Kinetic Studies in Strongly Basic Glycolic Solutions. Part II.† Alkaline Degradation of *p*-Dinitrobenzene

By **Lakshmi Aiyar** and **K. K. Kundu**,* Physical Chemistry Laboratories, Jadavpur University, Calcutta-32, India

The alkaline degradation of *p*-dinitrobenzene (*p*-DNB) has been studied in EG–LiOG, EG–NaOG, and EG–KOG systems (EG = ethylene glycol; OG = glycolate). The observed first-order rate constant (k) for the reaction for $c_{\mathrm{MOG}} \gg c_{p\text{-}\mathrm{DNB}}$ increased much more rapidly than c_{MOG} in each system. The plots of log k against the H_- acidity function for the respective system set up with amine indicators, $(H_-)^{\mathrm{EG}}_{\mathrm{Am}}$, were linear with slopes of 0·96, 0·98, and 0·90 respectively. The plots of log k against $(H_-)^{\mathrm{EG}}_{\mathrm{Am}}$ + log c_{GOH} (c_{GOH} being the concentration of free glycol) for the respective system were also found to be linear with slopes of 1·00, 1·04, and 1·00 respectively, suggesting an $S_{\mathrm{N}}2$ mechanism for the reaction as in the case of aqueous and methanolic media. The kinetics of the reaction have also been studied in the system EG–dimethylformamide–0·01M-NaOG and the mechanism in this medium seems to be same as in the EG–MOG systems.

We describe here our studies on the alkaline degradation of *p*-dinitrobenzene (*p*-DNB) in the systems EG–LiOG, EG–NaOG, EG–KOG, and EG–dimethylformamide (DMF)-0·01M-NaOG (EG = ethylene glycol; OG = glycolate); we also correlate reaction rates with the H_- acidity functions of the respective systems.[1,2] Schaal and his co-workers have studied the reaction in the systems water–ethylenediamine[3] and methanol–methoxide.[4] In the former system they correlated the the rate with $H_- + \log a_{\mathrm{H_2O}}$ and obtained a linear relationship. In the methanolic–methoxide (MOMe) systems (M = Li, Na, and K) they plotted log k values against the H_- function for the system measured with aniline indicators and obtained a unit slope for each of the three systems, NaOMe–MeOH, KOMe–MeOH, and LiOMe–MeOH. This result is surprising for two reasons. First, it is now increasingly recognised that the dependence of acidity function on reaction rates may be a function both of the reaction mechanism and of the structure of the reacting substrate.[5] Secondly, for the alkaline degradation of a very similar substrate, namely, *o*-dinitrobenzene, Schaal *et al.*[6] obtained straight lines of dissimilar slopes for plots of log k *vs.* H_- for the three MeOH–MOMe systems, whereas they obtained

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† Part I, K. K. Kundu and L. Aiyar, preceding paper.

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[2] K. K. Kundu and Lakshmi Aiyar, *J.C.S. Perkin II*, 1972, 715.

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[4] R. Schaal and F. Peure, *Bull. Soc. chim. France*, 1963, 2638.

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unit slopes in all the three systems for plots of log k vs. $H_- + \log c_{\mathrm{MeOH}}$ (where c_{MeOH} is the concentration of 'free methanol' in the solution). Recently, Bowden *et al.*[7] have studied the alkaline hydrolysis of *p*-DNB along with that of some other 1-substituted and 4-substituted nitrobenzenes in Me_2SO containing 0·1M-tetramethylammonium hydroxide. Thus, it was considered to be of interest to extend the study of the reaction to EG–glycolate systems in order to gain a better understanding both of the reaction mechanism as well as of the behaviour of the system itself. The results of the kinetic studies were utilised to furnish the 'kinetic' J_- function for the three MOG–EG systems in line with Rochester.[5]

EXPERIMENTAL

Materials.—EG was purified as described earlier[8] and LiOG, NaOG, and KOG solutions were prepared as described earlier.[1] DMF was purified by a standard method. The dark commercial sample of *p*-DNB was treated with activated charcoal during two crystallisations from benzene; a light yellow sample, m.p. 173° was obtained. It was dissolved in benzene–light petroleum (9 : 1) mixture and chromatographed on neutral alumina with light petroleum as eluant. The sample obtained on crystallisation from benzene was almost colourless with an extinction coefficient of 13,500 at 264·5 nm (Figure 1).

