Indian Journal of Chemistry
Vol. 15A, March 1977, pp. 220-225

A Generalized Treatment for the Kinetics of Two Consecutive Irreversible Second Order Reactions: Kinetics of Hydrolysis of Di-*n*-butyl Phthalate*

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Received 4 *March* 1975; *accepted* 7 *July* 1976

The rate constants of two-step competitive consecutive second order reactions of the type

$$A + B \xrightarrow{k_1} C + E$$
$$A + C \xrightarrow{k_2} D + E$$

have been determined employing a new graphical method developed by the authors (unpublished work) and applicable for the cases where the rate constant is unchanged or varies steadily with the progress of the reaction. The method is fully supported by the results of saponification of di-*n*-butyl phthalate by sodium hydroxide where the rate constant is unchanged with the progress of the reaction. Because of the unavailability of data for the rate constant varying continuously with the progress of the reaction, it is not possible to support it experimentally. From the various values of $\tau(=[B]_0k_1t)$ at different percentage reactions with different values of $\rho(=[A]_0/[B]_0)$ and $n(=k_2/k_1)$, a possible prediction of the experimental conditions has been described under which the kinetic study of such reactions will be more suitable. A probable mechanism has been suggested for the hydrolysis of di-*n*-butyl phthalate. The various activation parameters obtained corresponding to both consecutive steps are: $\Delta F^*_{30} = 22{\cdot}8$ (21·4) kcal mole^{-1}; $\Delta H^* = 10{\cdot}7 \pm 0{\cdot}5$ ($10{\cdot}9 \pm 0{\cdot}4$) kcal mole^{-1}; $\Delta S^* = -37{\cdot}2 \pm 1{\cdot}5$ ($-32{\cdot}3 \pm 1{\cdot}3$) cal deg^{-1} mole^{-1}; $E_a = 11{\cdot}3 \pm 0{\cdot}5$ ($11{\cdot}5 \pm 0{\cdot}4$) kcal mole^{-1}; ln $A = 11{\cdot}8 \pm 1{\cdot}5$ ($14{\cdot}3 \pm 1{\cdot}3$) in 80% aq. ethanol. The effects of the concentrations of alkali, ethanol and methanol on the rate of alkaline hydrolysis have also been investigated.

LITERATURE dealing with the hydrolysis of monoesters and monoamides is relatively more extensive than the hydrolysis of diesters and diamides. One of the reasons for lack of interest in the hydrolysis of diesters and diamides is due to difficulty in evaluating the rate constants of the consecutive steps from the complex kinetics equations which are usually encountered due to irreversible consecutive first or second order reactions. Different approximations[1-8] have been used for the determination of the rate constants in such cases. Recently, a more generalized solution for such kinetic systems has been described by Wen[9] as the modification of the Frost and Schwemer method[5] for the determination of rate constants without any restriction on the ratio of the initial [reactant].

A new graphical method (unpublished work) has been developed by the authors which can be applied for the evaluation of rate constants for the irreversible consecutive first-order reactions where the rate proceeds with or without the steady variation of rate constants with the progress of the reaction. This method as compared with the method of Wen[9] does not involve the use of the ratio of time intervals required for different percentage reactions, and hence does not involve the truncation error as is encountered in the time-ratio technique. Wen discussed his graphical treatment for the reaction monitored by measuring [reactant] only in the first step of hydrolysis, but did not discuss the case where the reaction is monitored by measuring the [reactant], in both the consecutive steps. In usual practice, the kinetics of hydrolysis of diesters[10-12] is followed by determining the total [alkali] which is involved in both the consecutive steps. The graphical treatment described in this paper takes into account the [reactant] involved in both the consecutive steps.

Literature search reveals that not a single paper has so far appeared on the effect of [OH$^-$] on the hydrolysis of diesters. The main reason for the lack of these studies is due to nonavailability of such numerical tables for the values of τ as a function of ρ, n and α as was given by Frost and Schwemer[5] at a particular value of ρ (= 2). To get rid of this difficulty, few such numerical tables are given in this manuscript. The method developed will be applicable under the conditions whether the rate constant is unchanged or not with the progress of the reaction as was observed by Bateman *et al.*[13]. in the hydrolysis of *ter*-butyl bromide. In the latter case the necessary condition is that the steady change in rate constants should not affect their ratio.

