

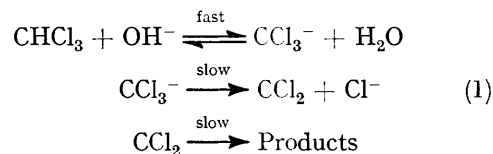
Kinetic Studies in Strongly Basic Glycolic Solutions. Part I. The Alkaline Solvolysis of Chloroform

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The acidity function behaviour of the alkaline solvolysis of chloroform has been investigated in the ethylene glycol (EG)-alkali-metal glycolate (MOG, M = Li, Na, and K) systems and the EG-Me₂SO-0.01M-NaOG system at 50 °C. The plots of log *k* (*k* = observed rate constant) against *H*₋ for the first three systems fall approximately on the same line, which is linear up to about 2M-NaOG with a slope of *ca.* 0.74, and curves down at higher concentrations. The mechanism of the reaction appears to be the same as in the aqueous and methanolic systems. The plot of log *k* vs. *H*₋ for the EG-Me₂SO-0.01M-NaOG system is much curved but the initial slope is again *ca.* 0.74. The curved nature of this plot has been explained in terms of increased dispersive interaction with increase in Me₂SO content.

ALKALINE solvolysis of chloroform has been studied by many workers in different basic media.¹⁻⁷ The mechanism for this reaction in aqueous solutions has been well established by the extensive work of Hine and his co-workers.¹ According to them the slow step is the heterolysis of the conjugate base (CCl₃⁻) to give dichlorocarbene (CCl₂), which then reacts with the solvent

to form carbon monoxide and formic acid [equation (1)].



¹ (a) J. Hine, *J. Amer. Chem. Soc.*, 1950, **72**, 2438; (b) J. Hine, Roy C. Peek, and Billy D. Oakes, *ibid.*, 1954, **76**, 827.

² S. Bose, *J. Indian Chem. Soc.*, 1960, **37**, 325.

³ P. S. Skell and I. Starer, *J. Amer. Chem. Soc.*, 1959, **81**, 4117.

⁴ J. Hine, A. D. Ketley, and Kozo Tanabe, *J. Amer. Chem. Soc.*, 1960, **82**, 1398.

⁵ R. A. More O'Ferrall and J. H. Ridd, *J. Chem. Soc.*, 1963, 5035.

⁶ J. Barbaud, C. Georgoulis, and R. Schaal, *Compt. rend.*, 1965, **260**, 2533.

⁷ C. Georgoulis, J. Pattaillet, M. Vial, and J. M. Valiry, *Compt. rend.*, 1969, **268C**, 761.

Reactions of this type are classified as *B-1* by analogy with the *A-1* reactions in acid solutions,^{5,8} whose rate constants are known to have a linear relation with the acidity function of the medium. More O'Ferrall and Ridd⁵ have studied the reaction in methanolic NaOMe and proposed a mechanism for the reaction in that medium similar to that in aqueous medium. These authors have plotted the values of $\log k$ (k being the observed first-order rate constant on keeping $C_{\text{NaOMe}} \gg C_{\text{CHCl}_3}$) against the H_- function of the system. The plot was curved, with a mean slope of *ca.* 0.8 in the region $1\text{M} < C_{\text{NaOMe}} < 3\text{M}$. Barbaud *et al.*⁶ obtained a linear plot of $\log k$ against H_- for the reaction in methanolic NaOMe and LiOMe although the slope (*ca.* 0.7) was much the same as in the earlier study. But again the linear correlation breaks down at high concentrations of methoxide.⁷ Hence a study of this reaction in basic glycolic or other similar systems should be interesting for it may provide additional information regarding the acidity function behaviour of the reaction. Recently, we have studied⁹ H_- acidity functions for the strongly basic systems of ethylene glycol (EG)–metal glycolates (MOG, $M = \text{Li, Na, or K}$) using nitro-substituted anilines and diphenylamines as indicator acids. Besides, more recently we have also determined H_- functions, for 0.01M-NaOG solutions in EG containing increasing mole % of different dipolar aprotic and protic solvents.¹⁰ This enabled us to take up the studies of the kinetics of the alkaline solvolysis of chloroform in the above EG–MOG systems as well as in the EG–Me₂SO–0.01M-NaOG system and to correlate the reaction rates with the acidity function of the respective system, which are described here.