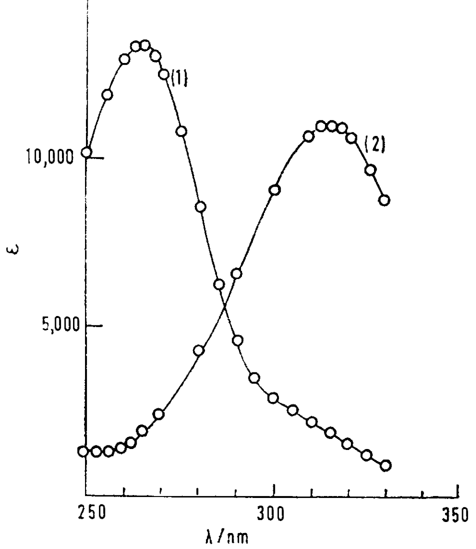

FIGURE 1 Absorption spectra of (1) *p*-dinitrobenzene in EG and (2) the degradation product in the NaOG–EG system

Kinetic Runs.—The solutions were prepared by weight, calculated amounts of a glycolic solution of *p*-DNB being added to weighed quantities of glycolate solutions of varying glycolate concentration or EG–DMF–NaOG solutions of varying compositions containing NaOG in such amounts as to bring the final concentration after addition of *p*-DNB solution to 0·01M. The substrate concentration ranged (constant for all runs of a particular experiment) between 6×10^{-5} and 8×10^{-5}M in the four experiments, and thus $c_{\mathrm{MOG}} \gg c_{p\text{-DNP}}$. The rates were followed by optical density measurements of the solutions with time. Spectral measurements were made as before,[1] at a room temperature of 27—28 °C; this was close to that (25 °C) at which the $(H_-)^{\mathrm{EG}}_{\mathrm{Am}}$ acidity scales had been set up. Measurements were made at 315 nm, the $\lambda_{\mathrm{max.}}$ of the product (ε 11,000). Since at this wavelength the substrate has an extinction coefficient of only 1850 (Figure 1) the wide difference in the absorption of the product and the reactant permitted easy study of the reaction. The change in optical density with time was noted in solutions of increasing alkali concentration or increasing mole % DMF and the final (infinite) readings were taken after several half-lives of the reaction. When the logarithm of the difference between the optical densities of a particular solution at infinite time and at time t, $\log (D_\infty - D_t)$, is plotted against t, straight lines were obtained; this confirms that the reaction is first order with respect to *p*-DNB.[4] From the slopes of these plots k was obtained by the relation, $k = -2{\cdot}303 \times$ slope.

RESULTS AND DISCUSSION

Table 1 gives the kinetic data for the reaction in the three EG–MOG systems. Plots of k against c_{MOG} rise very rapidly for all the three systems, but when log k is plotted against the $(H_-)^{\mathrm{EG}}_{\mathrm{Am}}$ function of the respective system (Figure 2) straight lines with slopes of 0·96, 0·98, and 0·90 for the LiOG–EG, NaOG–EG, and KOG–EG systems respectively were obtained. Thus not only are the slopes different, but at least one (KOG–EG) is appreciably less than unity.

