

## The Influence of the Solvent on Organic Reactivity. Part I. Kinetics and Mechanism of the Reactions of Carboxylic Acids with Diazodiphenylmethane in Donor Aprotic Solvents

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Apparent second-order rate coefficients have been determined for the reactions at 37 °C of diazodiphenylmethane with benzoic acid in 19 donor aprotic solvents. Values determined for various initial concentrations of acid,  $c$ , are analysed in terms of the equation  $k(\text{obs}) = k_0 + k'c$ . Reactions of acetic acid and of deuteriated benzoic and acetic acid ( $\text{PhCO}_2\text{D}$  and  $\text{MeCO}_2\text{D}$ ) have also been studied. We conclude that  $k_0$  corresponds to the reversible formation of a complex between monomeric acid and diazodiphenylmethane and its subsequent breakdown to products, while  $k'$  corresponds to the reaction of a small amount of highly reactive acid in the form of an open-chain dimer. The effect of a wide range of aprotic solvents on  $k_0$  and  $k'$  is interpreted in terms of the following solvent parameters: a function of dielectric constant and one of refractive index, and a measure of solvent nucleophilicity and one of electrophilicity. On including results from an earlier study, multiple linear regression of  $\log k_0$  on the four parameters gives an excellent correlation for 24 solvents ( $R = 0.975$ ,  $s = 0.209$ ). A similar analysis for the  $\log k'$  values for ten donor aprotic solvents is less satisfactory. Correlation analysis for  $\log k_0$  and  $\log k'$  values of the reaction in 11 ketones is very unsatisfactory: the hoped-for advantages of considering a homogeneous set of aprotic solvents were thus not realised. Apparent second-order rate coefficients have also been determined for the reactions at 37 °C of diazodiphenylmethane with substituted benzoic acids in seven donor aprotic solvents. Values of  $k_0$  and  $k'$ , and of the Hammett reaction constant for the two types of rate coefficient are discussed.

THE apparent second-order rate coefficients for the reactions of carboxylic acids with diazodiphenylmethane in many aprotic solvents depend on the initial concentration of acid. (In the usual spectrophotometric method of studying these reactions the acid is in at least ten-fold excess over the diazodiphenylmethane to ensure first-order kinetics.) We have already<sup>1</sup> presented values of  $k_0$ , the rate coefficient at  $[\text{acid}] = 0$ , for the reactions of benzoic acid in 22 aprotic solvents and discussed the dependence of  $k_0$  on the properties of the solvent. We now present detailed results for reactions in aprotic solvents in which the carboxylic acid is believed to be largely monomeric, *i.e.* we exclude most of the aromatic solvents and carbon tetrachloride. We also present results for the reactions of benzoic acid and substituted benzoic acids in further donor aprotic solvents, mainly ketones. Reactions of acetic acid and of deuteriated benzoic and acetic acid ( $\text{PhCO}_2\text{D}$  and  $\text{MeCO}_2\text{D}$ ) have also been studied. We defer to a later paper consideration of the more complicated situation for solvents in which the acid exists predominantly as a dimer.

Earlier papers<sup>1-3</sup> and those of other authors<sup>4</sup> give the mechanism of the reaction in alcohols. The rate-determining step involves a proton transfer from the carboxylic acid to form a diphenylmethyldiazonium-carboxylate ion-pair. Subsequent fast product-governing stages have been variously formulated.<sup>3-6</sup> The intervention of a benzhydryl-carboxylate ion-pair seems most likely; this may either 'collapse' to give the ester, or react with the solvent to give an ether.<sup>4-6</sup>

<sup>1</sup> N. B. Chapman, M. R. J. Dack, and J. Shorter, *J. Chem. Soc. (B)*, 1971, 834.

<sup>2</sup> A. Buckley, N. B. Chapman, M. R. J. Dack, J. Shorter, and H. M. Wall, *J. Chem. Soc. (B)*, 1968, 631.

<sup>3</sup> K. Bowden, A. Buckley, N. B. Chapman, and J. Shorter, *J. Chem. Soc.*, 1964, 3380.

<sup>4</sup> R. A. More O'Ferrall, W. K. Kwok, and S. I. Miller, *J. Amer. Chem. Soc.*, 1964, **86**, 5553.

<sup>5</sup> A. F. Diaz and S. Winstein, *J. Amer. Chem. Soc.*, 1966, **88**, 1318.

Until recently the reaction in aprotic solvents has been believed to follow a course analogous to that in alcohols, but with no possibility of ether formation.<sup>4,6</sup> Chapman *et al.*,<sup>7</sup> however, suggested that the reaction in toluene may involve the reversible formation of a complex between diazodiphenylmethane and the carboxylic acid, which subsequently breaks down to products, either spontaneously or under catalysis by a further molecule of acid. The present work examines the application of this suggestion to the reactions occurring in a wide range of aprotic solvents.

### DISCUSSION

*Kinetics of the Reaction between Benzoic Acid and Diazodiphenylmethane in Donor Aprotic Solvents at 37 °C.*—In 1953 Roberts and Regan reported<sup>8</sup> that the reaction between benzoic acid and diazodiphenylmethane in benzene, chloroform, 1,2-dichloroethane, acetonitrile, or acetone was not exactly of the first order in benzoic acid. They attributed this to partial dimerisation of the acid. These findings were not followed up until recently.<sup>1</sup> Indeed, the reaction in toluene has been assumed<sup>9</sup> to conform with second-order kinetics overall. Deviation from first order in benzoic acid for the reaction in toluene was first observed in 1963,<sup>4,10</sup> and for cinnamic and for phenylacetic acid in certain dipolar aprotic solvents (notably acetone and ethyl acetate, but not dimethyl sulphoxide) in 1968.<sup>2,11</sup>

Early in the present work the reaction in several donor aprotic solvents appeared to conform to equation (1).

$$k(\text{obs}) = k_0 + k'c \quad (1)$$

<sup>6</sup> D. Bethell and R. D. Howard, *Chem. Comm.*, 1966, 94.

<sup>7</sup> N. B. Chapman, A. Ehsan, J. Shorter, and K. J. Toyne, *Tetrahedron Letters*, 1968, 1049.

<sup>8</sup> J. D. Roberts and C. M. Regan, *Analyt. Chem.*, 1952, **24**, 360.

<sup>9</sup> A. B. Hoefelmeyer and C. K. Hancock, *J. Amer. Chem. Soc.*, 1955, **77**, 4746.

<sup>10</sup> K. Bowden, N. B. Chapman, and J. Shorter, *J. Chem. Soc.*, 1963, 5239.

<sup>11</sup> K. Bowden, M. Hardy, and D. C. Parkin, *Canad. J. Chem.*, 1968, **46**, 2929.

Here  $k(\text{obs})$  is the second-order rate coefficient when the [carboxylic acid] is  $c$ , and  $k_0$  and  $k'$  are constants characteristic of the carboxylic acid and the solvent,  $k_0$  being the second-order rate coefficient extrapolated to  $c = 0$ , and  $k'$  refers to a component of the overall reaction which is of the second order in carboxylic acid and first order in diazodiphenylmethane.

