

286. The Kinetics of Alkaline Hydrolysis of Substituted Ethyl 1-Naphthoates.

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Rates of alkaline hydrolysis, in 85% (w/w) ethanol-water, of ethyl 3- and 4-chloro-, 3-, 4-, and 5-bromo-, and 3- and 4-methyl-1-naphthoates and of ethyl 1-naphthoate have been measured within the temperature range 25—75°. The results allow an estimate to be made of the steric-hindrance effect of the fused ring in this reaction. A value for the Hammett reaction constant has been obtained from naphthoate hydrolysis alone.

RATES of alkaline hydrolysis of ethyl nitro-1-naphthoates have recently been reported.¹ We have now extended this work by kinetic studies on the esters listed above.

EXPERIMENTAL

New substituted 1-naphthoic acids were prepared as follows:

3-Chloro-1-naphthoic Acid.—*N-Acetyl-4-bromo-2-chloro-1-naphthylamine.* Chlorine was bubbled through a suspension of *N-acetyl-4-bromo-1-naphthylamine*² (165 g.) in glacial acetic acid (1 l.) at room temperature for 2 hr. The solid was filtered off, and water added to the filtrate. The resulting precipitate was recrystallised (charcoal) from ethanol, and then combined with the residue from the first filtration before being recrystallised twice from ethanol. The *N-acetyl-4-bromo-2-chloro-1-naphthylamine* was obtained as colourless crystals (125 g., 67%), m. p. 231° (Found: C, 48.5; H, 3.0; N, 4.6. $C_{12}H_9ONClBr$ requires C, 48.3; H, 3.0; N, 4.7%).

4-Bromo-2-chloro-1-naphthylamine. The naphthalide (125 g.) was refluxed with a mixture of ethanol (750 ml.), water (450 ml.) and concentrated sulphuric acid (300 ml.) until all the solid disappeared (*ca.* 6 hr.). The solution was poured into water, and the precipitate separated by filtration and recrystallised (charcoal) three times from acetic acid. **4-Bromo-2-chloro-1-naphthylamine** (77 g., 71%) was obtained, m. p. 113° (Found: C, 46.7; H, 2.9; N, 5.4. $C_{10}H_7NClBr$ requires C, 46.8; H, 2.7; N, 5.5%).

1-Bromo-3-chloronaphthalene. The foregoing amine (20 g.), dissolved in acetic acid (125 ml.), was added to a stirred, freshly prepared solution of sodium nitrite (7 g.) in concentrated sulphuric acid (45 ml.) below 20°. Stirring was continued for 30 min., and the mixture was then added during 30 min. to a stirred suspension of cuprous oxide (21 g.) in ethanol (180 ml.). After evolution of nitrogen had ceased the mixture was filtered, and the residue washed with boiling ethanol (100 ml.). The combined filtrate and washings were poured into water, and the precipitate recrystallised (charcoal) from methanol containing a little acetone to give crude 1-bromo-3-chloronaphthalene, m. p. 56.5°. The coloured impurities were removed by passing a solution of the product in hexane (100 ml.) through a short alumina column. Removal of the solvent and recrystallisation of the product from methanol-acetone yielded the compound as colourless crystals (13.5 g., 70%), m. p. 56.5°. This compound had previously been prepared³ in unstated yield from 3-chloro-1-naphthylamine, itself obtained by a laborious process.

3-Chloro-1-naphthoic acid. 1-Bromo-3-chloronaphthalene (24.2 g., 0.1 mole) in ether (50 ml.) was added to a solution of *n*-butyl-lithium (0.1 mole) in ether (96 ml.) at -35°. After vigorous shaking at -35° for 10 min. the mixture was stirred into a slurry of solid carbon dioxide and ether. Isolation by the usual method⁴ gave the crude *acid*, m. p. 218—221°. After three recrystallisations from aqueous ethanol and one from aqueous acetic acid it was obtained (8.9 g., 43%) as colourless crystals, m. p. 223° (Found: Cl, 17.3%; equiv., 206.6. $C_{11}H_7O_2Cl$ requires Cl, 17.2%; equiv., 206.5).