TABLE 1

Kinetic data for the alkaline degradation of *p*-DNB in the three MOG–EG systems

[MOG]/M	$(H_-)^{\mathrm{EG}}_{\mathrm{Am}}$ [a]	$10^5 k/\mathrm{s}^{-1}$
	MOG = NaOG	
0·292	15·24	3·185
0·523	15·53	6·409
0·755	15·74	9·596
0·928	15·88	13·97
1·269	16·10	22·72
1·644	16·34	36·12
2·037	16·58	62·79
	MOG = KOG	
0·141	15·03	1·279
0·324	15·52	3·492
0·766	16·09	10·66
0·985	16·30	16·69
1·219	16·49	24·83
1·389	16·61	33·37
	MOG = LiOG	
0·138	14·82	1·152
0·256	15·10	1·920
0·417	15·30	2·740
0·617	15·47	3·838
0·804	15·58	4·935
0·960	15·65	6·141
1·001	15·67	6·825

[a] Interpolated data from ref. 1.

Although a quantitative analysis of the products was not made, the spectrum of the resultant solution (Figure 1), which is very similar to that of *p*-nitroanisole in methanolic methoxide solutions,[4] and the observed positive test for the NO_2^- in the resultant solution, suggest that the reaction sequence should be similar

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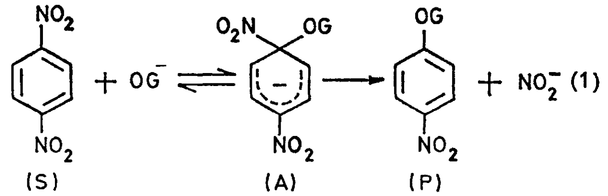
[8] Lakshmi Aiyar, Amar Nath Dutta (in part), and K. K. Kundu, *J.C.S. Perkin, II*, 1972, 1046.

to that in aqueous [3,7] and methanolic systems [4] [equation (1)] where the product P is evidently 2-(4-nitrophenoxy)-ethanol.



For the aqueous ethylenediamine [3] and methanolic media [4] Schaal *et al.* have proposed a fast pre-equilibrium involving the addition of base to the substrate to form an intermediate anion, and a slow rate-determining decomposition of the latter to products; in contrast Bowden *et al.*[7] propose that in aqueous Me_2SO the addition of hydroxide to the substrate is the rate-determining step. As Rochester has pointed out [5] for the S_N2 reaction of 2,4-dinitroanisole, either of the above two mechanisms will lead to the same rate equation, the only observable difference being in the rate constant; the acidity function behaviour of the reaction cannot distinguish between the two mechanisms. Bowden [7] has noted however that much evidence [9-13] clearly indicates a two-stage mechanism [see equation (1)] for similar substrates in basic media, and has suggested that for the particular reaction studied here, the addition step is rate determining. For such a mechanism it is known that when log *k* is plotted against the J_- function for the system it should give a straight line with unit slope.[14]

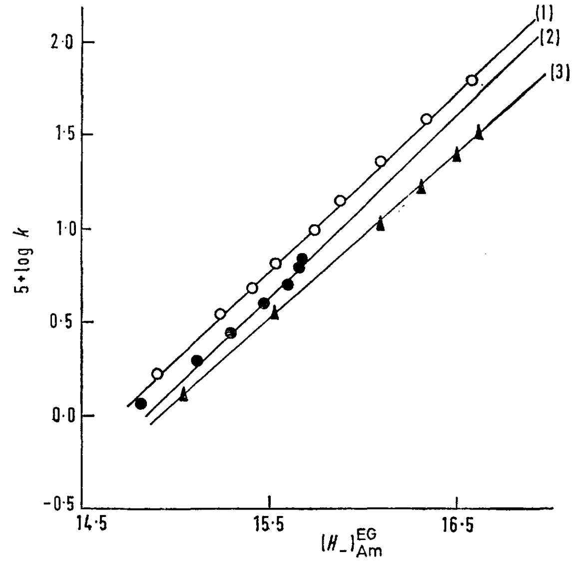


FIGURE 2 Plots of log *k* *vs.* $(H_-)^{EG}_{Am}$ for the alkaline degradation of *p*-DNB in the three systems: (1) NaOG–EG, (2) LiOG–EG, and (3) KOG–EG