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*A part of this paper was presented in the Annual Convention of Chemists held at Madurai University, 22-27 December 1974.

Theory

Consider the following chemical reactions:

$$A+B \xrightarrow{k_1} C+E \qquad \ldots(1)$$

$$A+C \xrightarrow{k_2} D+E \qquad \ldots(2)$$

where k_1 and k_2 are the rate constants of first and second steps of the reaction respectively, and solving the usual rate equations[9], the concentration of A can be given by Eq. (3).

$$[A] = [A_0]-2[B_0] + \frac{(1-2n)}{(1-n)}[B] + \frac{1}{(1-n)}\frac{[B]^n}{[B]_0^{n-1}} \qquad \ldots(3)$$

where $[A]_0$ and $[B]_0$ are the initial concentrations (mol litre^{-1}) of A and B. For the special case where $n = 1$, Eq. (3) reduces to Eq. (4)

$$[A] = [A]_0-2[B]_0-[B]\ln([B]/[B]_0)+2[B] \qquad \ldots(4)$$

The values of τ were calculated using Eq. (5)

$$\tau = \frac{1}{\rho}\int_{\beta}^{1}\frac{d\beta}{\alpha\beta} \qquad \ldots(5)$$

where $\tau = [B]_0\, k_1 t$; $\rho = [A]_0/[B_0]$; $\alpha = [A]/[A]_0$ and $\beta = [B]/[B]_0$.

Initially β was calculated for particular value of ρ, n and α from Eq. (3) using Newton-Raphson method[14] followed by substitution of Eq. (3) into Eq. (5). τ was calculated using Simpson's $\frac{1}{3}$ Rule with Richardson's Extrapolations[15]. These calculations were done using a Fortran programme developed for the IBM-1130 electronic computer which produced constancy in the values of β and τ up to nine and six decimal places respectively. When the value of β thus obtained for a particular value of ρ and n was inserted in Eq. (3) the resulting difference between left and right hand sides of the equation came out to be either zero or of the order of about 10^{-12} in each set of calculation.

Tables 1-3 give the values of τ at different values of n and ρ for 10, 20 and 30% reactions of A, respectively. Tables 2 and 3 also show that the values of τ are exactly similar to those obtained by Frost and Schwemer[5] at $\rho = 2$, though the calculation techniques are quite different. Similar tables can be constructed if the reaction is followed by measuring the concentrations of species other than A. Since τ is defined as $k_1[B_0]t$, a plot of t_{exp} versus τ for a run at a particular value of ρ and $1/n$ should yield a linear curve passing through the origin. Here t_{exp} and τ represent respectively the experimental time at various percentage reactions and the calculated values of time parameter at the same percentage reactions for a run. Any shift from linearity in the above plot may be due to (i) the shift from the exact value of n, and (ii) the steady variation of rate constants with the progress of percentage reactions for a run. The exact value of n can be obtained by choosing a curve from a family of plots of t_{exp} versus τ for which the deviation from linearity is either zero

TABLE 1 — VALUES OF τ AS A FUNCTION OF ρ AND n AT $\alpha = 0{\cdot}9$ (10% REACTION)

