# 32. *The Kinetics of the Alkaline Hydrolysis of Esters and Amides of 1- and 2-Naphthoic Acid.*

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The kinetics of alkaline hydrolysis, in alcohol–water solvents, of the methyl and ethyl esters of 1- and 2-naphthoic acid have been followed in the temperature range 30—60°. The order of reactivity found for the methyl esters is the reverse of that found by Bergmann and Hirshberg,[1] working with methanolic potassium hydroxide, and the order now found agrees with results for ethyl esters and with results here reported for the corresponding naphthamides at 70—80°. The relative rates of hydrolysis of ethyl and methyl esters for a given naphthoic acid are discussed and a value is derived, from results on ethyl 2-naphthoate, for the Hammett $\sigma$ constant for the fused benzene ring.

In accord with calculations showing that electron density at $C_{(1)}$ of naphthalene is greater than that at $C_{(2)}$,[2] reaction of naphthalene with electrophilic reagents occurs predominantly at position 1, provided that it is not complicated by exceptionally strong temperature- and solvent-dependence (as in, *e.g.*, sulphonation, Friedel–Crafts alkylation). The evidence concerning nucleophilic attack is, however, neither extensive nor unambiguous.

Few reactions involving nucleophilic displacement of groups at either position 1 or position 2 have been carried out and evidence for order of relative reactivity is inconclusive.[3] But the difference in electron density should be reflected in the relative reactivities of suitable side chains, and reactions of such derivatives may be chosen which are more amenable to kinetic study than are reactions involving direct substitution in the ring. In such reactions which have been investigated, it is possible to link greater reactivity of the 1-naphthyl compound (*e.g.*, neutral hydrolysis of bromomethylnaphthalenes [4]) with a preliminary rate-determining ionisation which would be aided by electron-donating groups, whilst greater reactivity of the 2-naphthyl compound (*e.g.*, acid hydrolysis of naphthalenesulphonyl chlorides [5]) may be associated with an $S_N2$ type mechanism in which the rate-determining step is attack by the nucleophilic agent. Such interpretations are compatible with calculated electron densities, but of special interest, however, are the results of Bergmann and Hirschberg [1] who determined the second-order rate constants for the alkaline hydrolysis of methyl 1- and 2-naphthoates in methanol at 60°. Hydrolysis of the 1-naphthoate was observed to occur at the higher rate (*ca.* 4 : 3). It is difficult to interpret these results, especially on the basis of a $B_{AC}2$ mechanism by which, it may be assumed, these reactions occur. In view of the greater electron-donating capacity of the 1-naphthyl group it would be expected, *a priori*, that methyl 2-naphthoate would undergo hydrolysis more rapidly than the 1-ester.

The alkaline hydrolysis of the two methyl naphthoates in methanol–water has been investigated by us and the results, together with those of similar hydrolytic studies on the ethyl esters in ethanol–water and on the corresponding amides in dioxan–water, are now reported.

## Experimental

*Materials.*—1- and 2-Naphthoic acid melted at 160° and 182° respectively. The esters were prepared by using the purified alcohols and dry hydrogen chloride. Methyl 2-naphthoate melted at 76°. B. p.s of the other three esters were: ethyl 1-, 194—196°/45 mm., and 2-naphthoate, 194—195°/37 mm.; methyl 1-naphthoate, 165—166°/17 mm., m. p. 36°. 1-Naphthamide melted at 207° and 2-naphthamide at 196—196·5°. Solvents were purified by standard methods, the alcohols being aldehyde-free (Schiff's reagent), and sodium hydroxide

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[1] Bergmann and Hirshberg, *J.*, 1936, 331.
[2] Jaffé, *J. Chem. Phys.*, 1952, **20**, 778.
[3] Cf., *inter al.*, Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 273; also ref. 2.
[4] Ingold and Patel, *J. Indian Chem. Soc.*, 1930, **7**, 95.
[5] Linetskaya and Sapezhorikova, *Zhur. priklad. Khim.*, 1948, **21**, 876.

solutions being free from carbonate. The temperature of the thermostat bath was maintained within ±0·02°.

*Ester Hydrolyses.*—The kinetic procedure was similar to that used by Evans, Gordon, and Watson.[6] The esters were hydrolysed in aqueous alcohol (85% of alcohol by wt.), the alcohol used being that corresponding to the alkyl group of the ester under study. Boiled-out distilled water was used and aliquots for analysis were kept under nitrogen. Amounts of ester and sodium hydroxide initially used were equivalent, and the simplified form $k = x/[ta(a - x)]$ of the second-order rate equation was found to apply in all instances (see Appendix). The minimum number of runs carried out under any chosen conditions was 2 and the average was 3—4. Runs with unequal concentrations of ester and alkali acted as a check on the assumed rate-dependence. Kinetics were followed at four temperatures and results of all runs are given in the Table. The mean values for rate constants led to satisfactory Arrhenius plots of log $k$ *versus* $1/T$ and values for the activation energy ($E$) and the temperature-independent term ($\log_{10} B$) are included in the Table.