For benzoic acid, equation (1) was closely obeyed up to  $c$  ca. 0.3M, but at higher concentrations departure from linearity was sometimes observed.\* We therefore accumulated results for a range of solvents, with  $c$  up to ca. 0.3M, and applied equation (1) by the method of least-squares. The values of  $k_0$  and  $k'$  are in Table I,

benzoic or any other carboxylic acid in any donor aprotic solvent. However, they must be several orders of magnitude smaller than those for carboxylic acids in non-polar solvents (*e.g.* benzene, carbon tetrachloride) since various authors have examined the spectroscopic or colligative properties of relevant solutions and have usually failed to establish the presence of dimer. Thus Lassetre<sup>12</sup> examined the colligative properties of solutions of benzoic acid up to ca. 0.5M and concluded that the acid was essentially monomeric in acetone, diethyl ether, and ethyl acetate. From u.v. spectral measurements Forbes and Knight<sup>13</sup> also concluded that the acid was monomeric in ether at 10<sup>-3</sup>M. Collings and

TABLE I

Kinetics of the reaction between benzoic acid and diazodiphenylmethane in various dipolar aprotic solvents at 37 °C

Solvent	$k_0/$ l mol <sup>-1</sup> min <sup>-1</sup> <sup>a</sup>	% Error <sup>b</sup>	$k'/$ l <sup>2</sup> mol <sup>-2</sup> min <sup>-1</sup>	% Error <sup>b</sup>	Number of points	$r$ <sup>c</sup>	$s$ <sup>d</sup>
1 Acetonitrile	3.73	2.1	19.0	5.7	18	0.975	0.134
2 Methyl acetate	0.276	8.2	2.59	7.8	5	0.991	0.0245
3 Ethyl acetate	0.174	6.1	2.49	3.4	9	0.996	0.0142
4 Dimethyl sulphoxide	0.072	1.2	0.00		4		
5 Dioxan	0.057	2.8	0.307	3.0	5	0.999	0.0017
6 <i>NN</i> -Dimethylacetamide	0.041	2.5	0.00		3		
7 Di- <i>n</i> -butyl ether	0.027	13.5	0.76	3.8	5	0.998	0.0038
8 1,8-Epoxy- <i>p</i> -menthane	0.0042	25.1	0.188	2.9	4	0.999	0.0070
Ketones							
9 Acetophenone	0.691	4.1	5.28	5.9	9	0.988	0.0291
10 Acetone	0.363	2.2	1.40	3.3	12	0.995	0.0150
11 Di-isopropyl ketone	0.322	5.4	3.62	4.5	6	0.996	0.0138
12 Ethyl methyl ketone	0.301	7.2	1.71	7.1	8	0.985	0.0277
13 Diethyl ketone	0.295	2.2	2.68	1.7	14	0.998	0.0121
14 Cyclopentanone	0.293	2.9	0.95	9.0	7	0.980	0.0091
15 Methyl <i>n</i> -propyl ketone	0.292	3.2	1.67	6.7	9	0.985	0.0102
16 Isopropyl methyl ketone	0.247	7.6	2.21	4.1	6	0.997	0.0219
17 Methyl <i>n</i> -butyl ketone	0.243	3.2	1.90	3.5	7	0.997	0.0077
18 Cyclohexanone	0.214	2.8	1.42	2.7	6	0.999	0.0075
19 Methyl <i>t</i> -butyl ketone	0.208	3.5	2.92	2.3	8	0.998	0.0074

\* For some of the solvents the values of  $k_0$  differ slightly from those published previously. This is due to the inclusion of additional points and to replacing graphical extrapolation by least-squares analysis. <sup>b</sup> Standard deviation. <sup>c</sup> Correlation coefficient. <sup>d</sup> Standard deviation of the estimate.

together with relevant statistical information. Conformity to equation (1) is usually satisfactory, although very small values of  $k_0$  may be subject to a considerable percentage error. Only for dimethyl sulphoxide or *NN*-dimethylacetamide was  $k(\text{obs})$  independent of  $c$  and therefore equivalent to  $k_0$ . The results for ten solvents (nos. 2–8, 10, 13, and 18) were previously used in discussion of the effect of solvent on  $k_0$ .<sup>1</sup> The additional values of  $k_0$  now presented enable us to discuss this further, together with the effect of solvent on  $k'$ .

*Mechanism of the Reaction between Carboxylic Acids and Diazodiphenylmethane in Donor Aprotic Solvents.*—In these solvents benzoic acid is probably present largely as monomer for the concentrations employed. Dimerisation constants,  $K_{12}$ , are rarely available for

\* Throughout our discussion of equation (1) we assume that it may be interpreted in terms of the reaction mechanism. Occasionally deviations from ideal behaviour may occur for  $c$  ca. 0.3M. However the general trend which equation (1) expresses is readily discernible at much lower concentrations, and the effect of change of concentration is usually so great that to attribute it to a significant extent to deviations from ideality is unreasonable. However, values of  $k'$  may contain a small contribution from such deviations. These considerations do not affect values of  $k_0$ .

Morgan<sup>14</sup> found the 'associated CO' i.r. band to be vanishingly weak in solvents more basic than dioxan. The amount of dimer is negligible in a molar solution of benzoic acid in acetonitrile.<sup>15</sup> Our own measurements with a vapour-pressure osmometer (Hitachi-Perkin-Elmer M115) have revealed benzoic acid to be essentially monomeric in acetone and ethyl acetate.

We therefore assume that in the solutions we have used the main species present is the monomeric acid, which is prevented from dimerising by extensive solvation of the carboxy-group by interaction of its hydrogen atom with basic centres in the solvent. We thus infer that the reaction corresponding to  $k_0$  is a bimolecular process involving diazodiphenylmethane and monomeric carboxylic acid.

There are two main possibilities for the reaction corresponding to the third-order constant,  $k'$ . Either the solution contains a relatively small amount of

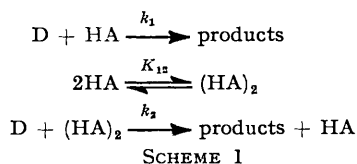
<sup>12</sup> E. N. Lassetre, *Chem. Rev.*, 1937, 20, 259.

<sup>13</sup> W. F. Forbes and A. R. Knight, *Canad. J. Chem.*, 1959, 37, 334.

<sup>14</sup> A. J. Collings and K. J. Morgan, *J. Chem. Soc.*, 1963, 3437.

<sup>15</sup> C. J. W. Brooks, G. Eglinton, and J. F. Morman, *J. Chem. Soc.*, 1961, 106.

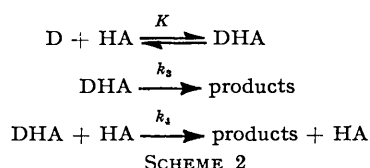
highly reactive dimer, or the usual reaction is catalysed by an additional molecule of monomer.<sup>7</sup> Both possibilities (Schemes 1 and 2) lead to kinetics which conform with equation (1). For Scheme 1 the total rate of



reaction,  $v_t$ , is given by  $v_t = k_1[\text{D}][\text{HA}] + k_2[\text{D}][(\text{HA})_2] = k_1[\text{D}][\text{HA}] + k_2K_{12}[\text{D}][\text{HA}]^2$  thus leading to equation (2).

$$k(\text{obs}) = k_1 + k_2K_{12}[\text{HA}] \quad (2)$$

[D represents diazodiphenylmethane, HA monomeric acid, and  $(\text{HA})_2$  dimeric acid.] Equation (2) is equivalent to equation (1) with  $k_0 = k_1$ ,  $k' = k_2K_{12}$ , and  $c = [\text{HA}]$ . {We assume  $[(\text{HA})_2] \ll [\text{HA}]$ .} For Scheme



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possible role of the intermediate complex and of catalysis. For the reactions of  $\text{PhCO}_2\text{D}$  and  $\text{MeCO}_2\text{D}$  in ethyl acetate and in acetone the results are summarised in Table 2. [Great care was taken to ensure that the results were not vitiated by exchange of deuterium for protium due to residual  $\text{H}_2\text{O}$  in the solvent or exchangeable hydrogen in the actual solvent molecules (see Experimental section).]