ρ	$1/n = 1$	$1/n = 2$	$1/n = 3$	$1/n = 4$	$1/n = 5$	$1/n = 6$	$1/n = 7$	$1/n = 8$
0·1	0·105361	0·105629	0·105719	0·105764	0·105791	0·105809	0·105822	0·105832
0·2	0·105367	0·105900	0·106080	0·106171	0·106226	0·106263	0·106289	0·106309
0·3	0·105376	0·106172	0·106445	0·106583	0·106666	0·106721	0·106761	0·106791
0·5	0·105404	0·106723	0·107183	0·107416	0·107558	0·107653	0·107721	0·107772
0·8	0·105471	0·107564	0·108312	0·108696	0·108930	0·109088	0·109201	0·109286
1·0	0·105532	0·108134	0·109080	0·109569	0·109869	0·110071	0·110216	0·110326
1·2	0·105606	0·108712	0·109861	0·110459	0·110827	0·111075	0·111255	0·111390
1·4	0·105692	0·109299	0·110655	0·111366	0·111805	0·112103	0·112318	0·112481
1·6	0·105791	0·109894	0·111462	0·112291	0·112804	0·113153	0·113406	0·113598
1·8	0·105902	0·110498	0·112283	0·113234	0·113825	0·114228	0·114521	0·114743
2·0	0·106025	0·111111	0·113118	0·114195	0·114868	0·115328	0·115663	0·115917
3·0	0·106813	0·114316	0·117519	0·119305	0·120447	0·121240	0·121823	0·122770
4·0	0·107888	0·117783	0·122335	0·124980	0·126715	0·127942	0·128857	0·129565
5·0	0·109252	0·121547	0·127631	0·131322	0·133813	0·135613	0·136976	0·138044

TABLE 2 — VALUES OF τ AS A FUNCTION OF ρ AND n AT $\alpha = 0{\cdot}8$ (20% REACTION)

ρ	$1/n = 1$	$1/n = 2$	$1/n = 3$	$1/n = 4$	$1/n = 5$	$1/n = 6$	$1/n = 7$	$1/n = 8$
0·1	0·223159	0·224308	0·224698	0·224895	0·225013	0·225092	0·225149	0·225191
0·2	0·223205	0·225489	0·226279	0·226679	0·226920	0·227082	0·227199	0·227286
0·3	0·223281	0·226687	0·227885	0·228496	0·228867	0·229116	0·220295	0·229429
0·5	0·223519	0·229133	0·231176	0·232234	0·232881	0·233317	0·233632	0·233869
0·8	0·224082	0·232936	0·236324	0·238116	0·239226	0·239981	0·240528	0·240942
1·0	0·224591	0·235566	0·239904	0·242234	0·243689	0·244685	0·245409	0·245960
1·2	0·225203	0·238275	0·243610	0·246520	0·248355	0·249617	0·250539	0·251242
1·4	0·225915	0·241068	0·247450	0·250986	0·253236	0·254794	0·255938	0·256813
1·6	0·226728	0·243950	0·251432	0·255643	0·258350	0·260237	0·261629	0·262698
1·8	0·227640	0·246926	0·255562	0·260504	0·263713	0·265967	0·267637	0·268926
2·0	0·228652	0·249999	0·259850	0·265582	0·269344	0·272007	0·273992	0·275530
3·0	0·235246	0·267062	0·284027	0·298117	0·302352	0·307934	0·312246	0·315681
4·0	0·244669	0·287682	0·313996	0·332468	0·346396	0·357378	0·366313	0·373753
5·0	0·257644	0·313350	0·352221	0·382593	0·407711	0·429228	0·448104	0·464952

TABLE 3 — VALUES OF τ AS A FUNCTION OF ρ AND n AT $\alpha = 0{\cdot}7$ (30% REACTION)

