1172. *The Kinetics of the Reactions of Diazodiphenylmethane with Some Methylnaphthoic and Acenaphthoic Acids in Ethanol or 2-n-Butoxyethanol*

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Rate coefficients have been determined for the reactions in ethanol or 2-n-butoxyethanol at 30° of diazodiphenylmethane with aromatic carboxylic acids derived from naphthalene, 1-methylnaphthalene, 1,8-dimethylnaphthalene, and acenaphthene. The results are discussed in terms of polar effects and secondary steric effects.

We recently studied the kinetics of the reactions of diazodiphenylmethane with various carboxylic acids in ethanol or another solvent.[1-5] Fischer, Mitchell, Packer, Topsom, and Vaughan [6] also measured pK values (in 20% dioxan) for aromatic carboxylic acids derived from naphthalene, 1-methylnaphthalene, 1,8-dimethylnaphthalene, and acenaphthene. Certain interesting structural effects were observed. The authors have kindly provided us with samples of some of the acids, the kinetics of the reactions of which with diazodiphenylmethane in ethanol or 2-n-butoxyethanol at 30° are now reported.

Second-order rate coefficients are assembled in the Table. Although these refer to the consumption of diazodiphenylmethane in concurrent esterification and etherification reactions,[1-5] we do not correct the measured rate coefficient (k_2^a) to give the " true " rate coefficient (k) for the esterification (cf. refs. 1, 2, and 5); k_2^a is now understood to relate to a common rate-determining proton transfer from the acid to the diazodiphenylmethane.[3,7] We have not measured the rate coefficients over a range of temperatures, but for reactions of other series of acids with diazodiphenylmethane the pattern of the results is unaltered by considerable changes of temperature.[3]

Second-order rate coefficients* for the reactions of diazodiphenylmethane with carboxylic acids in ethanol or 2-n-butoxyethanol at 30°

	Benzoic	1-Naphthoic	2-Naphthoic	1-Me-2-naphthoic	4-Me-1-naphthoic
Ethanol	0·992 (ref. 3)	1·53 (ref. 3)	1·12 (ref. 3)	1·92	1·21
2-n-Butoxyethanol	0·331	0·356	0·398	0·458	0·268

	5-Me-1-naphthoic	4,5-Me$_2$-1-naphthoic	3-Acenaphthoic	5-Acenaphthoic
Ethanol	1·37	1·07	—	—
2-n-Butoxyethanol	0·300	0·228	0·095	0·144

* Values of k_2^a (l. mole^{-1} min.$^{-1}$) are reproducible to ±2% or better.

Esterification with Diazodiphenylmethane in Ethanol.—The slightly enhanced reactivity of 2-naphthoic acid (compared with that of benzoic acid) is due to the electron-attracting influence of the fused ring system, while the considerably greater reactivity of 1-naphthoic acid is mainly due to the secondary steric effect of the 8-H atom.[3] 4-Methyl-1-naphthoic acid shows the electron-releasing influence of the 4-methyl group, which reduces k_2^a by about 20%, as in the case of the 4-methyl group in *p*-toluic acid;[1] the retarding influence of the 5-methyl group in 5-methyl-1-naphthoic acid is, as might be expected, smaller (10%). The cumulative effect of the two methyl groups in 4,5-dimethyl-1-naphthoic acid is additive;[5] $\Delta\log k_2^a$ (calc.) is $-0{\cdot}150$ and $\Delta\log k_2^a$ (obs.) is $-0{\cdot}155$. Fischer *et al.*,[6] however, found a substantial departure from additivity of substituent effects in the dissociation of this acid; they attributed this to mutual compression of the methyl groups. The introduction

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[1] N. B. Chapman, J. Shorter, and J. H. P. Utley, *J.*, 1962, 1824.
[2] K. Bowden, N. B. Chapman, and J. Shorter, *J.*, 1963, 5239.
[3] K. Bowden, A. Buckley, N. B. Chapman, and J. Shorter, *J.*, 1964, 3380.
[4] K. Bowden, N. B. Chapman, and J. Shorter, *Canad. J. Chem.*, 1964, **42**, 1979.
[5] A. Buckley, N. B. Chapman, and J. Shorter, *J.*, 1963, 178.
[6] A. Fischer, W. J. Mitchell, J. Packer, R. D. Topsom, and J. Vaughan, *J.*, 1963, 2892.
[7] R. A. More O'Ferrall, W. K. Kwok, and S. I. Miller, *J. Amer. Chem. Soc.*, 1964, **86**, 5553.

of a 1-methyl group into 2-naphthoic acid raises k_2^a by about 70%, whereas *o*-toluic acid is slightly less reactive than benzoic acid.[1] The secondary steric effect of the 1-methyl group is evidently enhanced by the buttressing effect of the 8-H atom in 1-methyl-2-naphthoic acid.

Esterification with Diazodiphenylmethane in 2-n-Butoxyethanol.—The influence on the reactivity towards diazodiphenylmethane of the fused ring system in 2-naphthoic acid and of the methyl group in 4- or 5-methyl-1-naphthoic acid is greater with 2-n-butoxyethanol as solvent than with ethanol as solvent. We attribute this tentatively to the lower dielectric constant of 2-n-butoxyethanol (12·8) compared with that of ethanol (24·3) increasing the susceptibility of the reaction to polar effects.[8] As with ethanol as solvent, the cumulative effect of the two methyl groups in 4,5-dimethyl-1-naphthoic acid is additive;[5] $\Delta\log k_2^a$ (calc.) is $-0{\cdot}197$ and $\Delta\log k_2^a$ (obs.) is $-0{\cdot}193$.

The accelerating influence of the 8-H atom in 1-naphthoic acid and of the 1-methyl group in 1-methyl-2-naphthoic acid is much lower than that observed with ethanol as solvent which suggests that there is a considerable solvent-dependence of the secondary steric effect. A related observation is that, in 2-methoxyethanol as solvent, benzoic acid and *o*-isopropylbenzoic acid are of comparable reactivity,[8] whereas the latter has a value of k_2^a about 50% greater with ethanol as solvent.[1]

3-Acenaphthoic acid reacts more slowly than 2-naphthoic acid by a factor of about 4, cf. 1-methyl-2-naphthoic acid. Similarly, Fischer *et al.*[6] observed that 3-acenaphthoic acid was much weaker than 2-naphthoic acid. They attributed this to a low steric requirement and substantial electron-donating ability of the ethylene bridge. The latter is also manifested in 5-acenaphthoic acid, which reacts more slowly than 1-naphthoic acid by a factor of about 2·5 and is likewise found by Fischer *et al.*[6] to be a considerably weaker acid (cf. 4,5-dimethyl-1-naphthoic acid).

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[8] A. Buckley, N. B. Chapman, J. Shorter, and H. M. Wall, unpublished results.