The ratio  $k_0(\text{H}) : k_0(\text{D}) (= R_0)$  for benzoic acid is *ca.* 1.1 for ethyl acetate and *ca.* 1.8 for acetone, the corresponding values of  $k'(\text{H}) : k'(\text{D}) (= R')$  being 7.3 and 4.2. For acetic acid  $R_0$  is *ca.* 1.0 for ethyl acetate and *ca.* 0.6 for acetone. These values are subject to considerable uncertainty, but the isotope effect on  $k_0$  is clearly very small and is possibly inverted. The values of  $R'$  for acetic acid are 4.8 and 5.9.

The second-order reaction is thus characterised either by a small 'normal' isotope effect or, for acetic acid, possibly an 'inverse' isotope effect, while the third-order reaction has a substantial normal isotope effect, larger than that observed for the reaction of diazodiphenylmethane with carboxylic acids in alcohols (Table 3).

The isotope effect for  $k_0$  accords with the reversible formation of a complex from diazodiphenylmethane and

TABLE 2

Isotope effect on the kinetics of the reactions between benzoic or acetic acid and diazodiphenylmethane in ethyl acetate or acetone at 37 °C

Acid	Solvent	$k_0/$ $\text{l mol}^{-1} \text{min}^{-1}$	% Error <sup>a</sup>	$k'/$ $\text{l}^2 \text{mol}^{-2} \text{min}^{-1}$	% Error <sup>a</sup>	Number of points	$r^b$	$s^c$
$\text{PhCO}_2\text{H}$	Ethyl acetate	0.174	6.1	2.49	3.4	9	0.996	0.0142
$\text{PhCO}_2\text{D}$	Ethyl acetate	0.154	4.5	0.341	8.9	10	0.970	0.0106
$\text{PhCO}_2\text{H}$	Acetone	0.363	2.2	1.40	3.3	12	0.995	0.0150
$\text{PhCO}_2\text{D}$	Acetone	0.203	5.4	0.332	13.0	6	0.968	0.0117
$\text{MeCO}_2\text{H}$	Ethyl acetate	0.0185	13.3	0.697	2.3	9	0.998	0.0039
$\text{MeCO}_2\text{D}$	Ethyl acetate	0.0190	10.7	0.146	2.7	11	0.997	0.0042
$\text{MeCO}_2\text{H}$	Acetone	0.0152	25.6	0.466	2.0	6	0.999	0.0052
$\text{MeCO}_2\text{D}$	Acetone	0.0242	5.9	0.0795	6.8	5	0.993	0.0019

<sup>a</sup> Standard deviation. <sup>b</sup> Correlation coefficient. <sup>c</sup> Standard deviation of the estimate.

2 the total rate of reaction is given by  $v_t = k_3[\text{DHA}] + k_4[\text{DHA}][\text{HA}] = k_3K[\text{D}][\text{HA}] + k_4K[\text{D}][\text{HA}]^2$  leading to equation (3). This is equivalent to equation (1) with

$$k(\text{obs}) = k_3K + k_4K[\text{HA}] \quad (3)$$

$k_0 = k_3K$  and  $k' = k_4K$ . (We assume dimer formation to be negligible, so that  $[\text{HA}] = c$ .)

The involvement of highly reactive dimer was suggested for the reaction between benzoic acid and diazodiphenylmethane in toluene by O'Ferrall *et al.*,<sup>4</sup> while the possible role of an intermediate complex undergoing acid-catalysed breakdown was suggested by Chapman *et al.*<sup>7</sup>

These ideas are conveniently discussed separately, but they are not necessarily mutually exclusive since a combination of Schemes 1 and 2 leads to an expression of the form of equation (1).

*The Protium-Deuterium Isotope Effect.*—The study of this isotope effect in various solvents sheds light on the

<sup>16</sup> See, e.g. R. P. Bell, 'Acid-Base Catalysis,' Clarendon Press, Oxford, 1941, p. 143.

the carboxylic acid. Inverse isotope effects in proton-transfer reactions are commonly 'solvent isotope effects,' i.e.  $\text{D}_3\text{O}^+$ -catalysed reactions in  $\text{D}_2\text{O}$  are often faster than

TABLE 3

Isotope effect on the second-order rate coefficient for the reactions of benzoic or acetic acid with diazodiphenylmethane in methanol or ethanol at 30 °C

Acid	Solvent	$k/\text{l mol}^{-1} \text{min}^{-1}$	Ratio $k_{\text{H}} : k_{\text{D}}$
$\text{PhCO}_2\text{H}$	MeOH	2.48	
$\text{PhCO}_2\text{D}$	MeOD	0.65	3.8
$\text{PhCO}_2\text{H}$	EtOH	1.03	
$\text{PhCO}_2\text{D}$	EtOD	0.396	2.6 <sup>a</sup>
$\text{MeCO}_2\text{H}$	EtOH	0.600	
$\text{MeCO}_2\text{D}$	EtOD	0.223	2.7 <sup>a</sup>

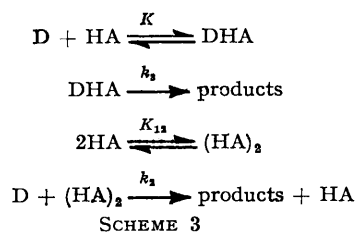
<sup>a</sup> Miller (ref. 4) found 3.6 at 35.4 °C for benzoic acid, and J. D. Roberts and C. M. Regan (*J. Amer. Chem. Soc.*, 1952, **74**, 3695) give *ca.* 3.6 for both acetic and benzoic acid at 30 °C.

$\text{H}_2\text{O}^+$ -catalysed reactions in  $\text{H}_2\text{O}$ , and the effects relate to a mechanism in which an intermediate complex, formed by rapid hydrogen ion addition to the substrate, undergoes rate-limiting conversion into products.<sup>16</sup> In

principle, however, an inverse isotope effect or an unusually small 'normal' effect could arise from the formation of an intermediate complex by fairly extensive transfer of a hydrogen ion from a weak acid to a base. In our work, the effect of the difference between the zero-point energy of the O-H bond and that of the O-D bond in the carboxylic acid could be considerably compensated by the zero-point energy difference for the C-H and the C-D bond in the intermediate ion-pair. Indeed, if the C-X levels are further apart than the O-X levels, the zero-point energy difference in the initial state might be outweighed. Thus there may be either a small normal or an inverse isotope effect on  $K$  (Scheme 2). If the stage of Scheme 2 characterised by  $k_3$  does not involve significant further change in the C-H or C-D bond,  $k_3$  would show no isotope effect, and that on  $k_0$  ( $= k_3K$ ) would directly reflect that on  $K$ .

The step of Scheme 1 characterised by  $k_1$ , is analogous to the rate-determining step for the reaction in alcohols as solvent. These processes should not differ markedly in their isotope effects.

*A Revised Scheme.*—If we accept the occurrence of the first and second step of Scheme 2, then it seems natural to account for the  $k'$  term in equation (1) by the third step. However, if we are to do this a mechanism whereby an additional molecule of acid can facilitate the decomposition of the intermediate complex must be suggested, and this mechanism must involve a rate-limiting proton transfer, because  $k'$  shows a substantial normal isotope effect, which in Scheme 2 must come from  $k_4$ . Further,  $k'$  depends markedly on the strength of the carboxylic acid; *cf.* the values for acetic and benzoic acid in Table 2, and those for substituted benzoic acids in Table 5. There is also the related matter of the kinetic stability of the intermediate complex, *i.e.* why a diphenylmethyldiazonium-carboxylate ion-pair does not immediately lose nitrogen to give the resonance-stabilised diphenylmethyl cation. Whatever the explanation of this it is difficult to suggest any plausible rate-limiting transfer of hydrogen ion from a carboxylic acid to the diphenylmethyldiazonium-carboxylate ion-pair. Neither a nitrogen nor a carboxylate-oxygen lone pair seems a likely centre for accepting the second hydrogen ion in a rate-limiting step.



