872. *The Kinetics of Alkaline Hydrolysis of Ethyl Nitro-1-naphthoates.*

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A study has been made of the kinetics of alkaline hydrolysis of the ethyl esters of 2-, 3-, 4-, 5-, 6-, and 8-mononitro- and of 4 : 5-dinitro-1-naphthoic acid, in ethanol–water, at four temperatures covering a range of 15°, 20°, or 30°. Results are compared with each other and with those obtained for benzoates, comments are made on Hammett σ values obtained in this and other work, and the steric effects connected with 2- and 8-nitro-substituents are discussed.

EXTENSIVE studies have been made of substituent effects on the reactivity of a side-chain in benzene derivatives.[1] Similar investigations on naphthalene derivatives have been few and, in pursuance of a general study of reactivity in the naphthalene series, we have examined the effect of the nitro-group on the rate of alkaline hydrolysis of ethyl 1-naphthoates in 85% ethanol–water (w/w). For the corresponding benzoate hydrolysis,

[1] Jaffé, *Chem. Rev.*, 1953, **53**, 191.

substituent effects are well understood; the mechanism is known to involve acyl–oxygen fission [2] and to be of the first order with respect to both ester and base.[3]

EXPERIMENTAL

Esters.—Ethyl 2- [4] and 8-nitro-1-naphthoate [5] were prepared by the action of excess of ethyl iodide on the corresponding silver salts. They melted at 92° and 68° respectively. 2-Nitro-1-naphthoic acid (m. p. 202°) was made from 1-methylnaphthalene.[4] 8- and 5-Nitro-1-naphthoic acid were obtained by nitration of 1-naphthoic acid: [6] treatment of the mixture of acids with hydrogen chloride and ethanol converted the 5-nitro-acid into its ethyl ester (m. p. 94°); [7] the purified 8-nitro-acid melted at 220°. Ethyl 3- (m. p. 87°) and ethyl 4-Nitro-1-naphthoate (m. p. 57°) were obtained from the corresponding acids through the acid chlorides, the acids themselves (m. p.s 269° and 225·5° respectively) having been prepared from acenaphthene.[8] Ethyl 6-nitro-1-naphthoate (m. p. 111°) was prepared by treatment of the crude 6-nitro-acid (obtained by the evaporation of the mother-liquor from the recrystallization of the 3-nitro-acid) with hydrogen chloride and ethanol.[8] Ethyl 4 : 5-dinitronaphthoate was made by nitration of ethyl 5-nitro-1-naphthoate by Koelsch and Hoffmann's method.[7] Analytical figures were obtained for this ester in view of the polymorphism indicated by its behaviour on heating (Found: C, 54·0; H, 3·6; N, 9·75. Calc. for $C_{13}H_{10}O_6N_2$: C, 53·8; H, 3·5; N, 9·65%). The ester melted sharply at 140°. Then (i) further heating led to solidification followed by a sharp m. p. at 145·5°, and (ii) cooling and reheating the solidified sample resulted in a single m. p. of 145·5°.

Solvent.—Ethanol was purified by a preliminary distillation from sulphuric acid (45 ml. of 4N-acid per litre of alcohol),[9] followed by several treatments with silver oxide [10] and a final fractional distillation in hydrogen.[11] Only the middle fraction was used for kinetic runs. Boiled-out distilled water was used for making up solutions, and sodium hydroxide solutions were free from carbonate.

Apparatus.—Bath temperatures were maintained (thermostat) within ±0·02°. The conductivity bridge consisted of (i) a regulated power supply, (ii) a Wien bridge oscillator, producing a current of frequency *ca.* 1 kilocycle per sec., (iii) the Wheatstone bridge, which had 450 ohm fixed-ratio arms and a decade resistance box with a compensating variable condenser across it for the measuring arm, (iv) a high-gain amplifier, and (v) a detector unit. Balance was indicated by zero reading of the microammeter in the detector unit. For resistances of the order measured in runs (300—1200 ohms) the bridge had a maximum sensitivity better than 1 part in 100,000 and a stability, measured over a greater period of time than the maximum time for a kinetic run, of better than 1 part in 20,000. The conductivity cells used were of the type described by Evans and Hamann.[12] They consisted of a compartment of 15—20 ml. capacity, containing bright platinum electrodes, and a smaller compartment of 2—3 ml. capacity joined to the first by a hollow elbow. Each compartment had a filling tube.