ρ	$1/n = 1$	$1/n = 2$	$1/n = 3$	$1/n = 4$	$1/n = 5$	$1/n = 6$	$1/n = 7$	$1/n = 8$
0·1	0·356732	0·359538	0·360499	0·360984	0·361277	0·361477	0·361614	0·361719
0·2	0·356901	0·362461	0·364417	0·365416	0·366022	0·366429	0·366721	0·366941
0·3	0·357178	0·365448	0·368435	0·369975	0·370916	0·371550	0·372006	0·372350
0·5	0·358042	0·371617	0·376776	0·379497	0·381179	0·382322	0·383149	0·383775
0·8	0·360072	0·381402	0·390126	0·394889	0·397893	0·399960	0·401471	0·402624
1·0	0·361897	0·388312	0·399639	0·405973	0·410025	0·412843	0·414916	0·416506
1·2	0·364093	0·395559	0·409693	0·417792	0·423055	0·426754	0·429497	0·431614
1·4	0·366658	0·403175	0·420336	0·430423	0·437088	0·441827	0·445372	0·448126
1·6	0·369598	0·411190	0·431623	0·443953	0·452244	0·458216	0·462728	0·466259
1·8	0·372921	0·419641	0·443615	0·458480	0·468667	0·476107	0·481790	0·486275
2·0	0·376642	0·428571	0·456348	0·474118	0·486520	0·495718	0·502829	0·508497
3·0	0·402082	0·482324	0·535113	0·574311	0·605287	0·630728	0·652187	0·670643
4·0	0·443381	0·559615	0·652429	0·733660	0·808222	0·878682	0·946577	1·01291
5·0	0·515509	0·686412	0·849632	1·01386	1·18214	1·35498	1·53179	1·71172

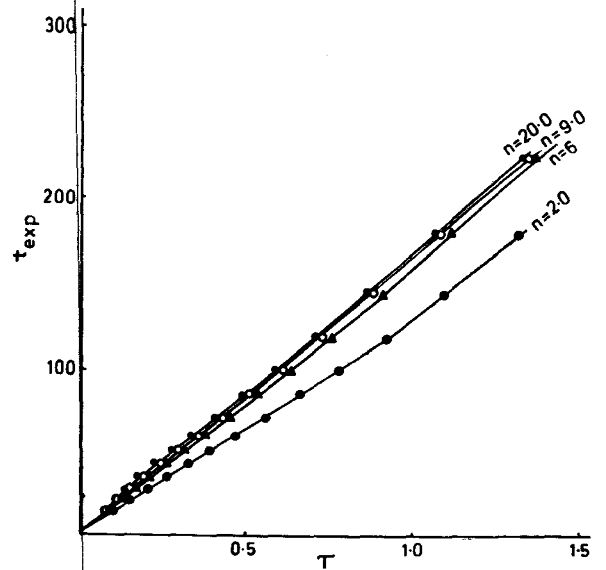


Fig. 1 — Plots of t_{exp} versus τ for various values of n (ρ= 1·8)

(i.e. the case where the rate constants remain unchanged throughout the run) or minimum (i.e. the case where there is a steady variation in rate constants). Fig. 1 shows the plots of t_{exp} versus τ for a kinetic run on the saponification of di-n-butyl phthalate which indicate that the exact value of n is 9·0 and any shift of n from 9·0 either towards lower or higher values causes a positive or negative deviation from linearity. Once the exact value of n is obtained, the values of k_1 are calculated by dividing τ at various percentage reactions by the corresponding product of $[B]_0$ and t_{exp} (Table 4).

Our calculations of β and τ versus α, and α and τ versus β, covered the ranges of 0·05-10 and 0·40-20 for ρ and of 0·02-50 for n. The following inferences were derived from the plot of ρ versus τ for 30% reaction with respect to A and B (Fig. 2).

Case I: Study of reaction following the concentration of reactant A — In this case if n lies within 1-50, the evaluation of rate constants is quite possible for those values of ρ which fall within the range of 0·50-6·4. For values of $n < 1{\cdot}0$, the sensitive range of ρ becomes 0·05-3·0. It has also been observed that along with the decrease in n, the value of β decreases with the increase in ρ. This technique can be most smoothly applied for the values of ρ between 0·1 and 3·0.

Case II: Study of reaction following the concentration of reactant B — In this case the possible range of ρ is 0·8-2·0 because at $\rho>2$, the values of τ becomes approximately the same for all the values of n between 1·0 aqd 0·02, and thus it will be much difficult to find out the exact value of n. Similar difficulty is also encountered if $\rho>6$ for n lying between 1 and 50. On the basis of these results it is clear that the accuracy in the evaluation of rate constants and freedom for the choice of variation of ρ is greater in Case I than in Case II which provides a very narrow range of ρ.

The method described here was successfully applied for studying the alkaline hydrolysis of di-n-butyl phthalate.

