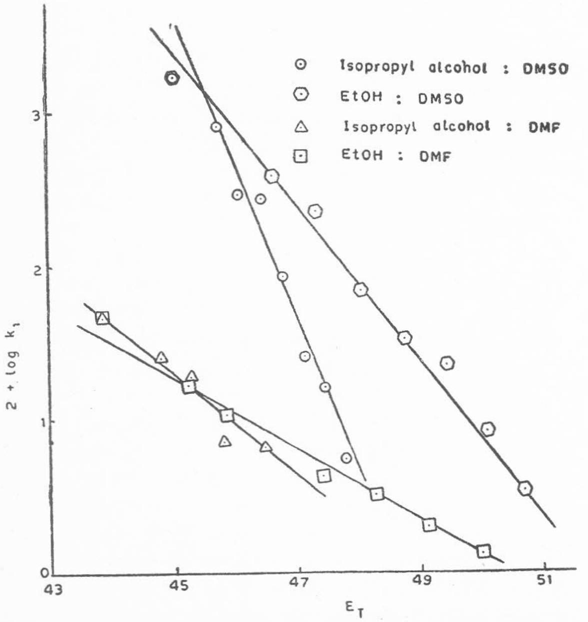


Fig. 2 — Plot of log k_1 (second order rate constant for the first step in the reaction of methylene iodide with alkoxide ion in different solvent mixtures) versus E_T.

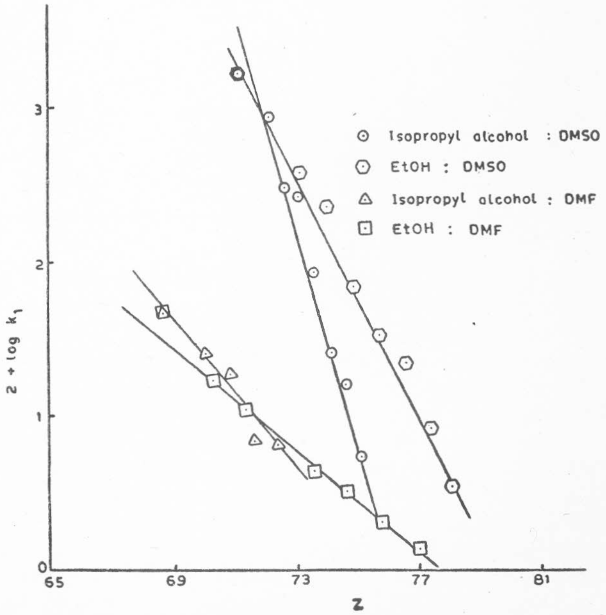


Fig. 3 — Plot of log k_1 (second order rate constant for the first step in the reaction of methylene iodide with alkoxide ion in different solvent mixtures) versus Z.

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