Hydrolyses.—For the 2-, 3-, 4-, and 8-nitro-esters, kinetics were followed by conductivity methods. The following method was employed for the 3- and 4-nitro-esters (*i.e.*, for fast reactions).

The solution (9—10 g.) of the ester in 95% ethanol was weighed into the larger cell compartment. From the exact weight of ester solution taken, the required volume of aqueous sodium hydroxide solution to make the reaction mixture [85% ethanol–water (w/w) with ester and base in equimolar amounts] was measured into the smaller compartment. After the cell had come to temperature equilibrium with the bath, the contents were mixed and left in the

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[2] Bender, *J. Amer. Chem. Soc.*, 1951, **73**, 1626.
[3] Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, Ithaca, **1953**, Chapter XIV.
[4] Topsom and Vaughan, *J.*, 1957, 2842.
[5] Ekstrand, *J. prakt. Chem.*, 1888, **38**, 155.
[6] *Idem, ibid.*, p. 139.
[7] Koelsch and Hoffmann, *J. Amer. Chem. Soc.*, 1943, **65**, 989.
[8] Leuck, Perkins, and Whitmore, *ibid.*, 1929, **51**, 1831.
[9] Danner and Hildebrand, *ibid.*, 1922, **46**, 2824.
[10] Dunlap, *ibid.*, 1906, **28**, 395.
[11] Riiber, *Z. Elektrochem.*, 1923, **29**, 335.
[12] Evans and Hamann, *Trans. Faraday Soc.*, 1951, **47**, 31.

electrode compartment. After an initial 15 min. interval, 30 resistance–time measurements (*i.e.*, R_1, t_1; R_2, t_2; · · · · · R_{30}, t_{30}) were made at approximately equal increments of resistance. Zero time was the time of mixing.

From (i) the simplified form of the second-order rate equation

$$\mathrm{d}x/\mathrm{d}t = k(A_0 - x)^2 \quad \ldots\ldots\ldots \quad (1)$$

(ii) the relation between the resistance (R) of the solution and concentration (x) of carboxylate ion

$$x = a/R + b \text{ (a and b are constants)} \quad \ldots\ldots \quad (2)$$

and (iii) the resistance–time values R_1/t_1, R_{11}/t_{11}, R_{21}/t_{21}, it follows that

$$A_0k = -\frac{\sum R_1R_{11}(t_{11} - t_1)}{\sum R_1R_{11}t_{21}(t_{11} - t_1)} \quad \ldots\ldots\ldots \quad (3)$$

where k is the rate constant, A_0 is the initial concentration of ester and base, and x (the concentration of carboxylate ion) is also the decrease in concentration of base or ester at time t (sec).

From expressions of type (3), ten values of A_0k were calculated for each run, and the mean was obtained.

The above method could not be satisfactorily applied to the very slow reactions of the 2- and 8-nitro-ester. A blank run, without added ester, indicated that the rate of increase of resistance (assumed to be caused by reaction of base and Pyrex cell-wall) was of the same order as that of rate of change in resistance observed in the hydrolysis of ethyl 8-nitro-1-naphthoate. This blank is insignificant with the 3- and the 4-nitro-ester (k values for these are *ca.* 5000 × k for the 8-nitro-ester). The following method was adopted for measuring hydrolysis of the two hindered esters. An 85% ethanol–water solution of sodium hydroxide was made up in the electrode compartment of a cell. After temperature equilibrium with the bath had been attained, eight measurements of the resistance were made during 1 hr. (blank run). The calculated quantity of ester was added and the cell resistance measured at frequent intervals covering 3 hr. after mixing.