We therefore conclude that while we must accept the role of the intermediate complex in Scheme 2, the  $k'$

\* We do not regard this matter as finally settled, *cf.* p. 976, following paper.

<sup>17</sup> Discussion, data, and references in M. M. Davis, 'Acid-Base Behavior in Aprotic Organic Solvents,' NBS Monograph 105, Washington, D.C., 1968, p. 40.

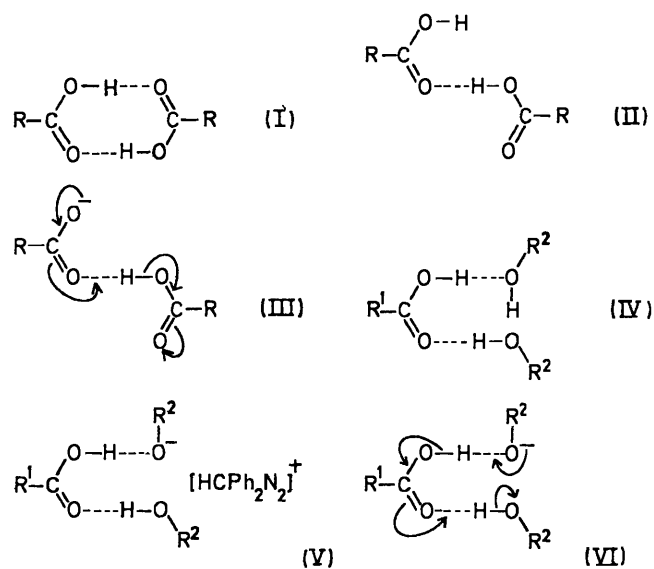
term of equation (1) is better explained in terms of the occurrence and reaction of a small amount of highly reactive dimer, *viz.* the second and third step of Scheme 1.\* If the dimer is highly reactive, then it may well react with diazodiphenylmethane in a rate-determining proton transfer, showing a normal protium-deuterium isotope effect, as for the reaction in alcohols.

We therefore combine features of Schemes 1 and 2 to give Scheme 3. The total rate coefficient is given by equation (4). This is equivalent to equation (1) with

$$k(\text{obs}) = k_3K + k_2K_{12}[\text{HA}] \quad (4)$$

$k_0 = k_3K$ ,  $k' = k_2K_{12}$ , and  $c = [\text{HA}]$ . The large normal isotope effect on  $k'$  would mainly reflect that on  $k_2$ , since dimerisation constants, so far as is known, are little affected by isotopic substitution.<sup>17</sup> Also  $k_2$  would increase with increasing strength of the acid, whereas  $K_{12}$  is likely to decrease as the strength of the acid increases; *cf.* dimerisation of carboxylic acids in non-polar solvents. (The structural effect is not very pronounced.)<sup>18</sup> On balance it seems that any effect of acid strength on  $K_{12}$  will be outweighed by that on  $k_2$ . Hence the observed dependence of  $k'$  on acid strength referred to above receives an explanation.

For non-polar solvents it is believed that the dimer has the ring structure (I) known to occur in the gas phase.<sup>18</sup> Occasionally<sup>19</sup> it has been suggested that a proportion of the dimer has the structure (II). The situation for donor aprotic solvents is largely unknown, but such dimerisation as occurs may involve the open-chain rather than the cyclic dimer,<sup>19a</sup> because



the necessary desolvation of the free OH group of the open-chain dimer may inhibit the conversion of open-chain dimer into cyclic dimer. The open-chain dimer

<sup>18</sup> G. Allen and E. F. Caldin, *Quart. Rev.*, 1953, **7**, 255; see also ref. 17, pp. 31 *et seq.*

<sup>19</sup> (a) T. S. S. R. Murty, *J. Phys. Chem.*, 1971, **75**, 1330; (b) ref. 17, p. 37.

may well be an extremely reactive species in a proton-transfer reaction, since the negative charge left behind might be delocalised throughout the system as in (III).

There remains the question why reaction of the monomer involves an intermediate complex but that of the dimer does not. Apparently some factor operates which stabilises the diphenylmethyldiazonium-carboxylate ion-pair with respect to decomposition to the benzhydryl-carboxylate ion-pair for the reaction of the monomer in donor aprotic solvents, but not for that of the dimer in the same solvents or for that of the monomer in alcohols. Possibly hydrogen-bonding interactions facilitate the onset of the 'completion' stages of the reaction. In alcohols the monomeric acid molecule must be extensively solvated, *e.g.* (IV).<sup>20</sup> We suggested previously<sup>1</sup> that the dependence of rate coefficient on protic or aprotic solvents is intimately connected with the strength of the solvation of the carboxy-hydrogen atom, since such solvation must be broken down during the transfer of the carboxy-proton to the diazodiphenylmethane. Possibly in protic solvents the proton which is actually transferred is that of the solvating alcohol molecule, as in (V). The negative charge can then be extensively delocalised throughout a solvated carboxylate ion, *i.e.* (VI). This is analogous to the ready delocalisation of charge suggested above to account for the apparent high reactivity of the dimer. When the monomer reacts in an aprotic solvent the negative charge is localised within the one carboxylate group. This disadvantageous situation may hinder the onset of the 'completion' stages.\*

For the reaction of benzoic acid in dimethyl sulphoxide or *NN*-dimethylacetamide,  $k(\text{obs})$  is independent of  $c$ .† Possibly these solvents solvate the carboxy-group so strongly that dimer formation is inappreciable in the concentration range studied. Moreover, the dependence of  $k(\text{obs})$  on concentration is more pronounced in the less basic solvents, *e.g.*  $k'$  tends to be small in ethers and is larger in ketones and esters, and in acetonitrile. The factors influencing  $k'$  are undoubtedly complex, however, and the matter is discussed again on p. 967.

*The Dependence of  $k_0$  and  $k'$  on the Solvent.*—In a previous paper<sup>1</sup> we examined the multiple correlation of  $\log k_0$  with the Kirkwood function  $f(\epsilon) = (\epsilon - 1)/(2\epsilon + 1)$  and with  $\Delta\nu_D$  for 22 aprotic solvents.  $\Delta\nu_D$  is the wave-number shift of the OD stretching vibration of  $\text{CH}_3\text{OD}$  on transfer from solution in benzene to solution in a given solvent and is a measure of solvent basicity.<sup>21</sup> Expression (5) was obtained with  $R$  0.905 and  $s$  0.388.

$$\log k_0 = -1.020 + 4.0f(\epsilon) - 0.0196\Delta\nu_D \quad (5)$$

\* This modified picture of the reaction in alcohols as solvents requires a slight alteration of the previous explanation of the solvent effect, *viz.* decreasing the basicity of the alcohol increases the rate coefficient by facilitating the transfer of the  $\text{R}^+\text{OH}$  proton, rather than by facilitating desolvation of the  $\text{R}^+\text{CO}_2\text{H}$  proton before its transfer to the diazodiphenylmethane.

† Similar results have been obtained for formic and for acetic acid in dimethyl sulphoxide.

‡ The I.C.L. 1905 statistical analysis package was used for these calculations.