3-Methyl-1-naphthoic Acid.—**4-Bromo-2-methyl-1-naphthylamine.** Bromine (8 ml.) in carbon

¹ Fischer, Murdoch, Packer, Topsom, and Vaughan, *J.*, 1957, 4358.

² Hodgson and Birtwell, *J.*, 1943, 321.

³ Hodgson and Hathway, *J.*, 1944, 538.

⁴ Hussey, *J. Amer. Chem. Soc.*, 1951, **73**, 1364.

tetrachloride (40 ml.) was added with stirring at -5° to a solution of 2-methyl-1-naphthylamine⁵ (23 g.) in carbon tetrachloride containing iodine and iron powder. After 10 minutes' stirring the precipitated amine hydrobromide was filtered off and dried under vacuum; when it was dissolved in hot ethanol and poured into aqueous sodium hydrogen carbonate, crude 4-bromo-2-methyl-1-naphthylamine (m. p. $68-74^{\circ}$) was obtained. Three recrystallisations from light petroleum (b. p. $50-70^{\circ}$) gave 4-bromo-2-methyl-1-naphthylamine (11 g., 31%), m. p. 78° . (If the crude product was heated in a solvent above 65° a tar was formed.) This amine has been prepared in very low yield by hydrolysis of *N*-acetyl-4-bromo-2-methyl-1-naphthylamine.⁶

1-Bromo-3-methylnaphthalene. 4-Bromo-2-methyl-1-naphthylamine was deaminated by the method described for 4-bromo-2-chloro-1-naphthylamine. The resulting mixture was steam-distilled. After ether extraction of the distillate and removal of ether from the extracts, the yellow, oily residue was distilled in vacuum to yield 1-bromo-3-methylnaphthalene (48%), b. p. $127/3.5$ mm. This preparation is simpler than that due to Vesely.⁷

3-Methyl-1-naphthoic acid. *n*-Butyl-lithium (0.025 mole) in ether (25 ml.) was added at room temperature to 1-bromo-3-methylnaphthalene (5.6 g., 0.025 mole) in ether (75 ml.). The mixture was shaken for 30 sec. and then stirred into a slurry of solid carbon dioxide and ether. After excess of carbon dioxide had evaporated, hydrochloric acid and ethanol were added and the ether was distilled off. On cooling, crude 3-methyl-1-naphthoic acid was obtained, m. p. $168-172^{\circ}$. Four recrystallisations from aqueous ethanol gave colourless crystals (3 g., 64%), m. p. 173.5° (Found: C, 77.4; H, 5.2%; equiv., 186.0. $C_{12}H_{10}O_2$ requires C, 77.4; H, 5.4%; equiv., 186.2).

Of the known acids, 1-naphthoic acid had m. p. 160° and 4-methyl-1-naphthoic acid,⁸ m. p. 174° . 4-Chloro-1-naphthoic acid (m. p. 225° ; yield 57%) and 4-bromo-1-naphthoic acid (m. p. 221° ; yield 80%) were prepared, by the method described for 3-chloro-1-naphthoic acid, from 1-bromo-4-chloronaphthalene⁹ (6 g.) and 1:4-dibromonaphthalene¹⁰ (14 g.) respectively. 3-Bromo-1-naphthoic acid (m. p. 236° ; yield 50%) was prepared from 3-nitro-1-naphthoic acid¹¹ through reduction to the amine sulphate¹² (not isolated) followed by diazotisation and subsequent formation of the diazonium mercuribromide, which was decomposed to the required acid by heating at 110° with sodium bromide (cf. ref. 13).