From the limiting conditions (i) $x = 0$, $R = R_0$, and (ii) $x = A_0$, $R = R_\infty$, and equations (1) and (2),

$$R = \frac{R_0}{R_\infty}A_0k(R_\infty - R)t + R_0 \quad \ldots\ldots\ldots \quad (4)$$

When k is small, $(R_\infty - R)$ is approximately constant and thus R is a linear function of t. Plots of R against t were made for the blank and the hydrolysis runs. The " hydrolysis " plot was extrapolated back to the time of ester addition ($t = 0$) to find R_0. The difference in slopes of " hydrolysis " and " blank " plots gave the rate of change in resistance for ester hydrolysis alone, *i.e.*, $(R_\infty - R)A_0kR_0/R_\infty$. As a measure of R_∞ the resistance was measured of the corresponding solution of the sodium salt of the acid. Substitution of values for R_0, R_∞, R, and A_0 in the last expression gave k. It is to be noted that for faster reactions, when $(R_\infty - R)$ is no longer constant and the R–t plot no longer linear, it is possible to plot $(R - \alpha t)$ against $(R_\infty - R + \alpha t)t$ to give a linear plot with intercept R_0. Here α is the slope of the " blank " plot and $(R - \alpha t)$ is thus the resistance (at time t) caused by the hydrolysis alone. The slope of this plot is A_0kR_0/R_∞, and k is obtained by substituting values of R_0, A_0, and R_∞.

A titration method was used in following the hydrolysis of the 5- and 6-nitro- and 4 : 5-dinitro-ester. Solutions were made up as described for hydrolysis of the 3- and 4-nitro-ester and Evans, Gordon, and Watson's procedure [13] was followed in analysing reaction mixtures. Blank runs (without added ester) indicated no significant consumption of alkali. Runs were followed to 50% hydrolysis, good second-order kinetics being obtained. A few runs, using the titration method and with unequal concentrations of ester and base, were carried out on the 3-, 4-, and 5-nitro- and 4 : 5-dinitro-ester. The reaction was thereby shown to be of the first order with respect to both ester and base. Satisfactory agreement was found when the rate constants for the 3- and 4-nitro-esters were determined by both the conductivity and the titration method.

For each compound, kinetics were followed at a minimum of four temperatures. Use of the

[13] Evans, Gordon, and Watson, *J.*, 1937, 1430.

Arrhenius equation (log $k = \log B - E/\mathbf{R}T$) led to linear plots of log k against $1/T$ in every case except that of the 2-nitro-ester. With this ester a distinct curvature indicated that k was increasing more rapidly with T than would be indicated by the best straight-line fit to the points. Mean rate data and probable errors for all esters are listed in Table 1, together with derived values of Arrhenius parameters. The latter values have a probable error of 1%, except those for the 2-nitro- (5%) and 8-nitro- (2%) esters. Beneath each mean value of k, the number of runs is given in parentheses.

TABLE 1.

10^3k (l. mole^{-1} sec.$^{-1}$).

Ethyl x-*nitro*-1-*naphthoates.*

x	20°	30°	35°	40°	50°	55°	60°	65°
2	—	—	—	—	0·332 ±0·002 (2)	0·44 ±0·02 (2)	0·65 ±0·02 (4)	1·05 ±0·04 (2)
3	—	17·1 ±0·6 (5)	26·9 ±0·3 (5)	41·0 ±0·1 (3)	92·3 ±0·1 (2)	—	—	—
4	—	19·0 ±0·0 (2)	28·8 ±0·1 (3)	44·4 ±0·2 (5)	101±2	—	—	—
5	2·61 ±0·02 (3)	6·37 ±0·09 (6)	9·5 ±0·2 (3)	15·1 ±0·1 (4)	34·5 ±0·1 (4)	—	—	—
6	2·40 ±0·04 (3)	5·91 ±0·05 (3)	—	13·7 ±0·1 (3)	29·9 ±0·1 (3)	—	—	—
8	—	—	—	—	0·0256 ±0·0001 (3)	0·041 ±0·002 (2)	0·066 ±0·002 (3)	0·097 ±0·004 (2)