| | $10^3k$ (l. mole$^{-1}$ sec.$^{-1}$) | | | | $E$ (kcal.) | $\log_{10} B$ |
|---|---|---|---|---|---|---|
| | Ethyl esters in 85% ethanol–water (w/w) | | | | | |
| | 30° | 40° | 50° | 60° | | |
| 1-Naphthoate | 0·68, 0·63, 0·59 | 1·67, 1·60, 1·57,<br>1·70, 1·50 | 2·63, 2·67,<br>3·10, 3·10 | 5·8, 5·9, 5·9 | 14·5 | 7·3 |
| 2-Naphthoate | 1·50, 1·63, 1·61,<br>1·54 | 3·52, 3·58, 3·47,<br>3·77, 3·66 | 8·0, 8·3,<br>8·3 | 17·3, 17·5, 17·3 | 16·1 | 8·8 |
| | Methyl esters in 85% methanol–water (w/w) | | | | | |
| 1-Naphthoate | 0·152, 0·152, 0·148 | 0·52, 0·48, 0·50 | 1·22, 1·24 | 2·48, 2·45, 2·50 | 18·7 | 9·7 |
| 2-Naphthoate | 0·36, 0·33, 0·37,<br>0·35, 0·38, 0·37 | 0·97, 0·87, 0·96,<br>0·83, 0·96, 0·93 | 2·65, 2·66 | 6·5, 6·4, 6·5 | 19·4 | 10·5 |
| | Naphthamides in 20% dioxan–water (v/v) | | | | | |
| | 70° | 80° | | | | |
| 1-Naphthamide | 0·0103 | 0·0236 | — | — | 20·0 | 7·7 |
| 2-Naphthamide | 0·146 | 0·253 | — | — | 13·3 | 4·6 |

*Amide Hydrolyses.*—The reaction vessels used and the methods of analysis followed have been described.[7, 8] The analytical procedure was checked for the solvent (20% dioxan–water, v/v) and no interference could be detected. With 2-naphthamide the extent of reaction with hypobromite was sufficiently small to allow use of direct titration after correction for the slight amide–hypobromite reaction. With 1-naphthamide, the interaction with hypobromite was extensive and the distillation procedure was used with satisfactory results. The molar ratio of alkali : amide was >100 : 1 in every run and the kinetics were of the first order with respect to amide. Variation of amide concentration confirmed the expected pseudounimolecular kinetics. Kinetics were followed at 70° and 80° and at each temperature rates were measured at five different alkali concentrations (0·4—1·6M for 1-naphthamide and 0·15—0·65M for 2-naphthamide). Duplicate runs showed agreement as good as that previously reported for aliphatic amides.[8] For each amide, when $k_1$ (first-order rate constant) was plotted against [NaOH], the resulting graph was linear, the slope $k$ being the second-order rate constant for the reaction. Values for $k$, $E$, and $\log_{10} B$ are in the Table.

## DISCUSSION

Comparison of the present results for methyl esters with those of Bergmann and Hirshberg [1] shows a difference in absolute values, and the order of reactivity now found is the reverse of that indicated by them. The earlier, much lower values are understandable in the light of the solvent used, which appears to have been almost 100% methanol, in which hydroxyl-ion concentration is extremely low (see below). The difference in order, on the other hand, is difficult to accept without the arbitrary assumption of a reversal in order within the range 85—100% methanol. In estimating the importance of the discrepancy, however, it must be borne in mind that Bergmann and Hirshberg's figures

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

[7] Ivory, McKenzie, and Vaughan, *J.*, 1952, 3264.

[8] Packer, Thomson, and Vaughan, *J.*, 1955, 2601.

are the result of kinetic work at one temperature and appear to be derived from single runs followed only for a very small degree of hydrolysis; furthermore Bergmann and Hirshberg used the simplified form of the second-order rate equation, which appears not to be applicable in nearly absolute methanolic sodium hydroxide. The order of reactivity now reported finds a parallel in the results on the ethyl esters, and similar work on the corresponding amides also shows the same relative rate order. Unexpectedly, in the ester hydrolyses the slower reaction (that of the 1-naphthoates) has the smaller Arrhenius energy of activation although in the amide hydrolyses the slower reaction (again that of the 1-derivative) has the higher energy of activation. There appears to be no obvious explanation of this difference; the results do suggest, however, that there may be no simple correlation between electron density and Arrhenius energy of activation in the naphthalene series.