As the reaction in the glycolic system was rather too slow at 25 °C, we have studied the reaction at 50 °C as More O'Ferrall and Ridd⁵ have done in the methanolic media, whereas our H_- functions for the systems studied are set up at 25 °C. In order to check the change in the H_- function with temperature we have set up¹¹ the $(H_-)_{\text{Am}}^{\text{EG}}$ scale for the NaOG–EG system at 50 °C up to a concentration of 2.5M-NaOG using the nitro-substituted amine indicators as before.⁹ It can be seen from the Table that the $(H_-)_{\text{Am}}^{\text{EG}}$ function at 50 °C is almost parallel to that at 25 °C in the range of NaOG concentration studied. Again in order to check the temperature dependence of the acidity-function correlation of the reaction in the glycolic system we have also studied the reaction in the NaOG–EG system at 40 °C.

EXPERIMENTAL

EG was purified and NaOG, LiOG, and KOG solutions were made as earlier.⁹ Chloroform (E. Merck, G.R.) was distilled twice in all-glass apparatus, Me₂SO was purified by a standard method.

⁸ C. H. Rochester, 'Acidity Functions,' Academic Press, London, 1970.

⁹ K. K. Kundu and Lakshmi Aiyar, *J. Chem. Soc. (B)*, 1971, 40.

¹⁰ K. K. Kundu and Lakshmi Aiyar, *J.C.S. Perkin II*, 1972, 715.

The reaction mixtures for LiOG–EG, NaOG–EG, and KOG–EG systems were prepared by adding calculated amounts (by weight) of a glycolic CHCl₃ solution to weighed quantities of glycolic MOG solutions of varying MOG concentrations, cooled to nearly 0 °C. In the case of the EG–Me₂SO–0.01M-NaOG system a standard ($\approx 0.1\text{M}$) NaOG solution in EG was added to the EG–Me₂SO mixtures of varying composition in such amounts as to bring the final NaOG concentration after addition of CHCl₃ solution to 0.01M. CHCl₃ solution was added after the mixture had been cooled to *ca.* 0 °C. The final CHCl₃ concentrations in all the reaction mixtures were kept constant at *ca.* 0.015M. The reaction was started (*i.e.* the reaction vessels were thermostatted at 50 °C) as soon as possible after mixing of the CHCl₃. The vessels were removed after different time intervals, chilled to *ca.* 0 °C, and the contents completely transferred into a vessel containing HNO₃ to neutralize the base. The solutions were titrated potentiometrically for the Cl⁻ formed using standard AgNO₃ solution. The reaction was carried out in the presence of a large excess of alkali, so that first-order kinetics were obtained.

The initial composition of the solutions were calculated by applying the known densities of the LiOG, NaOG, and KOG solutions in EG.¹¹ In the case of the EG–Me₂SO solutions, since the NaOG content was small, densities of EG¹² and DMSO¹³ were applied to calculate the volumes, 'excess volumes' being taken to be zero. As the aliquots were not all of the same volume, the titrant values of AgNO₃ were normalized to obtain that volume required for 10 ml of the aliquot. This gives V_t , the volume of AgNO₃ required to titrate 10 ml of the reaction mixture at time t . V_∞ , The corresponding volume of AgNO₃ required after completion of the reaction was obtained by calculation. The values of k were deduced from the slopes of the linear plots of $\log (V_\infty - V_t)$ against time.

RESULTS AND DISCUSSION

The k values thus obtained are given in the Table together with the MOG concentration or mole % Me₂SO of the solutions and the corresponding $(H_-)_{\text{Am}}^{\text{EG}}$ values. Figure 1 compares the plots of $\log k$ (50 °C) *vs.* H_- (25 °C), $\log k$ (50 °C) *vs.* H_- (50 °C),^{11,14} and $\log k$ (40 °C) *vs.* H_- (40 °C). Values of H_- (40 °C) were obtained by interpolation from those at 25 and 50 °C.

According to More O'Ferrall *et al.*,⁵ one of the reasons for the low slope for the plot of $\log k$ *vs.* H_- may be the difference in temperature between the kinetic studies and the indicator measurements. But later work by Barbaud *et al.*⁶ rules out this contention, at least for the methanolic system, for it is seen that the acidity function behaviour of methanolysis of CHCl₃ is independent of temperature in the region 20 °C < t < 80 °C. Now Figure 1 shows that the acidity function behaviour of the reaction in the NaOG–EG system is independent of temperature at least in the range 25 °C $\leq t \leq$ 50 °C. From the Table we see that the $(H_-)_{\text{Am}}^{\text{EG}}$ functions for

¹¹ Lakshmi Aiyar, Ph.D. Thesis, Jadavpur University, 1972.

¹² K. K. Kundu, P. K. Chatterjee, D. Jana, and M. N. Das, *J. Chem. Eng. Data*, 1970, 15, 209.

¹³ A. J. Parker, *Chem. Rev.*, 1969, 69, 1.

