Transmission of Polar Effects. Part 16.[1] Ionisation of 8-Substituted 1-Naphthoic Acids and the Alkaline Hydrolysis of their Methyl Esters

Socrates Acevedo and Keith Bowden *
Department of Chemistry, University of Essex, Wivenhoe Park, Colchester CO4 3SQ, Essex

Kirkwood–Westheimer calculations were carried out for the ionisation of three 8-substituted 1-naphthoic acids in 80% (w/w) 2-methoxyethanol–water at 25 °C. The reversed substituent polar effects are accounted for qualitatively and quantitatively for the 8-chloro and 8-bromo acids. For the 8-nitro acid the critical nature of the assumptions regarding the geometry is discussed. The rate coefficients for the alkaline hydrolysis of six methyl 8-substituted 1-naphthoates have been determined in 70% (v/v) dimethyl sulphoxide–water at 83.3 °C. All 8-substituents show very large steric 'bulk' retardations and their significance is discussed.

In earlier studies [2,3] it has been both shown and confirmed that reversed dipolar substituents effects occur in the ionisation of 8-substituted 1-naphthoic acids. 1-Naphthoic acid is a weaker acid than any of the 8-substituted derivatives. This arises from steric inhibition of resonance between the carboxy group and the ring, caused by the *peri*-substituent, leading to an acid-strengthening effect. All the 8-substituted 1-naphthoic acids have the carboxy group completely or very extensively deconjugated from the ring, and the steric effect can be considered to be approximately constant for all the substituents.

In this study the polar effects of 8-substituents on the acidity of 1-naphthoic acids are assessed by using the theory of Kirkwood and Westheimer.[4] Further, a study of the effects of 8-substituents on the alkaline hydrolysis of methyl 1-naphthoate has been made in order to evaluate such effects which might be relevant to related systems such as methyl 5-substituted triptycene-7-carboxylates.[5]

Results and Discussion

pK_a *Values*.—The reference compound in the series of 8-substituted 1-naphthoic acids can be taken to be the 8-methyl derivative, in order to allow for deconjugation of the carboxy group.[2] However, this 8-substituent itself will have a small but definite polar effect. The ΔpK_a values for 80% (w/w) aqueous 2-methoxyethanol shown in Table 1 are corrected for the latter effect (*i.e.* by -0.1 pK_a unit).

Calculations (see Experimental section) of the field effect of the 8-substituents in 1-naphthoic acid have been carried out by using the Kirkwood and Westheimer theory for a spherical, two-point charge model[4] (Table 1). Both the sign and the magnitude of the observed polar effect for the 8-chloro and -bromo derivatives are predicted. However, the results for the nitro group are apparently very poor; they clearly illustrate the difficulties inherent in the method. The theory[4] is a very appropriate model when both the dipole and reaction site are on or near to a common diameter of the model cavity shape and sufficiently far apart that approximations to point or two-point dipole systems are realistic. In the present model system, the reaction site and the substituent come into close contact, and the approximations approach their useful limit. It is perhaps surprising that such reasonable agreement is found for the 8-chloro- and -bromo-substituted acids, in view of the crucial dependence noted for disposition of the dipole in the 8-nitro acid.

Alkaline Hydrolysis.—The rate coefficients for the alkaline hydrolysis of a series of methyl 8-substituted 1-naphthoates in 70% (v/v) dimethyl sulphoxide–water at 83.3 °C are shown in Table 2. These results show that a steric 'bulk' effect is the main factor determining the relative reactivity. The steric effect results from 'crowding' in the reactant being greatly magnified in the transition state for alkaline hydrolysis. Crystallographic studies[6] on 1,8-disubstituted naphthalenes have shown that non-bonded interactions between the *peri*-substituents lead to considerable distortion to relieve steric compression. Such interactions should be considerably increased in the transition state, owing to the 'tetrahedral' nature of the reaction site. With dipolar *peri*-substituents the situation is further complicated by electrostatic interactions between the dipole and incipient charges at the reaction site. However, it seems that the main effect is purely one of steric 'bulk'. The effect of the 8-methyl group appears to be much larger than the effects of the other substituents. This appears to be associated with out-of-plane bending (the in-plane twisting is inhibited by the β-hydrogen atom[6]) of the substituent, the C–Me bond being stronger than the other C–X bonds. Further, the rotational freedom of the methyl group, which may be hindered in the reactant state, will be highly or completely inhibited in the transition state. All substituent effects are much greater than those observed for the *ortho*-substituted benzoate esters.[7,8] However, the small range in the effects noted for the 8-chloro, -bromo and -methoxy groups shows the dominance of the severe, but similar, 'lateral' *peri*-interaction for these three substituents.

Experimental

Materials.—The methyl 8-substituted 1-naphthoates had been previously prepared[9,10] and were recrystallised or redistilled until their physical properties were identical with or close to those reported. The solvent was prepared as previously described.[11]

Measurements.—The rate coefficients for the alkaline hydrolysis of the methyl esters were measured in aqueous dimethyl sulphoxide by a u.v. spectrophotometric method as previously described.[12] For the unsubstituted and 8-nitro esters, the substrate and hydroxide anion concentrations were 2.5×10^{-4} and 1×10^{-3} to 1×10^{-2}M, respectively. At these base concentrations the other esters were hydrolysed very slowly. An aqueous solution of tetramethylammonium hydroxide (0.782M) in dimethyl sulphoxide was used for hydrolysis of all the esters; the kinetic equivalent concentration of base was determined from the known k_2 values for the unsubstituted and 8-nitro esters as 4.08M. This technique allowed for any activity, or salt, or specific salt effects on the rates in the presence of high base concentrations. Satisfactory

Table 1. Kirkwood–Westheimer calculations for the 8-substituted 1-naphthoic acids in 80% (w/w) 2-methoxyethanol–water at 25 °C[a]

Substituent	ΔpK_a	
	Calc.	Found
Cl	−0.20	−0.15
Br	−0.37	−0.27
NO_2 (i)	−0.83	−0.11
(ii)	−0.86	−0.11

[a] Positive end of dipole located (i) midway between the ring carbon and the nitrogen or (ii) on the nitrogen atom.