Ethyl 4 : 5-*dinitronaphthoate*

Temp.	10^3k
5°	38·0 + 0·5 (5)
10	62·4 ± 0·1 (3)
15	98 ± 2 (3)
20	158 ± 2 (4)

x	*E* (kcal. mole^{-1})	log *B*
2	16·6	7·7
3	16·4	10·0
4	16·3	10·0
5	16·2	9·5
6	15·8	9·2
8	19·7	8·7
4 : 5-Di	15·3	10·6

DISCUSSION

Evans, Gordon, and Watson[13] have shown that for the alkaline hydrolysis of unsubstituted and of *meta*- and *para*-substituted ethyl benzoates in 85% ethanol–water, log B is constant within experimental error. For hydrolysis of *ortho*-substituted ethyl benzoates log B is smaller and is not constant. For the alkaline hydrolysis of ethyl benzoate in 87·83% ethanol, log $k_{30} = -3{\cdot}08$, log $B = 7{\cdot}3$, and $E = 14{\cdot}4$ kcal. mole^{-1}.[14] In 85% ethanol, log $k_{30} = -2{\cdot}98$, log $B = 9{\cdot}8$, and $E = 17{\cdot}7$ kcal. mole^{-1}.[13] A small solvent change thus has an extremely large effect on the Arrhenius parameters (but not on log k_{30}). In the present work log B values for the 3- and the 4-nitro-compounds are slightly higher than might have been expected. For work on these two compounds a fresh solvent batch was used and although care was naturally exercised a slight variation in make-up of batches may have existed. It is therefore suggested that the alkaline hydrolyses of mononitronaphthoates here reported (with the exception of the 2- and 8-nitro-compounds) can also be regarded as iso-entropic, within the limits of experimental error. Values of $\Delta\Delta G^‡$ ($= -\mathbf{R}T \ln k/k_0$), $\Delta\Delta H^‡$ ($= \Delta E$), $T\Delta\Delta S^‡$ ($= -\mathbf{R}T \ln B/B_0$), and Hammett substituent constant [$\sigma = (1/\rho) \log k/k_0$] for both benzoates and naphthoates are collected in Table 2. The values for nitro-1-naphthoates are relative to ethyl 1-naphthoate ($E = 17{\cdot}22$; log $B = 9{\cdot}01$).[15] The values for nitrobenzoates are relative to ethyl benzoate ($E = 17{\cdot}79$; log $B = 9{\cdot}83$).[13] Values of the Hammett reaction constant ρ, used to evaluate substituent constants, were taken from Jaffé's review. The figures for ethyl nitrobenzoates are

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[14] Herbst and Jacox, *J. Amer. Chem. Soc.*, 1952, **74**, 3004.

[15] Personal communication from J. E. Packer.

calculated from the *rate constants* of Evans, Gordon, and Watson,[13] who appear to have made an error in calculating E and log B for the *o*-nitrobenzoate.

The values, in parentheses, for $\Delta\Delta H^{\ddagger}$ have been derived from values of $\Delta\Delta G^{\ddagger}$, on the assumption that $\Delta\Delta S^{\ddagger} = 0$. Over small temperature ranges, experimental errors in E and log B tend to be self-cancelling in their effect on k. Hence, in these cases $\Delta\Delta G^{\ddagger}$ is more reliable than ΔE as a measure of $\Delta\Delta H^{\ddagger}$.