¹⁴ K. K. Kundu and Lakshmi Aiyar, *Indian J. Chem.*, in the press.

the system at 25 and at 50 °C are almost parallel, *i.e.* $d(H_-)/dt$ is constant for all NaOG concentrations.

TABLE

Kinetic data for the solvolysis of CHCl_3 in the different systems at the various MOG or mole % Me_2SO concentrations and the corresponding $(H_-)_{\text{Am}}^{\text{EG}}$ values

[NaOG]/M	$(H_-)_{\text{Am}}^{\text{EG } 11,14}$ (50 °C)	$(H_-)_{\text{Am}}^{\text{EG } 9}$ (25 °C)	$10^6 k^{40-50^\circ}/s^{-1}$
0.515	15.05	15.53	6.40
0.916	15.41	15.87	11.4
1.295	15.66	16.13	18.0
1.680	15.89	16.37	25.6
2.110	16.13	16.63	35.2
2.505	16.38	16.88	41.4

[KOG]/M	$(H_-)_{\text{Am}}^{\text{EG } 9}$ (25 °C)	$10^6 k^{50^\circ}/s^{-1}$
0.450	15.72	7.68
0.767	16.10	13.5
1.163	15.45	25.6
1.573	16.72	39.6

[LiOG]/M	$(H_-)_{\text{Am}}^{\text{EG } 9}$ (25 °C)	$10^6 k^{50^\circ}/s^{-1}$
0.390	15.31	3.98
0.690	15.59	5.75
1.078	15.82	8.71

[NaOG]/M	$(H_-)_{\text{Am}}^{\text{EG}}$ (40 °C)	$10^6 k^{40^\circ}/s^{-1}$
0.500	15.23	1.02
0.896	15.59	2.19
1.450	15.94	3.72
1.696	16.09	4.90
2.100	16.33	6.46
2.510	16.61	8.51

Mole % Me_2SO	$(H_-)_{\text{Am}}^{\text{EG } 10}$ (25 °C)	$10^6 k^{50^\circ}/s^{-1}$
34.73	15.73	1.66
39.78	16.02	2.89
44.40	16.32	3.98
49.44	16.67	5.97
54.48	17.10	8.71

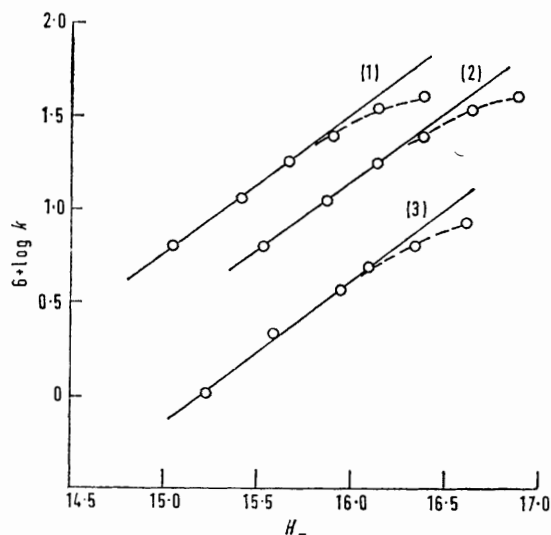


FIGURE 1 Plots of (1) $\log k$ (50 °C) vs. H_- (50 °C), (2) $\log k$ (25 °C) vs. H_- (25 °C), and (3) $\log k$ (40 °C) vs. H_- (40 °C)

From Figure 1 it is seen that $d(\log k)/dt$ is also constant for all NaOG concentrations, thus resulting in the parallel plots of $\log k$ (t °C) vs. H_- (t °C) or H_- (t' °C). The same may be taken to apply for the other systems studied

as well, and hence we are justified in using the H_- function for the system measured at 25 °C for correlation with rate at 50 °C, for it is the slopes of these correlations that concern us most.

It is seen from Figure 1 that the plot of $\log k$ vs. H_- for the NaOG-EG system is linear only up to *ca.* 2.0M NaOG and curves down beyond this concentration. The slope of the linear portion of the plot is *ca.* 0.74. Thus it seems that the reaction path in the NaOG-EG system is similar to that in methanolic and aqueous media and probably follows a scheme similar to equation (1), the first step being given by equation (2). Besides,



it is interesting to note that the points for the plots of $\log k$ vs. $(H_-)_{\text{Am}}^{\text{EG}}$ for all the three systems fall approximately on the same line with a slope of *ca.* 0.74 (Figure 2). This seems to provide extra evidence against