The introduction of a refraction (polarisability) term<sup>22</sup> effected only a slight improvement. Expression (6) was obtained with  $R$  0.930 and  $s$  0.346.

$$\log k_0 = -2.994 + 3.775f(\epsilon) - 0.0179\Delta\nu_D + 9.311f(n^2) \quad (6)$$

The analysis of these results has been taken further by Koppel and Palm,<sup>23</sup> by using  $f(\epsilon)$ ,  $f_1(n^2)$ ,  $B$ , and  $E$  in a four-parameter equation.  $f_1(n^2)$  is the function  $(n^2 - 1)/(n^2 + 2)$ .  $B$  is directly related to  $\Delta\nu_D$ , but the standard system is gas-phase  $\text{CH}_3\text{OD}$ .  $E$  measures the electrophilic solvating power of the solvent and is derived from the  $E_T$  scale (Dimroth),<sup>24</sup> corrected for dielectric effects. Koppel and Palm obtained expression (7) with  $R$  0.981, for 16 solvents.

$$\log k_0 = -2.14 + 4.06f(\epsilon) + 6.98f_1(n^2) + 0.182E - 0.0189B \quad (7)$$

The positive regression coefficient of  $E$  implies the relative stabilisation of the activated complex by electrophilic solvation, as previously suggested tentatively by us.<sup>1</sup> The negative coefficient for  $B$  indicates the relative stabilisation of the initial state by nucleophilic solvation. If  $f(n^2)$  is used instead of  $f_1(n^2)$  for the 16 solvents expression (8) is obtained [*N.B.*  $f(n^2)$  is of the same form as  $f(\epsilon)$ , whereas  $f_1(n^2)$  is not].

$$\log k_0 = -2.74 + 3.905f(\epsilon) + 12.05f(n^2) + 0.1975E - 0.01928B \quad (8)$$

We have extended the correlation to 24 solvents for which  $B$  and  $E$  values are available or have  $E$  values assumed to be zero. The solvents are those of the earlier paper<sup>1</sup> omitting diethyl ketone, together with acetonitrile, ethyl methyl ketone, and acetophenone. ( $E = 0$  is assumed for methyl acetate, diethyl carbonate, 1,8-epoxy-*p*-menthane, mesitylene, and iodobenzene.) The regression equation is (9) with  $R$  0.975 and  $s$  0.209.

$$\log k_0 = -1.94 + 4.185f(\epsilon) + 8.391f(n^2) + 0.224E - 0.0212B \quad (9)$$

A plot of  $\log k_0(\text{calc})$  versus  $\log k_0(\text{obs})$  is in Figure 1. Stepwise regression ‡ shows that the order of decreasing significance of the terms is  $B$ ,  $f(\epsilon)$ ,  $E$ , and  $f(n^2)$ ,  $R$  for the successive one-, two-, and three-parameter equations being 0.780, 0.901, and 0.954. In an equation such as (9) the regression coefficients do not give directly an indication of the relative importance of the various terms. Thus in (9) the  $B$  term, with the smallest coefficient, is the most important term because the values of  $B$  are large compared with those of  $f(\epsilon)$ ,  $f(n^2)$ , and  $E$ , and vary much more for the solvents employed. Further

<sup>20</sup> J. Lascombe, M. Haurie, and M.-L. Josien, *J. chim. Phys.*, 1962, **59**, 1233.

<sup>21</sup> T. Kagiya, Y. Sumida, and T. Inoue, *Bull. Chem. Soc. Japan*, 1968, **41**, 767.

<sup>22</sup> E. M. Kosower, 'Physical Organic Chemistry,' Wiley, New York, 1968, p. 272.

<sup>23</sup> I. A. Koppel and V. A. Palm in 'Advances in Linear Free Energy Relationships,' eds. N. B. Chapman and J. Shorter, Plenum Press, London, 1972, ch. 5.

<sup>24</sup> C. Reichardt, *Angew. Chem. Internat. Edn.*, 1965, **4**, 29.

the number of significant figures given in the regression coefficients is not to be taken as an indication of their precision, but is simply as provided by the computer.  $R$  0.975 for the final four-parameter equation with 24

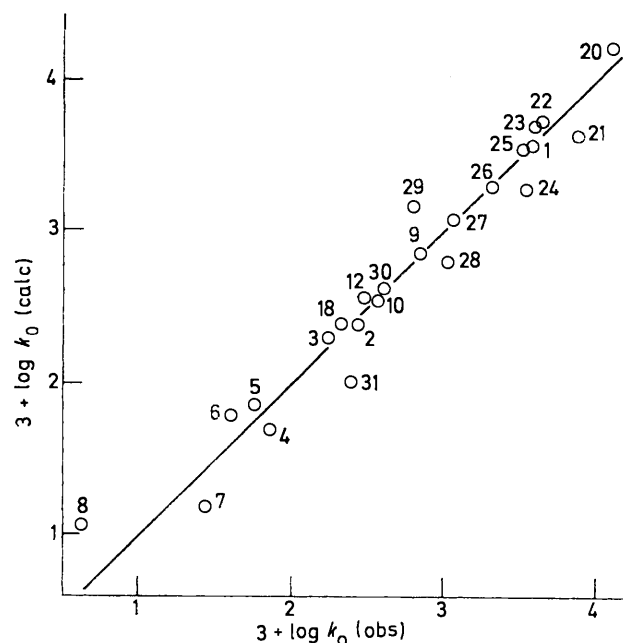


FIGURE 1 Plot of  $\log k_0$  (calc) according to equation (8) against  $\log k_0$  (obs). For some point numbers, see Table 1; also 20, chloroform; 21, nitrobenzene; 22, fluorobenzene; 23, iodobenzene; 24, benzene; 25, chlorobenzene; 26, benzonitrile; 27, toluene; 28, anisole; 29, carbon tetrachloride; 30, mesitylene; 31, diethyl carbonate

data sets and 19 degrees of freedom corresponds to a confidence level of over 99.9%. The partial  $r$  (0.68) for the introduction of the fourth parameter,  $f(n^2)$ , corresponds to a confidence level of *ca.* 99.9%. The introduction of  $f(n^2)$  thus accounts for *ca.* 46% [*i.e.*  $100 \times (0.68)^2$ ] of what is left unexplained by the three-parameter equation.

This correlation is much more successful than any we devised previously. The main improvement is due to the electrophilicity term. The possible importance of such a term was recognised then by us<sup>1</sup> but no suitable scale of electrophilicity was available. The high correlation coefficient indicates a substantial degree of 'explanation' (95% of the variance) but as a summary of data the expression is inadequate since  $s = 0.209$ , a rather high value. Some solvents are placed wrongly in the pattern, *e.g.* for  $\log k_0$ (obs), benzene  $\gg$  carbon tetrachloride, but the  $\log k_0$ (calc) values are very close together. Doubtless there are special effects of which the above correlation takes no account.<sup>1</sup> However, its degree of success is probably all that can be expected for such a variety of solvents, particularly in view of the complex significance of  $k_0$ .

The essential qualitative chemical conclusion to be drawn is, that despite the mechanistic complexity of the reactions studied, the influence of the solvent on 'reactivity' for this system can be related primarily to the

nucleophilicity of the solvent, with a much weaker contribution from its electrophilicity, and some contribution from its properties as a continuum (mainly dielectric constant).

The factors which influence  $k_0$  should also influence  $k'$ , but not necessarily in the same way.\* At present we can attempt a full correlation analysis for only ten dipolar aprotic solvents, the limitation being mainly lack of  $E$  values. The solvents are nos. 1–3, 5, 7–10, 12, and 18; expression (10) was obtained with  $R$  0.914 and  $s$  0.286.

$$\log k' = 0.830 + 2.863f(\epsilon) + 0.0859E - 0.0165B \quad (10)$$

No significant contribution would be made by a  $f(n^2)$  term. A plot of  $\log k'$ (calc) versus  $\log k'$ (obs) is in Figure 2. Stepwise regression shows that, as with  $k_0$ , the order of decreasing significance of the terms is  $B$ ,  $f(\epsilon)$ , and  $E$ , the relevant  $R$  values being 0.783 and 0.872.  $R$  0.914 for equation (10) with 10 data sets and 6 degrees of freedom corresponds to a confidence level of *ca.* 99%. The partial  $r$  for the introduction of the third parameter,  $E$ , is 0.56, which corresponds to the rather poor confidence level of a little below 90%.