Esters.—These were all prepared by the Fischer-Speier method. Physical constants, etc., were as follows: Ethyl 1-naphthoate, b. p. $116^{\circ}/1$ mm.; ethyl 3-methyl-1-naphthoate, b. p. $155^{\circ}/2$ mm.; ethyl 4-methyl-1-naphthoate, b. p. $172^{\circ}/4.5$ mm.; ethyl 4-bromo-1-naphthoate, m. p. 43.5° ; ethyl 5-bromo-1-naphthoate, m. p. 48° ; ethyl 4-chloro-1-naphthoate, m. p. 27.5° ; ethyl 3-chloro-1-naphthoate, b. p. $133^{\circ}/0.75$ mm. (Found: Cl, 15.1. $C_{13}H_{11}O_2Cl$ requires Cl, 15.1%); ethyl 3-bromo-1-naphthoate, needles from aqueous alcohol, m. p. 28° (Found: Br, 28.1. $C_{13}H_{11}O_2Br$ requires Br, 28.6%).

Hydrolyses.—The purification of solvent ethanol and of reagents has been described, as has the general titration method of following kinetics.¹ At temperatures above 55° , corrections were required for alkaline attack on the glass wall of the reaction vessel; these were obtained from blank runs, with ester omitted. For ethyl 3- and 4-bromonaphthoates, use of stainless-steel reaction vessels eliminated the blank. Rate constants for these two esters are fully comparable with those for the other esters; rate constants for ethyl 1-naphthoate measured by both techniques were in good agreement (see Table I).

For each ester, runs were carried out at four temperatures, good second-order kinetics being obtained. Runs with unequal concentrations of ester and base showed that reactions were of first order with respect to each reactant. Good Arrhenius plots of $\log k$ versus $1/T$ were obtained. Rate constants and Arrhenius parameters (in $\log k = \log B - E/RT$) are given in Table I. The probable error in each of these parameters is ca. 0.1 in every case. For ethyl naphthoate three sets of results, obtained by three different individuals, are given.

⁵ Adams and Albert, *J. Amer. Chem. Soc.*, 1942, **64**, 1476.

⁶ Shoesmith and Rubli, *J.*, 1927, 3103.

⁷ Vesely and Kapp, *Rec. Trav. chim.*, 1925, **44**, 360.

⁸ Mayer, Sieglitz, *et al.*, *Ber.*, 1922, **55**, 1835.

⁹ Fieser and Desreux, *J. Amer. Chem. Soc.*, 1938, **60**, 2261.

¹⁰ Zalkind and Faerman, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 1021.

¹¹ Leuck, Perkins, and Whitmore, *J. Amer. Chem. Soc.*, 1929, **51**, 1831.

¹² Jacobs and Gould, *J. Biol. Chem.*, 1937, **120**, 141.

¹³ Newman and Wise, *J. Amer. Chem. Soc.*, 1941, **63**, 2847.

Results in the first two rows of Table 1 were derived from runs in glass reaction flasks. The third set of results was obtained by using stainless steel reaction vessels.

TABLE 1. Rates of hydrolysis (10^3k , with k in l. mole⁻¹ sec.⁻¹) of ethyl X-1-naphthoates at various temperatures.

X	25°	35°	45°	55°	65°	75°	E *	log B
H	—	0.704, 0.718	1.67, 1.72 1.74	3.67, 3.82 3.84	—	—	16.7	8.7
H	—	—	1.51, 1.53 1.56	3.53, 3.61 3.68	7.76, 7.79 7.88	16.0, 16.0	17.2	9.0
H	0.240, 0.241 0.242	0.716, 0.719	—	3.40, 3.43 3.45, 3.45	8.07, 8.07 8.12, 8.12	—	17.3	9.1
3-Cl	2.01, 2.09 2.14	5.04, 5.06 5.13	11.1, 11.2 11.3, 11.4	25.5, 25.6	—	—	16.1	9.1
4-Cl	—	2.45, 2.45	6.02, 6.02 6.05	13.2, 13.2	30.3, 30.5	—	17.2	9.6
3-Br	2.10, 2.13 2.16	—	11.2, 11.3 11.3	—	49.6, 52.0 52.4	—	15.8	8.9
4-Br	1.04, 1.05	2.72, 2.77 2.83	—	13.2, 13.3 13.3, 13.5	31.6, 31.8 32.0	—	16.7	9.3
5-Br	1.04, 1.04 1.05	—	5.45, 5.57 5.57	12.6, 12.7	25.6, 25.9 25.9	—	16.2	8.9
3-CH ₃	—	—	1.13, 1.16 1.17	2.71, 2.71	6.05, 6.15 6.24	12.8, 12.9 13.1	17.8	9.3
4-CH ₃	—	—	0.750, 0.750 0.754	1.69, 1.69 1.72	3.90, 3.90 3.95	8.65, 8.80 8.86	18.1	9.3

* In kcal. mole⁻¹.