Although a conventional J_- function measured with indicators which undergo addition of base in the medium is not known for the glycolic systems, an approximate $(J_-)^{EG}$ function can be computed using relation (2).[5,15] In absence of activity data for glycol in the systems studied, we may tentatively substitute the 'free glycol' concentration for a_{GOH}.[16,17] Thus relation (2) takes the form (3),

$$(J_-)^{EG} = (H_-)^{EG} + \log a_{GOH} \qquad (2)$$

$$\approx (H_-)^{EG} + \log c_{GOH} \qquad (3)$$

Hence a plot of log *k* *vs.* $(H_-)^{EG} + \log c_{GOH}$ should give a linear plot with almost unit slope, as Anbar *et al.*[18] predicted for similar reactions in aqueous solutions. The concentration of 'free glycol', c_{GOH} (Table 2) in these systems have been obtained after Yagil [17] using the 'best fit' empirical values of $n = 0$, 2, and 3·5 for the EG–LiOG, EG–NaOG, and EG–KOG systems [19] respectively (*n* is a solvation parameter). The $(J_-)^{EG}$ values for the three systems calculated by equation (3) are given in Table 2. The slopes of the linear plots of log *k* *vs.* $(J_-)^{EG}$ are 1·00, 1·04, and 1·00 for the LiOG–EG, NaOG–EG, and KOG–EG systems respectively. This appears to suggest that as in the other solvent systems,[3,7] the mechanism of the reaction

TABLE 2

Values of c_{GOH} calculated with empirical *n* values,[19] $(J_-)^{EG}$ $[=(H_-)^{EG}_{Am} + \log c_{GOH}]$, and $(J_-)^{EG}_k$, with increasing concentration of MOG

[MOG]/M	c_{GOH}	$(J_-)^{EG}$ $[=(H_-)^{EG}_{Am} + \log c_{GOH}]$	$(J_-)^{EG}_k$
		MOG = NaOG	
0·10	0·98	14·74	14·75
0·25	0·96	15·15	15·17
0·50	0·92	15·48	15·52
0·75	0·88	15·68	15·74
1·00	0·84	15·86	15·93
1·25	0·80	16·01	16·09
1·50	0·76	16·14	16·24
1·75	0·72	16·26	16·34
2·00	0·68	16·39	16·53
		MOG = KOG	
0·10	$0·97_5$	14·81	14·75
0·25	0·94	15·30	15·20
0·50	0·88	15·76	15·57
0·75	0·82	15·98	15·81
1·00	0·76	16·18	16·03
1·25	0·70	16·33	16·21
1·50	$0·63_5$	16·47	16·37
		MOG = LiOG	
0·10	0·995	14·72	14·72
0·25	0·99	15·11	15·06
0·50	0·98	15·41	15·30
0·75	0·97	15·62	15·46
1·00	0·96	15·77	15·61

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in these systems also conforms to equation (1), with the addition of glycolate to the substrate as the rate-determining step.

Kinetic J_- *Functions.*—The kinetic data for the solvolysis of *p*-DNB in the three MOG–EG systems can be utilised to derive ' kinetic J_- '[5] functions for the systems, which will be more plausible than the J_- functions calculated after Anbar *et al.*,[18] since, apart from some assumptions regarding the activity coefficient terms, the former function is mainly based on experimental data whereas the latter function is partly empirical.

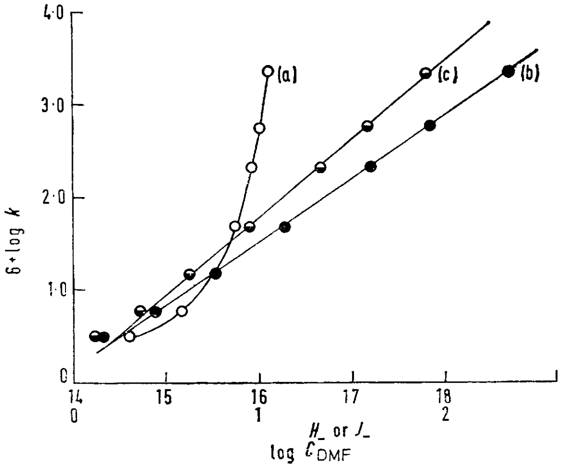

FIGURE 3 Plots of (a) log k *vs.* log c_{DMF}, (b) log k *vs.* $(H_-)^{\mathrm{EG}}_{\mathrm{Am}}$, and (c) log k *vs.* $(H_-)^{\mathrm{EG}}_{\mathrm{Am}}$ + log c_{GOH} for the EG–DMF–0·01M-NaOG system