Our results on ester hydrolysis also serve for a comparison of the reaction rates of methyl and ethyl esters of a given naphthoic acid. At any one temperature the rate constant for ethyl 1- or 2-naphthoate in 85% ethanol is higher than that for methyl 1- or 2-naphthoate respectively in 85% methanol. Bearing in mind the assumed mechanism for such ester hydrolysis it would be expected that, had the reactions been carried out in the same solvent, the more highly positive-inductive ethyl group should lead to a comparatively slower reaction for the ethyl ester. Ingold,[9] for example, found this effect in the hydrolyses of methyl and ethyl acetate. Comparison of rate constants obtained in different solvents is clearly complicated by many factors but in the present case a major effect, tending to favour faster reaction of the ethyl ester, can be discerned. Caldin and Long [10] studied the replacement, at 25°, of hydroxide ion by ethoxide ion in solutions made by dissolving sodium or sodium hydroxide in ethanol–water mixtures. It is clear, from their measurement of equilibrium constants, that ethoxide-ion concentration in 85% ethanol at 25° is high (*ca.* 60% total base).

A somewhat similar relation, with a different equilibrium constant, is likely to hold for hydroxide ions in methanol. Woodland, Carlin, and Warner [11] demonstrated the greater acidity of methanol than of water, and Hine and Hine [12] have given the values for the relative acidities of ethanol, methanol, and water in propan-2-ol solution as 0·95, 4·0, and 1·2 respectively. Clearly, addition of equal amounts of alkali to methanol and ethanol leads to a higher concentration of *hydroxide* ions in ethanol than in methanol. Because attack by methoxide ion on the methyl ester merely produces another ester molecule, the lower hydroxide-ion concentration in the methanolic solution results in a lower rate of hydrolysis than might be expected from the amount of sodium hydroxide introduced. The extent of such lowering of rate would be less in the corresponding case of ethanol and ethyl ester. From the experimental figures on relative rates, it appears possible that this factor is much more important than the difference in inductive effects displayed by the alkyl groups concerned. Other factors, such as difference in dielectric constant of the medium, will doubtless play their parts.

From the present results on ethyl 2-naphthoate a value may be obtained for the Hammett $\sigma$ constant of the fused benzene ring in the 2-naphthyl derivative. Calculations were based on Jaffé's equation,[13] and rate constants were taken from the Arrhenius plot to obtain figures for $\sigma$ at temperatures for which other data are available. The relevant values, together with the probable errors, are $\sigma_{25} = 0{\cdot}079 \pm 0{\cdot}017$, $\sigma_{35} = 0{\cdot}055 \pm 0{\cdot}021$, $\sigma_{50} = 0{\cdot}051 \pm 0{\cdot}019$. Two values have previously been reported. Hammett [14] gives $\sigma_{25} = 0{\cdot}170 \pm 0{\cdot}10$ and Price and Michel [15] give $\sigma_{25} = 0{\cdot}019$. In checking the calculation of the latter workers, we obtained 0·001, although recalculation of other $\sigma$ constants given in the same paper confirmed the values quoted.

[9] Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, New York, **1953**, p. 758.

[10] Caldin and Long, *J.*, 1954, 3737.

[11] Woodland, Carlin, and Warner, *J. Amer. Chem. Soc.*, 1953, **75**, 5835.

[12] Hine and Hine, *ibid.*, 1952, **74**, 5266.

[13] Jaffé, *Chem. Rev.*, 1953, **53**, 254.

[14] Hammett, " Physical Organic Chemistry," McGraw-Hill, New York, 1940, p. 188.

[15] Price and Michel, *J. Amer. Chem. Soc.*, 1952, **74**, 3653.

## APPENDIX

In our system for ester hydrolysis the concentrations of alcohol and water change by negligible amounts and the ionic strength remains constant. The equilibrium constant ($K$) for the equation $OH^- + EtOH \rightleftharpoons H_2O + EtO^-$ may be written as $[H_2O][EtO^-]/[OH^-][EtOH]$. The linear plots which occur owing to the use of the simplified form of the second-order rate equation arise from the proportionality between the amount of hydroxide ion and the total amount of base present (hydroxide and ethoxide ions). It will be seen from the expression for $K$ that this will only be true if changes in $[H_2O]$ and $[EtOH]$ are negligible. Use of 85% ethanol–water is satisfactory in this respect but it appears that in a solvent of very high alcohol concentration (*e.g.*, $>99\%$) and with base concentration greater than, say, 0·01M some drift from linearity of plots might be expected. The general argument appears true for use of both ethanol and methanol, which give rise to values of $K$ which, while different numerically, are of the same order of magnitdue. Further, for alcohol–water systems to which the simple second-order equation is applicable the derived rate constant, $k$, is not the same as that which would be obtained from the unsimplified form with knowledge of the actual hydroxide-ion concentration. It is readily demonstrable that the relation, which in theory should hold between the two rate constants, is $k = k_{\text{true}} \cdot s/(1 + s)$ where $s = [OH^-]/[EtO^-]$. Provided that the mixed solvent remains the same, however, $k$ values found by use of the simple equation are fully adequate for the main purpose of such measurements, *i.e.*, the comparison of rates.

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