TABLE 4 — RATE CONSTANTS FOR THE HYDROLYSIS OF DI-n-BUTYL PHTHALATE BY SODIUM HYDROXIDE AT 50° IN 80% AQ. ETHANOL ($\rho = 1{\cdot}8$; $n = 9{\cdot}0$; $[B_0] = 0{\cdot}025M$ AND $\mu = 0{\cdot}4$)

Reaction (%)	t_{exp} (min)	τ	$k_{1(obs)} \times 10^2$ (litre mole^{-1} min^{-1})
10	15·2	0·0785919	29·7
15	21·5	0·115615	21·5
20	28·0	0·154785	22·1
25	35·5	0·197420	22·2
30	43·5	0·298166	23·2
40	60·5	0·359295	23·8
45	71·5	0·430258	24·1
50	86·0	0·513876	23·9
55	100·0	0·614054	24·6
60	119·0	0·736415	24·8
65	145·0	0·889392	24·5
70	180·0	1·08630	24·1
75	224·5	1·34953	24·0
80	282·0	1·72008	24·6
		Av.	23·5

10 $k_{2(obs)} = 21{\cdot}4 \pm 0{\cdot}9$ litre mole^{-1} min^{-1} calculated from

$$n = \frac{k_{2(obs)}}{k_{1(obs)}}$$

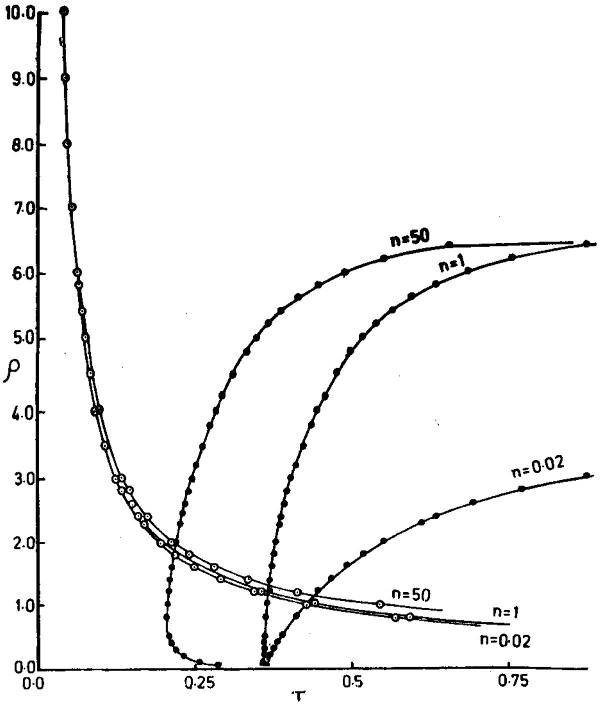


Fig. 2 — Plots of ρ versus τ for various values of *n* (●, 30% reaction with respect to reactant A; ⊙, 30% reaction with respect to reactant B)

Materials and Methods

Di-*n*-butyl phthalate (BDH) and methanol (E. Merck) were used as such. Absolute ethanol was prepared as described by Vogel[17]. Other chemicals used were of reagent grade. Carbon dioxide-free doubly distilled water was used for the preparation of solutions. The kinetics were followed at the desired temperature maintained with an accuracy of ±0·1°. The reaction was initiated by adding the appropriate volume of NaOH solution and the zero time taken when half of NaOH solution was transferred into the reaction vessel. The ionic strength was kept constant at 0·2*M* and 0·4*M* to minimize the possibility of any changes in the medium caused by changes in ionic strength as diacid anions were produced in the final stage of the hydrolysis. Evaporation was prevented by using a double surface condenser. Efficient shaking of the reaction mixture was done by bubbling oxygen-free nitrogen gas which also served to keep an inert atmosphere. The reaction was monitored by withdrawing periodically 5 ml of the reaction mixture and quenching it in a standard solution of HCl. The unreacted HCl was titrated quickly against standard NaOH solution.

Evaluation of the rate constants was followed according to the above method and the results for a kinetic run are given in Table 4.