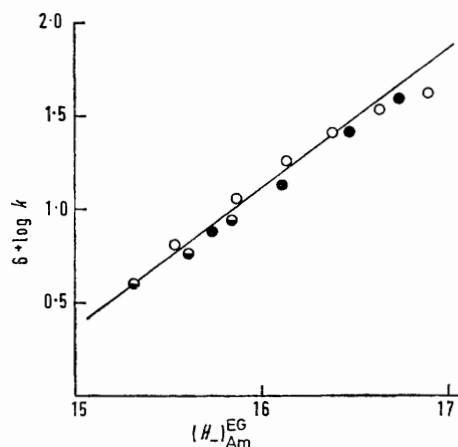


FIGURE 2 Plots of $\log k$ vs. $(H_-)_{\text{Am}}^{\text{EG}}$ for \circ = NaOG-EG, \bullet = KOG-EG, and \ominus = LiOG-EG systems

the possibility of the proton-abstraction step⁸ being rate determining, especially when the slope is rather less than unity in these systems; otherwise, the activities of glycol, which are expected to be different for the three glycolate systems, should have made the slopes different.

The rather large deviation of the slopes of the plots of $\log k$ vs. H_- from unity for the reaction in the three systems as well as in the methanolic NaOMe and LiOMe systems seems to stem from the large difference in size and structure between CHCl_3 and the nitro-anilines and diphenylamines used as indicators,⁵ the latter being much more polar. This may lead to a large difference in the solvation requirements of the transition state, *i.e.* CCl_3^- and the indicator anions. In other words, the Zucker-Hammett hypothesis,¹⁵ $f_{\text{SH}}/f^\ddagger = f_{\text{HA}}/f_{\text{A}^-}$, where f_i values are the activity coefficients of the species concerned, SH is the substrate, HA and A^- the indicator acid and its anion, and f^\ddagger represents the activity coefficient of the transition state, is not fully valid in this case. It is possible that the ratio $f_{\text{HA}}/f_{\text{A}^-}$

¹⁵ F. A. Long and M. A. Paul, *Chem. Rev.*, 1957, **57**, 935.

becomes larger and larger compared to the ratio f_{SH}/f^\ddagger with increase in base concentration,¹⁶ resulting in a decrease in the activity coefficient of factor, $\frac{f_{A^-}}{f_{HA}} \cdot \frac{f_{SH}}{f^\ddagger}$ in the rate-expression (ref. 8) and hence in a slope smaller than unity. Further, Rochester's idea⁸ that the low value of the slope may, in part, be due to the fact that chloroform is a carbon acid whereas the indicators used are nitrogen acids does not seem to be tenable, since it has now been confirmed that nitrogen acids and carbon acids behave similarly in basic solutions.¹⁷ Further, the acidity function rate correlation of alkaline degradation of *p*-dinitrobenzene in the system (see Part II of this series) probably indicates that the size and structure of the substrate compared to the indicator used is even more important than the reaction site.

The Table also includes the values of k (50 °C) and $(H_-)_{Am}^{EG}$ (25 °C) for the different mole % in EG–Me₂SO–0.01M–NaOG system. Here also the rate was too slow at 25 °C and the kinetics had to be studied at 50 °C. A simple plot of $\log k$ (50 °C) *vs.* $(H_-)_{Am}^{EG}$ (25 °C) of this system also would furnish a curved line with an initial slope of *ca.* 0.74. Assuming a similar mechanism in this system as in the MOG–EG systems the curved

nature of that plot can be interpreted in the following terms. First, although the second step of equation (1), involving a large dispersed reactant anion (CCl₃⁻) compared to the product anion (Cl⁻), is favoured by the increasing dielectric constant of the medium as Me₂SO is added, CCl₃⁻ may be more solvated by Me₂SO due to dispersive interaction than Cl⁻, thus leading to the reaction. Secondly, the Zucker–Hammett hypothesis (above) may be even less valid in this mixed solvent system where the activity coefficient of the various species are likely to be affected to greater and varied extents. The possibility that f_{HA}/f_{A^-} becomes increasingly greater than f_{SH}/f^\ddagger with increasing content of Me₂SO is even more likely in this mixed protic-dipolar aprotic solvent system than in a pure glycolic system.¹⁰ This seems to justify the decrease of the activity coefficient factor $f_{A^-}f_{SH}/f_{HA}f^\ddagger$ in the rate-expression and hence explain the observed decreased slope with increasing content of Me₂SO.

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¹⁶ Lakshmi Aiyar, Amar Nath Datta (in part), and K. K. Kundu, *J.C.S. Perkin II*, 1972, 1046.

¹⁷ J. R. Jones, *Progr. Phys. Org. Chem.*, 1972, 9, 241.