Further data sets are needed for a fully satisfactory analysis but clearly the various factors operate much as expected. We recall that  $k' = k_2 K_{12}$ . Solvent basicity should decrease both  $k_2$  and  $K_{12}$ , so the importance and sign of the  $B$  term are understandable. Increase in  $\epsilon$  should increase  $k_2$  and decrease  $K_{12}$ , and the former

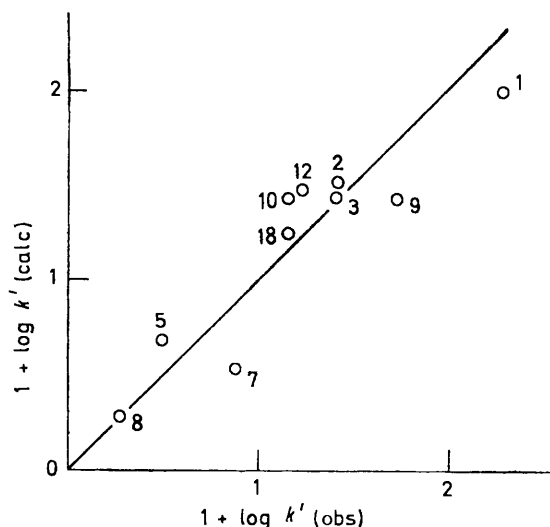


FIGURE 2 Plot of  $\log k'$ (calc) according to equation (10) against  $\log k'$ (obs). For point numbers, see Table 1

effect is the more important, the regression coefficient being positive. Solvent electrophilicity should also increase  $k_2$  and decrease  $K_{12}$ , and again the former effect is more important, the regression coefficient being positive.

Dimethyl sulphoxide and *NN*-dimethylacetamide were not included in the regression since  $k'$  was indistinguishable from zero. According to the above

\* Cf. comments on  $k'$  in the footnote on p. 963.

expression the values of  $k'$  should both be *ca.* 0.2. Such a value of  $k'$  would have been easily detectable. Thus there must be some special influence(s) suppressing the concentration dependence of the observed second-order rate coefficient with these two solvents.

*Ketonic Solvents.*—We have previously suggested<sup>1</sup> that 'further progress in understanding the effect of aprotic solvents on the reaction . . . will involve more homogeneous sets of solvents chemically . . . as in the case of the alcohols.' To this end, additional ketones were studied; results for 11 ketones are in Table 1 (nos. 9—19).

The values of  $k_0$  cover only a small range: apart from acetophenone (0.69) they all lie between *ca.* 0.21 and *ca.* 0.36, *cf.* a sixty-fold range in  $k$  shown by a series of alcohols.<sup>1</sup> The prospects for a detailed interpretation of these results are not good. However, they show certain rational trends. Thus, lengthening the chain or chain-branching at the  $\alpha$ -carbon atom in the series of alkyl methyl ketones both lead to a fall in  $k_0$ , which might be due to increasing the electron-releasing power of the group and thereby increasing the basicity of the ketone.

Maryott and Smith's compilation.<sup>26</sup> We now deemed it important to use the most modern and reliable values, and to correct them to 37 °C. Reliable data at various temperatures are now available for ten of the ketones. The two-parameter equation for the eleven ketones is (11) with  $R$  0.883 and  $s$  0.074.

$$\log k_0 = -2.503 + 0.408\Sigma\sigma^* + 4.482f(\epsilon) \quad (11)$$

A small improvement is produced by introducing  $n_H$ , the number of  $\alpha$ -hydrogen atoms as an additional parameter [equation (12) with  $R$  0.925 and  $s$  0.065].

$$\log k_0 = -3.380 + 0.387\Sigma\sigma^* + 6.75f(\epsilon) - 0.037n_H \quad (12)$$

$R$  for equation (12) corresponds to a confidence level of *ca.* 99.9%. The partial  $r$  for the introduction of the third parameter is 0.58, *i.e.* a confidence level of *ca.* 90%. The introduction of  $n_H$  accounts for *ca.* 34% of what is left unexplained by equation (11). The regression coefficient of  $f(\epsilon)$  has a standard error of 3.49, and the value of 6.75 is thus essentially similar to the values of

TABLE 4  
Solvent parameters for ketones

Ketone	$\Sigma\sigma^*$ <sup>a</sup>	$\epsilon$		$n_D^{20}$	$B^j$	$n_H^k$
		20°	37°			
9 Acetophenone	+0.60	18.66 <sup>e</sup>	17.9	1.535	119 (108)	3
10 Acetone	0.00	21.45 <sup>d</sup>	19.8	1.359	122 (116)	6
11 Di-isopropyl ketone	-0.38	16.2 <sup>e</sup>	~14.9	1.400	92	2
12 Ethyl methyl ketone	-0.10	18.51 <sup>d</sup>	17.1	1.379	108 (109)	5
13 Diethyl ketone	-0.20	17.00 <sup>d</sup>	15.6	1.398	99 (108)	4
14 Cyclopentanone	-0.20 <sup>b</sup>	13.80 <sup>f</sup>	13.1	1.437	123	4
15 Methyl n-propyl ketone	-0.115	15.38 <sup>f</sup>	14.3	1.390	108	5
16 Isopropyl methyl ketone	-0.19	16.57 <sup>f</sup>	15.6	1.388	101	4
17 Methyl n-butyl ketone	-0.13	14.56 <sup>f</sup>	13.1	1.401	109	5
18 Cyclohexanone	-0.215 <sup>c</sup>	16.10 <sup>f</sup>	15.2	1.451	132	4
19 Methyl t-butyl ketone	-0.30	12.73 <sup>f</sup>	11.4	1.395	95	3

<sup>a</sup> R. W. Taft, in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, ch. 13. <sup>b</sup> Assumed equivalent to 2Et. <sup>c</sup> Assumed equivalent to Et + Pr<sup>n</sup>. <sup>d</sup> R. H. Cole, *J. Chem. Phys.*, 1941, **9**, 251. <sup>e</sup> J. H. Calderwood and C. P. Smyth, *J. Amer. Chem. Soc.*, 1956, **78**, 1295. <sup>f</sup> E. L. Grove and G. E. Walden, *J. Chem. Eng. Data*, 1965, **10**, 98. <sup>g</sup> Determined by Mr. C. E. Reed, Physics Department, University of Hull. <sup>h</sup> From the observed temperature coefficient except for di-isopropyl ketone, for which  $\epsilon$  was assumed to have the mean temperature coefficient of other aliphatic ketones in the Table; additional uncertainty should not exceed  $\pm 0.3$ . <sup>i</sup> 'Handbook of Chemistry and Physics,' The Chemical Rubber Co., Cleveland, 51st edn., 1970. <sup>j</sup> Determined by Mr. G. Collier. Values in parentheses from ref. 23 and based on T. Kagiya, Y. Sumida, and T. Inoue, *Bull. Chem. Soc. Japan*, 1968, **41**, 767. <sup>k</sup> Number of  $\alpha$ -C-H bonds.

A decrease in  $\epsilon$  through the same series would have an effect reinforcing that of basicity. The enhanced reactivity for acetophenone might result from decreased basicity. That the  $k_0$  values for diethyl ketone, cyclopentanone, and methyl propyl ketone are very similar also seems rational. On the other hand, in these terms there is no obvious reason why di-isopropyl ketone should give a  $k_0$  value lying between the values for acetone and ethyl methyl ketone.