Results and Discussion

The effect of temperature on the hydrolysis of di-*n*-butyl phthalate was studied in the range 36° to 60° in 80% ethanol-water. The observed second-order rate constants for both the consecutive steps were found to be in good agreement with Arrhenius and Eyring equations as was evident from the linear plots of $-\ln k_{obs}$ versus $1/T$. Various activation parameters were evaluated using least-squares technique and are given in Table 5. The reproducibility of the data in using the least squares fit in the Arrhenius and Eyring equations is evident from the root mean square deviations and maximum deviations given in Table 5.

A series of kinetic runs were carried out at different [NaOH] keeping the ionic strength constant at 0·2*M*. The results summarized in Table 6

TABLE 6 — EFFECT OF VARYING [NaOH] ON THE RATE OF HYDROLYSIS OF DI-*n*-BUTYL PHTHALATE {[DI-*n*-BUTYL PHTHALATE] = 0·025*M*; μ = 0·2*M*; SOLVENT = 80% ETH ANOL; TEMP. = 55°}

[NaOH] *M*	$10^2 k_{1(obs)}$ (litre mole^{-1} min^{-1})	$10 k_{2(obs)}$ (litre mole^{-1} min^{-1})*	ρ	$\frac{k_{2(obs)}}{k_{2(obs)}}$
0·020	22·2 ± 1·5	19·8 ± 1·4	0·8	8·9
0·025	23·2 ± 1·8	21·1 ± 1·7	1·0	9·1
0·030	22·0 ± 0·6	19·6 ± 0·6	1·2	8·9
0·035	22·6 ± 0·6	20·2 ± 0·5	1·4	8·9
0·040	24·7 ± 1·9	22·5 ± 1·7	1·6	9·2
0·045	22·8 ± 0·7	20·2 ± 0·6	1·8	8·8
0·050	23·9 ± 0·8	21·7 ± 0·7	2·0	9·1

*Error limits are standard deviations.

TABLE 5 — ACTIVATION PARAMETERS {[DI-*n*-BUTYL PHTHALATE] = 0·025*M*; [NaOH] = 0·05*M*; μ = 0·2*M*; SOLVENT = 80% ETHANOL}

ΔF^{*}(a) kcal mole^{-1}	ΔH^{*} kcal mole^{-1}	$-\Delta S^{*}$ cal deg^{-1} mole^{-1}	E_a kcal mole^{-1}	ln *A* (ainmol^{-1} sec^{-1})	$10^4 R_{ms}^{(b)}$	Max. dev. (%)(c)
			$A + B \xrightarrow{k_1(obs)} C+E$			
22·8	10·7 ± 0·5(d)	37·2 ± 1·5(d)	11·3 ± 0·5(d)	11·8 ± 1·5(d)	9·7	−12·8
			$A + C \xrightarrow{k_2(obs)} D+E$			
21·4	10·9 ± 0·4	32·3 ± 1·3	11·5 ± 0·4	14·3 ± 1·3	539·0	−10·9

(a) Calculated from equation $k_{obs} = KbT/h \exp(-\Delta F^{*}/RT)$ at 50°. (b) Root mean square deviation between observed and calculated values. (c) Maximum deviation between observed and calculated values. (d) Error limits are standard deviations.