Table 2. Rate coefficients (k_2) for the alkaline hydrolysis of methyl 8-substituted 1-naphthoates in 70% (v/v) dimethyl sulphoxide–water at 83.3 °C[a]

Substituent	k_2/l mol^{-1} min^{-1}
H	248
Me	<0.0001
Cl	0.004 87
Br	0.0140
NO_2	1.24
OMe	0.008 99

[a] Rate coefficients were reproducible to within ±3%.

rates of hydrolysis were then obtained for the 8-chloro, 8-bromo and 8-methoxy esters. No significant hydrolysis was observed for the 8-methyl ester but an upper limit could be estimated. The reactions were followed at the λ value showing maximum difference between substrate and product, *i.e.* 300—320 nm. The reaction was observed to be first-order in substrate and, where it could be tested, first-order in base. As the reaction was carried out in excess of base, the resulting first-order behaviour was observed without deviation for at least three 'half-lives' for the faster reactions. For the slower reactions Guggenheim's method[13] was used. The products (the anions of the corresponding acids) were obtained quantitatively from preparative-scale reactions and their identities were confirmed by u.v. spectral comparison with the acids in basic solution.

Kirkwood and Westheimer Calculations.—These calculations for a spherical, two-point charge model[4] were carried out for the 8-chloro-, 8-bromo-, and 8-nitro-1-naphthoic acids. The molecular parameters required were taken from the literature[6,14] where possible. In naphthalene the distance between C-1 and C-8 has been reported to be 2.44 Å.[6] At this distance strong non-bonding electron repulsions appear between the substituent and the reaction site, which cause molecular distortions and lead to a considerable rise over 2.44 Å for the distance between the 8-substituent and the reaction site (substituted at position 1). A reasonable choice is to take this distance as equal to 80% of the sum of the van der Waals radii of the atoms concerned; *cf.* the 'contact' radii employed in Catalin models. This approach was used for the 8-chloro- and 8-bromo-1-naphthoic acids. The distance for the nitro derivative was taken equal to that reported for 1,8-dinitronaphthalene, *i.e.* 2.93 Å.[6] However, if the former geometry is used for the 8-nitro acid, the results are not significantly changed.

In general, the calculations were carried out as before.[1] However, in the model, the embedding distance of 1.6 Å suggested by Ehrenson[15] is reduced to 1.0 Å. This is because of the unrealistic nature of the former assumption in describing the present system in which the substituent and reaction site are so close. The cavity wall was placed 1.2 Å from the proton attached to C-4, this distance being the van der Waals radius of hydrogen.[15,16] These parameters define the spherical cavity the centre of which is located at C-9. The dipole moments and dipole bond lengths were taken from the literature for substituted benzenes.[14,17] The nitro group presents special problems particularly evident in this study. The positive end of the dipole can be located (i) midway between the ring carbon and the nitrogen or (ii) on the nitrogen atom. The dielectric constant of the molecular cavity was taken as 2 and that of the solvent [80% (w/w) aqueous 2-methoxyethanol] as 32.[18]

Acknowledgements

We are grateful to CONICIT for the support of one of us (S. A.).

References

1 Part 15, preceding paper.

2 K. Bowden and D. C. Parkin, *Chem. Commun.*, 1968, 75; *Can. J. Chem.*, 1969, **47**, 185.

3 K. Bowden, G. R. Taylor, and M. J. Price, *J. Chem. Soc. B*, 1970, 1022.

4 J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, 1938, **6**, 506, 513.

5 S. Acevedo and K. Bowden, following paper.

6 V. Balasubramaniyan, *Chem. Rev.*, 1966, **66**, 567.

7 N. B. Chapman, J. Shorter, and J. H. P. Utley, *J. Chem. Soc.*, 1963, 1291.

8 R. W. Taft in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, ch. 13, 1956.

9 K. Bowden, M. J. Price, and G. R. Taylor, *J. Chem. Soc. B*, 1970, 1022.

10 K. Bowden, D. Law, and R. J. Ranson, *J. Chem. Soc., Perkin Trans. 2*, 1977, 1799.

11 K. Bowden, M. Hardy, and D. C. Parkin, *Can. J. Chem.*, 1968, **46**, 2929.

12 K. Bowden and A. M. Last, *J. Chem. Soc., Perkin Trans. 2*, 1973, 345.

13 E. A. Guggenheim, *Phil. Mag.*, 1926, **2**, 538.

14 'Tables of Interatomic Distances and Configurations in Molecules and Ions,' ed. L. E. Sutton, Chem. Soc. Special Publ. No. 18, London, 1965.

15 S. Ehrenson, *J. Am. Chem. Soc.*, 1958, **80**, 2436.

16 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441.

17 L. E. Sutton in 'Determination of Organic Structures by Physical Methods,' eds. E. A. Braude and F. C. Nachod, Academic Press, New York, ch. 9, 1955.

18 W. Simon, *Angew. Chem., Int. Ed. Engl.*, 1964, **3**, 661.

Received 27th March 1986; *Paper* 6/609