TABLE 2.

x	Temp. (° K)	$\Delta\Delta G^{\ddagger}$ (kcal. mole^{-1})	$\Delta\Delta H^{\ddagger}$ (kcal. mole^{-1})	$T\Delta\Delta S^{\ddagger}$ (kcal. mole^{-1})	σ
		Ethyl x-*nitro*-1-*naphthoates*			
2	323·2	+1·3	−0·6	−2·0	—
3	323·2	−2·4	(−2·4)	—	0·68
4	323·2	−2·4	(−2·4)	—	0·70
5	323·2	−1·7	(−1·7)	—	0·50
6	323·2	−1·7	(−1·7)	—	0·48
8	323·2	+3·0	+2·5	−0·5	—
4 : 5-di	298·2	−4·1	(−4·1)	—	1·18
		Ethyl x-*nitrobenzoates*			
2	323·2	−1·2	−2·6	−1·4	—
3	308·2	−2·5	(−2·5)	—	0·73
4	308·2	−2·8	(−2·8)	—	0·81

Examination of tabulated σ values reveals three interesting features. (i) The nitro-substituent exerts a slightly smaller polar effect in the naphthoates than it does in the corresponding position in benzoates. (ii) However, for the 3-position, and for the 4-position, in benzoates and naphthoates, the polar effects are sufficiently similar to justify the assumption that the same general mechanism applies to both series. (iii) Polar effects of the 3- and 4-nitro-substituents are much closer in magnitude in the naphthoates than in the benzoates. Concerning (iii), if the nitro-group is to exert its full $-T$ effect it must lie approximately in the plane of the ring. Stuart models indicate that in the 4-position of naphthalene it is prevented from doing so by the adjacent *peri*-hydrogen atom. It follows that the $-T$ effect is reduced and the σ value is also reduced, in the direction of σ for the 3-nitro-substituent. Comparison of σ values for the 5- and the 6-nitro-substituent apparently reveals a similar effect. The 5-nitro-substituent, which is conjugated with the 1-position, has only a little greater polar effect than the 6-nitro-, which is not conjugated with the 1-position. However, an additional factor can be considered in this case. Examination of possible resonance structures indicates that the contribution of the $-T$ effect to the total σ value for the 5-nitro-substituent should be less than that of the $-T$ effect for a 4-nitro-substituent in 1-naphthyl compounds.

It is noteworthy that σ for the " dinitro "-substituent is approximately equal to the sum of the σ values for 4- and 5-mononitro-substituents. This apparent additivity might be taken to imply that any further deviation from coplanarity (resulting from substitution of *peri*-H by NO_2) has little effect on these σ values.

Table 3 summarises all available σ values for nitro-substituents in 1-naphthyl derivatives. Values in columns 2 and 3 are those given by Price *et al.*[16] Figures in column 4 are calculated from Schreiber and Kennedy's results, [17] and values in the last column are similarly calculated from Bryson's data.[18] The symbol in parentheses, $\sigma-$, conforms with the symbolism recently agreed on by Brown, Deno, Jaffé, Taft, and others.[19] It is equivalent to the symbol σ^* adopted earlier by Hammett.

Values for σ in the last column are lower than those elsewhere in the Table, but otherwise agreement is as good as that found for benzene derivatives. It is to be noted that

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[16] Price, Mertz, and Wilson, *J. Amer. Chem. Soc.*, 1954, **76**, 5131.

[17] Schreiber and Kennedy, *ibid.*, 1956, **78**, 153.

[18] Bryson, *Trans. Faraday Soc.*, 1949, **45**, 257; 1951, **47**, 528.

[19] Taft, personal communication, and *J. Amer. Chem. Soc.*, 1957, **79**, 1045.

the work on naphthols and on naphthylammonium ions does not indicate the necessity for a $\sigma-$ value in the case of the 5-nitro-substituent. Thus with 1-naphthyl derivatives, the $-T$ effect of a 5-nitro-substituent appears to be much less important than that of a 4-nitro-group, as tentatively suggested earlier in this discussion

TABLE 3.