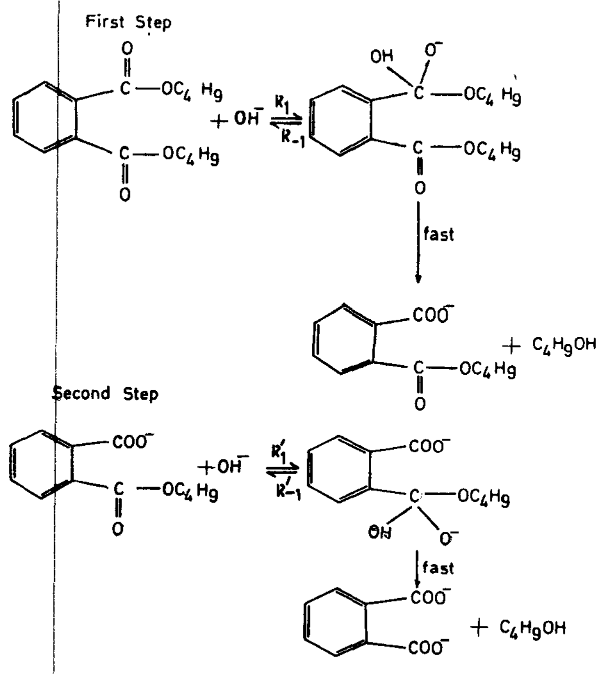
TABLE 7 — LINEAR PARAMETERS CORRESPONDING TO $\ln k_{obs} = B_1 + B_2/D$ AND $\ln k_{obs} = C_1 + C_2/D$ IN ETHANOL-WATER AND METHANOL-WATER SYSTEMS ([DI-*n*-BUTYL PHTHALATE] = 0·025*M*; [NaOH] = 0·045*M*; $\mu = 0{\cdot}4M$; TEMP. = 50°]

Reaction	B_1 (C_1) (litre mole^{-1} sec^{-1})	B_2 (C_2)	$10^4 R_{ms}$ (a)	Max. dev. (%)(b)
		ETHANOL-WATER		
$A+B \xrightarrow{k_{1(obs)}} C+E$	$-1{\cdot}93 \pm 0{\cdot}43$(c)	$1{\cdot}09 \pm 0{\cdot}12$(c)	2·17	5·0
$A+C \xrightarrow{k_{2(obs)}} D+E$	$(0{\cdot}42 \pm 0{\cdot}40)$	$(1{\cdot}14 \pm 0{\cdot}11)$	147·6	4·8
		METHANOL-WATER		
$A+B \xrightarrow{k_{1(obs)}} C+E$	$-14{\cdot}0 \pm 1{\cdot}2$(c)	$2{\cdot}09 \pm 0{\cdot}33$(c)	2·14	−6·2
$A+C \xrightarrow{k_{2(obs)}} D+E$	$(-12{\cdot}0 \pm 1{\cdot}3)$	$(2{\cdot}15 \pm 0{\cdot}34)$	186·7	6·2

(a) Calculated from equations $k_{obs} = \frac{K_b T}{h} \exp(-\Delta F^*/RT)$ at 50°.

(b) Root mean square deviation between observed and calculated values.

(c) Maximum deviation between observed and calculated values.



Scheme 1

indicate that rate constants are almost unaffected by the initial [NaOH] supporting the consecutive irreversible second-order hydrolysis.

The solvent effect on hydrolysis was carried out using different percentages by weight of ethanol-water and methanol-water systems. The linear plots of $-\ln k_{1(obs)}$ and $-\ln k_{2(obs)}$ versus $1/D$ showed that there was an increase in rates of both the consecutive steps with increasing concentration of ethanol while the reverse was true in the case of methanol. The results are summarized in Table 7, and were found to fit well in the empirical equations (6) and (7). The slope values were found to be positive for ethanol-water system and negative for methanol-water system.

$$\ln k_{1(obs)} = B_1 + \frac{B_2}{D} \qquad \ldots(6)$$

$$\ln k_{2(obs)} = C_1 + \frac{C_2}{D} \qquad \ldots(7)$$

where D refers to dielectric constant of the medium and B_1, B_2, C_1 and C_2 are the arbitrary constants which were determined using least-squares treatment.

In the alkaline hydrolysis of di-*n*-butyl phthalate, it was observed that in all the sets of observations the rate constants corresponding to first step were smaller than those of second step. This is probably the first such report on the hydrolysis of dicarboxylic ester. The reason for such abnormality is probably due to the steric effects. The bulky butyl group resists the approach of nucleophile to the second reactive butoxy carbonyl-carbon centre in the first step of hydrolysis and this effect predominates over the unfavourable electrostatic interaction experienced by the nucleophile in attacking at the butoxy carbonyl carbon centre in the second step. The rate limiting step is presumably the attack of hydroxide ion on the carbonyl-carbon of acyl substrate (first step) to form the tetrahedral intermediate and the subsequent expulsion of butoxide ion in a fast step. A plausible mechanism consistent with the observed results is shown in Scheme 1.