A treatment analogous to that used for the reaction in alcohols<sup>1</sup> may be employed, primarily involving correlation with  $\Sigma\sigma^*$  for the groups of the ketone<sup>25</sup> and  $f(\epsilon)$ . Values of  $\Sigma\sigma^*$  and  $\epsilon$  are in Table 4. Hitherto we have used values of  $\epsilon$  at 20 or 25 °C, often taken from

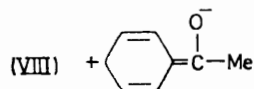
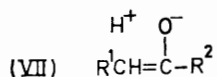
<sup>25</sup> R. W. Taft, in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, ch. 13.

4—5 found for the corresponding coefficient in the regressions for the series of alcohols<sup>1</sup> and for the broad range of aprotic solvents. The physical significance of the  $n_H$  term may be a moderation of the ketone basicity by  $\alpha$ -C-H hyperconjugation. The expression reproduces faithfully the main effects of chain-lengthening and branching, but fails on other details.

Extension to these ketones of the type of correlation used for aprotic solvents in general requires values of  $B$  determined as precisely as possible for all 11 ketones. Measurement of  $\nu_D$  (see Experimental section) gave results in the form of the  $B$  values shown in Table 4. Except for ethyl methyl ketone the agreement with earlier values<sup>21</sup> is poor, and some  $\nu_D$  or  $B$  values should

<sup>26</sup> A. A. Maryott and E. R. Smith, 'Table of Dielectric Constants of Pure Liquids,' N.B.S. Circular 514, Washington, D.C., 1951.

be regarded cautiously.\* The  $B$  values for the 11 ketones present a rational pattern, albeit somewhat surprising. In the alkyl methyl ketones branching at the  $\alpha$ -carbon atom decreases basicity, and diethyl ketone and di-isopropyl ketone also show behaviour consistent with this, whereas lengthening the alkyl chain beyond two carbon atoms has almost no effect. All this suggests that the dominating structural influence on the basicity of the carbonyl group is hyperconjugative interaction involving  $\alpha$ -C-H bonds, *cf.* (VII). The high basicity



of acetophenone compared with that of methyl *t*-butyl ketone confirms the importance of conjugative interaction [*cf.* (VIII)] for acetophenone. The basicity of the cyclic ketones appears substantially enhanced compared with those of the open-chain ketones; this may be due to a diminished steric effect in the cyclic structure.<sup>25</sup>

For the 11 ketones the  $B$  values help little in accounting for the reactivity of benzoic acid towards diazodiphenylmethane. Stepwise regression on  $f(\epsilon)$ ,  $f(n^2)$ , and  $B$  leads to the introduction of the terms in this order, and the final three-parameter equation is (13) with

$$\log k_0 = -7.38 + 13.39f(\epsilon) + 5.95f(n^2) - 0.0034B \quad (13)$$

$R$  0.853 and  $s$  0.0884, but the  $B$  term is significant only at the 75% level. Effectively the correlation is with  $f(\epsilon)$  and  $f(n^2)$  and is in complete contrast to the correlation for aprotic solvents in general when the  $B$  term is dominant. Values of  $E$  are available for only four of the ketones, but inclusion of  $E$  in the correlation would not affect the situation.

Useful as  $B$  is for a wide range of aprotic solvents, it is inadequate to deal with the fine details of the solvent effects for ketones and one must question whether in such a series the variations of  $B$  correspond entirely to real variations in solvent basicity, or perhaps also reflect some other aspect of the interaction between  $\text{CH}_3\text{OD}$  and the carbonyl group.

For the general series of aprotic solvents  $k_0$  and  $k'$  were governed by essentially the same factors, so that  $k_0$  and  $k'$  vary approximately in parallel. For the ketones, while the highest value of  $k_0$  is associated with the highest value of  $k'$  (acetophenone), for the open- and the branched-chain aliphatic ketones,  $k'$  appears to increase as  $k_0$  is decreased. There is no possibility of meaningful correlations with any of the solvent para-

meters used above, and the approach used so fruitfully for the wide range of aprotic solvents fails when applied to this more homogeneous set of solvents.

*Reaction of Substituted Benzoic Acids with Diazodiphenylmethane in Several Aprotic Solvents. Hammett  $\rho$  Values for  $k_0$  and  $k'$ .*—The analysis of the results in terms of equation (1) is in Table 5. Polar *meta*- or *para*-substituents produce changes in  $k_0$  and  $k'$  which are usually in the same direction. The structural effect on  $k_0$  results from the influence of substituents on the acid strength of the monomeric acid, and if  $k'$  is taken as  $k_2K_{12}$  (see above) then it is evident that the effect of acid strength on  $k_2$  outweighs the opposing effect on  $K_{12}$ .

The results in Table 5 have been examined in terms of the Hammett equation<sup>27</sup> (Table 6). For both  $k_0$  and  $k'$  conformity to the Hammett equation is adequate and for several solvents very good. Since the experimental error in  $k_0$  is usually much smaller than in  $k'$ , worse conformity to the Hammett equation might be expected for the latter. For acetone, ethyl acetate, and dimethyl sulphoxide values of  $\rho$  from  $k(\text{obs})$  at  $c = 0.03M$  (30 °C) were previously given as 1.93, 2.10, and 1.21 respectively.<sup>2</sup>

Usually  $\rho'$  (from  $k'$ ) is considerably lower than  $\rho_0$  (from  $k_0$ ), which is rational in view of the complex nature of  $k'$ , but acetophenone is exceptional. There is no simple relationship between  $\rho_0$  or  $\rho'$  and  $\log k_0$  or  $\log k'$  respectively of the parent benzoic acid, and these quantities must be governed in quite different ways by the properties of the solvent. Conceivably, the dielectric constant is more important for  $\rho_0$  or  $\rho'$  than for  $\log k_0$  or  $\log k'$  of the parent acid, for the Hammett reaction constant partly reflects the influence of the solvent on the transmission of the field effect of the substituent. The application of multiple regression to the  $\rho_0$  or  $\rho'$  values of the limited series of solvents is not justified.

#### EXPERIMENTAL

*Materials.*—Pure samples of many of the carboxylic acids were available from earlier work.<sup>1-3</sup> AnalaR acetic acid was purified by the method of Pohl *et al.*<sup>28</sup> Commercial  $\text{MeCO}_2\text{D}$  (deuterium content >99.7%) was used without further purification.  $\text{PhCO}_2\text{D}$  was prepared by refluxing benzoyl chloride with an excess of deuterium oxide (deuterium content >99.8%) with the exclusion of atmospheric moisture. The excess of  $\text{D}_2\text{O}$  was pumped off and the deuteriated acid purified by vacuum sublimation, m.p. 118—119° (lit.,<sup>29</sup> 118.5°), deuterium content by i.r. >98%. Small quantities of  $\text{PhCO}_2\text{D}$  were made as required, stored in a dry-box under nitrogen, and used within a few days. Diazodiphenylmethane, prepared by the method of Schroeder and Katz,<sup>30</sup> was stored over potassium hydroxide in a desiccator in a refrigerator.

The purification of several of the solvents has been

<sup>27</sup> L. P. Hammett, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1970, 2nd edn., ch. 11.

<sup>28</sup> H. A. Pohl, M. E. Hobbs, and P. M. Gross, *J. Chem. Phys.*, 1941, **9**, 408.

<sup>29</sup> H. Erlenmeyer, A. Epprecht, H. Lobeck, and H. Gärtner, *Helv. Chem. Acta*, 1936, **19**, 354.

<sup>30</sup> W. Schroeder and L. Katz, *J. Org. Chem.*, 1954, **19**, 718.

\* Professor T. Kagiya, personal communication, has recently redetermined  $\nu_D$  values for acetone, diethyl ketone, cyclohexanone, and acetophenone, which are in closer agreement with our values.