The kinetic J_- function for the systems under study, $(J_-)^{\mathrm{EG}}_{k}$, according to Rochester[5] is given by equation (4), in which $(K_s)_{\mathrm{GOH}}$ is the autoprotolysis constant of

$$(J_-)^{\mathrm{EG}}_{k} = \log k - \log k_0(K_s)_{\mathrm{GOH}} \qquad (4)$$

ethylene glycol and $k_0 = k_2k_1/(k_{-1} + k_2)$ [*cf.* equation (1)]. The k_0 values were obtained (*cf.* ref. 5) by plotting log k/c_{MOG} against c_{MOG} and extrapolating the linear plots to $c_{\mathrm{MOG}} = 0$. Utilising the k_0 values thus obtained from the intercepts of these plots ($k_0 = 9{\cdot}77 \times 10^{-5}$ l mol^{-1} s^{-1} for the NaOG–EG system and $8{\cdot}91 \times 10^{-5}$ l mol^{-1} s^{-1} for the other two systems) and the known value of $(K_s)_{\mathrm{GOH}}$,[20] the kinetic J_- functions, $(J_-)^{\mathrm{EG}}_{k}$, have been computed for the three systems and are presented in Table 2.

DMF–EG System.—For the alkaline degradation of *p*-DNB in the EG–DMF–0·01M-NaOG system with increasing mole % DMF, (Figure 3) a non-linear plot is obtained for reaction rate *vs.* the base concentration of the system (plot a) (taken as the molar concentration of DMF in this case), data for c_{DMF} are given in Table 3.

TABLE 3

Kinetic data for the alkaline degradation of *p*-DNB in the EG–DMF–0·01M-NaOG system

Mole % DMF	10^6k/s^{-1}	[DMF]/M	$(H_-)^{\mathrm{EG}}_{\mathrm{Am}}$ [a]	$(H_-)^{\mathrm{EG}}_{\mathrm{Am}}$ + log c_{GOH}
11·48	3·072	1·97	14·33	14·26
23·30	5·757	3·87	14·88	14·73
36·00	14·62	5·63	15·52	15·27
50·37	46·92	7·52	16·28	15·90
64·86	217·2	9·25	17·20	16·65
73·57	561·2	10·23	17·85	17·16
82·45	2303	11·12	18·68	17·80

[a] Interpolated data from the ref. 2.

When plotted against the $(H_-)^{\mathrm{EG}}_{\mathrm{Am}}$ function for the system[2] log k gives a straight line (plot b) with a slope of *ca.* 0·72. This probably suggests a similar S_N2 mechanism for the reaction in this medium as in the MOG–EG systems. A plot of log k *vs.* $(H_-)^{\mathrm{EG}}_{\mathrm{Am}}$ + log c_{GOH} gives a straight line with a slope of *ca.* 0·90 (plot c). As the concentration of NaOG in this case is very small, it was not necessary, in calculating c_{GOH}, to allow for the glycol molecules which solvate the glycolate ions.[21] The glycol concentration was calculated dividing the molar concentration by 1000 d/M, where d[19] is the density and M is molecular weight of EG. The observed deviation of the slope from unity is not surprising since (1) DMF is known to form complexes with hydroxylic solvents[22] and such formation of a complex with glycol will naturally reduce the ' free glycol ' concentration and (2) the validity of the Zucker–Hammett hypothesis in this polar–dipolar aprotic solvent system may be less than that in the pure solvent system because of possibly enhanced dispersive and other interactions.[2,22,23]

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