Similar conclusion was drawn recently by Bruice and Bruice[18] in the alkaline hydrolysis of a series of substituted phenylquinoline-8- and 6-carboxylates.

The results on the effect of varying methanol content of the solvent on the reaction rate were consistent with the modified Amis-Jaffe[19] equation derived for the ion-dipole reaction. This equation, however, was not applicable in the case of ethanol-water mixture. Such abnormality in the effect of solvents is not amazing because of the various unknown specific properties of the solvents[19]. The increased rates of both the steps in mixed solvents containing water-ethanol might be attributed qualitatively to the poorly solvated state of hydroxide ions and an increased solvation of the transition state.

The various activation parameters were found to be of the same order as those reported for other related diesters[12].

TABLE 8 — COMPARISON OF THE RATE CONSTANTS OBTAINED BY THE PRESENT METHOD WITH THOSE CALCULATED BY THE DATA OF INGOLD AND OTHER METHODS

Method	k_1(litre mole^{-1} min^{-1})	k_2(litre mole^{-1} min^{-1})
Ingold[1]	7·24	1·123
Wideqvist[16]	7·277	1·12
Wen[6]	7·334	1·107
This work	7·271	1·136

The rate constants obtained by the present method compared well with those calculated from the data of Ingold[1] and by other methods[9,16] (Table 8).

Acknowledgement

The authors feel pleasure to thank Prof. Wasiur Rahman, Head of the Department of Chemistry, for providing necessary facilities. One of them (M.N.K.) thanks the CSIR, New Delhi, for the award of a junior research fellowship.

References

1. Ingold, C. K., *J. chem. Soc.*, (1931), 2170.
2. Ritchie, M., *J. chem. Soc.*, (1931), 3112.
3. French, D., *J. Am. chem. Soc.*, **72** (1950), 4806.
4. Schwemer, W. C. & Frost, A. A., *J. Am. chem. Soc.*, **73** (1951), 4541.
5. Frost, A. A. & Schwemer, W. C., *J. Am. chem. Soc.*, **74** (1952), 1268.
6. McMillan, M. C., *J. Am. chem. Soc.*, **79** (1957), 4838.
7. Saville, B., *J. phys. Chem.*, **75** (1971), 2215.
8. Wells, P. R., *J. phys. Chem.*, **63** (1959), 1978.
9. Wlater, Y. Wen, *J. phys. Chem.*, **76** (1972), 704.
10. Rao, G. V. & Venkatasubramanian, N., *Aust. J. Chem.*, **24** (1971), 201.
11. Radhakrishnamurti, P. S. & Patro, P. C., *J. Indian chem. Soc.*, **46** (1969), 903.
12. Radhakrishnamurti, P. S. & Patro, P. C., *Indian J. Chem.*, **7** (1971), 1098.
13. Bateman, L. C., Church, M. G., Hughes, E. D., Ingold, C. K. & Taher, N. A., *J. chem. Soc.*, (1940), 979.
14. Margenau, H. & Murphy, G. M., *The mathematics of physics and chemistry*, Vol. I, 2nd edn (Van Nostrand, Princeton, NJ), 1963, 492.
15. McCormick, John M. & Salvadori Mario, G., *Numerical methods in Fortran*, (Prentic-Hall, India, New Delhi), 1971, 165.
16. Wideqvist, S., *Acta chem. Scand.*, **4** (1950), 1216.
17. Vogel, A. I., *A text-book of practical organic chemistry*, (Longmans, Green, London), ELBS edn, 1968, reprinted 1971, 166.
18. Bruice, P. Y. & Bruice, T. C., *J. Am. chem. Soc.*, **96** (1974), 5523.
19. Amis, E. S., *Solvent effects on reaction rates and mechanisms* (Academic Press, New York), 1966, 41, 300.