TABLE 5

Kinetics of the reactions between substituted benzoic acids and diazodiphenylmethane in various dipolar aprotic solvents at 37 °C

Solvent/Substituent	$k_0$ / l mol <sup>-1</sup> min <sup>-1</sup>	% Error <sup>a</sup>	$k'$ / l <sup>2</sup> mol <sup>-2</sup> min <sup>-1</sup>	% Error <sup>a</sup>	Number of points	$r$ <sup>b</sup>	$s$
Acetone							
<i>p</i> -NO <sub>2</sub>	8.09	5.2	<i>d</i>		5		
<i>m</i> -NO <sub>2</sub>	9.21	4.8	<i>d</i>		6		
<i>m</i> -Cl	2.54	0.3	3.08	3.1	4	0.999	0.007
<i>p</i> -F	0.713	0.6	2.53	1.4	4	1.000	0.0035
H	0.363	2.2	1.40	3.3	12	0.995	0.015
<i>p</i> -Me	0.184	2.7	1.13	3.6	5	0.998	0.0054
<i>p</i> -OMe	0.125	1.9	0.887	2.7	4	0.999	0.0016
<i>p</i> -NH <sub>2</sub>	0.0228	8.2	0.179	5.1	4	0.997	0.0020
Ethyl methyl ketone							
<i>p</i> -NO <sub>2</sub>	7.19	1.7	<i>d</i>		10		
<i>m</i> -NO <sub>2</sub>	8.56	2.6	<i>d</i>		13		
<i>m</i> -Cl	2.04	2.1	4.92	7.8	5	0.991	0.037
H	0.301	7.2	1.71	7.1	8	0.985	0.0277
<i>p</i> -Me	0.153	1.1	1.18	1.0	5	1.000	0.0016
<i>p</i> -OMe	0.118	4.1	0.722	7.8	9	0.979	0.0045
Methyl t-butyl ketone							
<i>m</i> -Cl	1.79	1.9	7.93	3.9	5	0.998	0.0309
<i>p</i> -F	0.564	1.0	2.99	2.1	5	0.999	0.0041
H	0.208	3.5	2.92	2.3	8	0.998	0.0074
<i>p</i> -Me	0.120	4.5	1.54	4.1	5	0.997	0.0040
Acetophenone							
<i>m</i> -Cl	3.18	1.7	17.96	3.3	4	0.999	0.0420
H	0.691	4.1	5.28	5.9	9	0.988	0.0291
<i>p</i> -Me	0.388	3.2	3.16	4.3	7	0.995	0.0109
<i>p</i> -NH <sub>2</sub>	0.0623	2.6	0.261	4.4	6	0.996	0.0012
Acetonitrile							
<i>p</i> -F	6.56	2.4	27.66	10.4	4	0.989	0.102
H	3.73	2.1	19.0	5.7	18	0.975	0.134
<i>p</i> -Me	2.27	2.4	13.02	7.5	12	0.973	0.0719
<i>p</i> -NH <sub>2</sub>	0.345	2.3	2.07	3.4	6	0.978	0.0093
Ethyl acetate							
<i>m</i> -NO <sub>2</sub>	7.24	2.1	21.07	10.9	9	0.961	0.119
<i>m</i> -Cl	1.46	4.6	8.96	9.6	8	0.973	0.0559
H	0.174	6.1	2.49	3.4	9	0.996	0.0142
<i>p</i> -Me	0.120	3.1	1.32	3.7	6	0.997	0.003
<i>p</i> -NH <sub>2</sub>	0.0110	4.9	0.112	3.4	4	0.999	0.0004

$k_{\text{obs}}$  was also determined for the reactions of several substituted benzoic acids at various concentrations in dimethyl sulphoxide. While there was some variation of  $k_{\text{obs}}$  with concentration in certain cases, this was probably to be attributed to experimental error arising from the low reaction rates. Approximate values of  $k_0$  are as follows: *p*-NO<sub>2</sub>, 0.82; *m*-Cl, 0.32; H, 0.072; *p*-Me, 0.04.

<sup>a</sup> Standard deviation. <sup>b</sup> Correlation coefficient. <sup>c</sup> Standard deviation of the estimate. <sup>d</sup> High reaction rates make the determination of meaningful values of  $k'$  impossible.

TABLE 6

Hammett  $\rho$  values for the reactions between substituted benzoic acids and diazodiphenylmethane in various dipolar aprotic solvents at 37 °C

Solvent	For $k_0$				For $k'$			
	$\rho_0$ <sup>a</sup>	$n$ <sup>b</sup>	$r$ <sup>c</sup>	$s$ <sup>d</sup>	$\rho'$ <sup>a</sup>	$n$ <sup>b</sup>	$r$ <sup>c</sup>	$s$ <sup>d</sup>
Acetone	1.846	8	0.995	0.097	1.220	6 <sup>e</sup>	0.961	0.137
Ethyl methyl ketone	1.845	6	0.995	0.094	1.251	4 <sup>e</sup>	0.995	0.045
Methyl t-butyl ketone	2.224	4	0.971	0.151	1.296	4	0.995	0.037
Acetophenone	1.650	4	0.999	0.028	1.790	4	0.991	0.126
Acetonitrile	1.689	4	0.994	0.072	1.524	4	0.997	0.050
Ethyl acetate	2.060	5	0.998	0.087	1.653	5	0.989	0.151
Dimethyl sulphoxide	1.409	4	0.992	0.095	<i>f</i>			

<sup>a</sup> Calculated by the method of least squares from  $\sigma$  values based on ionisation of benzoic acid. <sup>b</sup> Number of data sets. <sup>c</sup> Correlation coefficient. <sup>d</sup> Standard deviation of the estimate. <sup>e</sup> *m*-NO<sub>2</sub> and *p*-NO<sub>2</sub> omitted (see Table 5). <sup>f</sup>  $k(\text{obs})$  does not show a significant dependence on concentration (see Table 5).

described earlier.<sup>1,2</sup> The ketones were dried ( $K_2CO_3$ ) for several days and then over a molecular sieve (Linde type 4A) for three days before fractional distillation. Acetonitrile was treated with a molecular sieve, then phosphoric oxide, and then fractionated over fresh phosphoric oxide. Solvents to be used for making solutions of deuteriated carboxylic acids were dried initially in the normal way, then washed with  $D_2O$ , and finally dried again. This ensured that any small amount of water left in the solvent was present as  $D_2O$ , thus eliminating H-D exchange between  $H_2O$  and deuteriated acid. Without this procedure the observed rate coefficient could be too high by as much as a factor of two. Commercial  $CH_3OD$  and  $C_2H_5OD$  (deuterium content  $>99\%$ ) were used without further purification.

All solvents were stored and manipulated under dry nitrogen and were of adequate purity by g.l.c. (usually  $>99.5\%$  and often  $>99.8\%$  pure). Wherever possible water content was examined by the Karl Fischer method,<sup>31</sup> and was always  $\leq 0.02\%$  (w/v) and usually  $\leq 0.01\%$  (w/v).

**Measurements.**—Values of  $k$  were determined spectrophotometrically as described previously.<sup>1</sup> In working with deuteriated acids in ethyl acetate and acetone, the possible

occurrence of H-D exchange was examined. Kinetic experiments with a given solution were carried out at *ca.* 24 h intervals over the course of several days. Successive values of  $k$  increased slightly but it was clear that H-D exchange was of negligible importance for freshly prepared solutions of deuteriated acid in the aprotic solvents.

Values for the O-D stretching frequency of  $CH_3OD$  dissolved in 11 ketones were measured by Mr G. Collier. The solutions were 0.4M in  $CH_3OD$ . A Unicam SP 100 instrument was used in most cases.

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<sup>31</sup> W. Seaman, W. H. McComas, and G. A. Allen, *Analyt. Chem.*, 1949, **21**, 510.