DISCUSSION

It has already been shown¹ that, within experimental error, the alkaline hydrolyses of ethyl 1-naphthoate and of ethyl 3-, 4-, 5-, and 6-nitro-1-naphthoate are isoentropic (log B is constant). This conclusion can now be extended to include the hydrolyses of ethyl 3- and 4-chloro-, 3-, 4-, and 5-bromo-, and 3- and 4-methyl-1-naphthoates. These extensive results suggest that for the alkaline hydrolyses of all simple 3-, 4-, 5-, 6-, and 7-substituted 1-naphthoates, log B is likely to be constant. In such substituted naphthoates the substituents should be held rigidly at relatively large distances from the reaction centre. Thus, as in the *meta*- and *para*-substituted benzoates, there should be negligible steric interference, by the substituent, with the approach of the attacking hydroxide ion.

The mean of 14 values for log B obtained from the alkaline hydrolysis of *meta*- and *para*-substituted ethyl benzoates^{14,15} in 85% ethanol is 9.7 with a probable error of ± 0.02 . The mean of the 14 values of log B , obtained from the similar hydrolysis of the specific naphthoates listed above, is 9.3 ± 0.07 . The difference, which is equivalent to 0.65 kcal. mole⁻¹ in $T\Delta\Delta S_{50}^\ddagger$, is a measure of the steric hindrance of a 2:3-benzo-substituent in this reaction.* This measure of steric hindrance is sufficient to explain the difference in rate of hydrolysis of a *meta*- or *para*-substituted ethyl benzoate and a corresponding naphthoate. In Table 2 are listed, for correspondingly substituted ethyl benzoates and naphthoates, values of $-RT \ln k_{50}^\ddagger$ and values of the relative free energy of activation, $\Delta\Delta G_{50}^\ddagger$, *i.e.*,

$$\Delta\Delta G_{50}^\ddagger_{\text{naphthoate}} - \Delta\Delta G_{50}^\ddagger_{\text{benzoate}} = -RT \ln k_{50}^\ddagger_{\text{naphthoates}} + RT \ln k_{50}^\ddagger_{\text{benzoates}}$$

Data for the 4-nitro-substituent, although available, are not included in this Table because of the demonstrated complication of steric inhibition of resonance in a 4-nitronaphthoate.¹ Values of $\Delta\Delta G_{50}^\ddagger$ given in Table 2 are constant within experimental error. In the case of

* This value compares with a value of 0.6 kcal. mole⁻¹ otherwise determined in these laboratories.¹⁶

¹⁴ Ingold and Nathan, *J.*, 1936, 222.

¹⁵ Evans, Gordon, and Watson, *J.*, 1937, 1430.

¹⁶ Wong, Thesis, University of New Zealand, 1957.

the 3-nitro-substituent, an extrapolation, from published data at 25° and 35° only, was required to obtain $\log k_{50^\circ}$. The resultant uncertainty in this value is probably reflected in the rather large deviation, from the mean, of $\Delta\Delta G_{50^\circ}^\ddagger$ for this substituent. The mean value of $\Delta\Delta G_{50^\circ}^\ddagger$ is 0.61 kcal. mole⁻¹. Within experimental error this is equal to the $T\Delta\Delta S_{50^\circ}^\ddagger$ value of 0.65 kcal. mole⁻¹. Thus the relative heat of activation, $\Delta\Delta H^\ddagger$, for

TABLE 2.