	Ester hydrolysis (85% EtOH)	Ester hydrolysis (70% dioxan)	pK_a (naphthoic acids)	pK_a (naphthols)	pK_a (naphthyl-ammonium ions)
3-Nitro	0·68	—	—	—	0·61
4-Nitro	0·70	0·67	0·64	1·71 ($\sigma-$)	1·23 ($\sigma-$)
5-Nitro	0·50	0·49	0·43	0·57	0·40
6-Nitro	0·48	—	—	0·43	0·30
7-Nitro	—	—	—	—	0·70
4 : 5-Dinitro	1·18	—	—	—	—

Steric effects are of importance in the hydrolysis of the 2- and 8-nitro-1-naphthoate and the available data allow a rough comparison of the steric contributions in the two cases. Two types of primary steric effect must be distinguished:[20] (i) steric strain, arising from overlap between non-bonded atoms, and (ii) steric interference with motions. Other things being equal, an increase in steric strain in going from reactant to transition state will result in an increase in the heat of activation, whereas an increase in the " steric interference with motions " factor will lead to a decrease in the entropy of activation. Both will cause an increase in the free energy of activation. For the 2-nitro-1-ester, a rough estimate may be made of steric effects, on the assumption that the polar contribution to the relative heat of activation is not substantially different from that in the case of *o*-nitrobenzoate ($-2{\cdot}6$ kcal. mole^{-1} from Table 2). This, of course, also carries the further assumption that there is little change in steric strain, for *o*-nitrobenzoate, in passing from reactant to transition state. Models, and the comparable $\Delta\Delta H^{\ddagger}$ values for ethyl nitrobenzoates (Table 2), support this. Thus the steric contribution to $\Delta\Delta H^{\ddagger}$ is *ca.* $+2$ kcal. mole^{-1} (*i.e.*, $\Delta\Delta H^{\ddagger} + 2{\cdot}6$). From Table 2 the steric hindrance contribution to the total steric effect is $+2$ kcal. mole^{-1}, *i.e.*, the two steric contributions are comparable in magnitude.

Steric effects for the 8-nitro-substituent may be estimated by assuming that the polar contribution is somewhat similar to that of a 6-nitro-substituent ($-1{\cdot}7$ kcal. mole^{-1}). The steric strain contribution to $\Delta\Delta H^{\ddagger}$ is *ca.* 4·2 kcal. mole^{-1} (*i.e.*, $\Delta\Delta H^{\ddagger} + 1{\cdot}7$). In this case, unlike that of the 2-nitro-ester, the steric hindrance contribution (0·5 kcal. mole^{-1} from Table 2) to the total steric effect is almost negligible compared with the contribution of the steric strain term. Examination of models, in fact, suggests that in going from the 2-nitro-ester to the transition state there is little increase in strain whereas in the case of the 8-nitro-ester the corresponding increase is great.

Two further comments may be made on the 2-nitro-ester hydrolysis. First, the fact that $\Delta\Delta G^{\ddagger}$ is large and positive, whereas $\Delta\Delta G^{\ddagger}$ for *o*-nitrobenzoate is large and negative, appears to illustrate the so-called " buttress " effect. Presumably, in *o*-nitrobenzoate some of the steric interaction is relieved by deformation of bond angles. In the 2-nitronaphthoate the ethoxycarbonyl group cannot bend away from the 2-nitro-substituent without more serious interference with the *peri*-hydrogen atom. Secondly, the discernible curvature of the Arrhenius plot for the 2-nitronaphthoic ester is consistent with reaction by two mechanisms over the temperature range covered. With increase in temperature it might be expected that the reaction mechanism will change from predominantly acyl–oxygen fission to alkyl–oxygen fission. It is intended to carry out further work on the hydrolysis of 2- and of 8-substituted 1-naphthoic esters.

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[20] Taft, personal communication, and *J. Amer. Chem. Soc.*, 1953, **75**, 4534.