Substituent	H	3-NO ₂	3-Cl	4-Cl	4-Br	3-CH ₃	4-CH ₃
$-RT \ln k_{50^\circ, \text{benzoate}}$	3.30	0.73	2.07	2.47	2.35	3.46	3.80
$-RT \ln k_{50^\circ, \text{naphthoate}}$	3.88	1.52	2.62	3.03	2.99	4.07	4.37
$\Delta\Delta G^\ddagger$	0.58	0.79	0.55	0.56	0.64	0.61	0.57

corresponding benzoates and naphthoates, is negligible. This, of course, does not mean that the 2:3-benzo-substituent has no polar, steric strain, or "resonance" effect¹⁷ but rather that the algebraic sum of these effects is approximately zero. Sufficient data are now available to allow accurate evaluation of the Hammett reaction constant ρ for the alkaline hydrolysis of the ethyl 1-naphthoate series. By Jaffé's method,¹⁸ two regression lines were fitted to the $\log k_{50^\circ}$ versus σ (Hammett substituent constant) data from Table 3. In this table values of $\log k_{50^\circ}$ were derived from the Arrhenius relationship fitted to the data in Table 1. Values for σ are those of Jaffé.

The value of ρ_{50° so obtained is 2.21, the correlation coefficient r is 0.998, the calculated $\log k_0$ value is 2.59, and the slope of second regression line is 0.451. New σ values are

TABLE 3.

Substituent	H	H	H	3-NO ₂	3-Cl	4-Cl	3-Br
$-\log k_{50^\circ}$	2.59	2.62	2.64	1.03	1.77	2.05	1.77
σ	0.000	0.000	0.000	0.710	0.373	0.227	0.391
σ_n	—	—	—	0.706	0.372	0.246	0.372
Substituent	4-Br	3-CH ₃	4-CH ₃	4-NO ₂	5-NO ₂	6-NO ₂	5-Br
$-\log k_{50^\circ}$	2.02	2.75	2.95	0.99	1.46	1.51	2.07
σ	0.232	-0.069	-0.170	0.778	—	—	—
σ_n	0.259	-0.070	-0.160	0.724	0.512	0.489	0.236

ven by the expression * $\sigma_n = 1.170 + 0.451 \log k_{50^\circ}$. By using the experimental $\log k_{50^\circ}$ data in the latter expression, σ_n values were computed and are tabulated in the third line Table 3. For the reason mentioned above the data for the 4-nitro-substituent were not used in determining the regression lines.

For alkaline hydrolysis of ethyl 1-naphthoates in 85% ethanol, ρ_{50° is slightly smaller than ρ_{50° for similar hydrolysis of ethyl benzoates,¹⁸ *viz.*, 2.21 as compared with 2.32. The difference between the values is small and, without data on other reaction series, it is doubtful whether this difference is significant. It has been concluded,¹ from similar rate data on 3- and 4-nitro-benzoates and -naphthoates, that the same hydrolytic mechanism (A_{OC}2) applies to both aromatic series. The close similarity in ρ values confirms this conclusion.

The data in Table 3 show that the 5-bromo-substituent has a σ_n value not very different from that of the 4-bromo-substituent ($\sigma_4 - \sigma_5 = 0.023$). For the nitro-substituent, however, a change from position 4 to position 5 results in a much greater decrease ($\sigma_4 - \sigma_5 = 12$) in σ_n . In position 5, both *I* and *T* effects of a substituent are expected to be smaller than in position 4. In the case of the bromo-substituent it appears that the decrease in

* The subscript n (= naphthalene) merely denotes the different origin of the substituent constant in its expression. Its purpose is only to simplify present comparison of σ values, obtained from studies on benzene series, with corresponding values derived from the naphthalene series.

¹ Taft, in Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons Inc., New York, 1956.

¹⁸ Jaffé, *Chem. Rev.*, 1953, **53**, 191.

magnitude of its $-I$ effect is almost fully compensated by the reduction in its $+M$ effect. With the nitro-substituent, on the other hand, the reductions in its $-I$ and $-T$ effects are cumulative.

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