The Separation of Polar and Steric Effects. Part 14.[1] Kinetics of the Reactions of Benzoic Acid and of *ortho*-Substituted Benzoic Acids with Diazodiphenylmethane in Various Alcohols

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The main results now discussed are rate coefficients for the reactions of benzoic acid and 32 *ortho*-substituted benzoic acids with diazodiphenylmethane (DDM) at 30.0 °C in 11 alcohols including 2-methoxyethanol. The reaction involves a rate-determining proton transfer. The results have been subjected to correlation analysis in two ways. (*a*) For the reactions of a given acid in the various alcohols, the log *k* values are correlated through multiple regression on appropriate solvent parameters. (*b*) For reactions in a given alcohol, the log *k* values for the various acids are correlated by using the appropriate form of the extended Hammett equation involving inductive, resonance, and steric parameters. Analyses of type (*a*), as in earlier work, involve the σ^* value of the group R in the alcohol ROH, the Kirkwood function of dielectric constant, $f(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1)$ and $n_{\gamma H}$, the number of hydrogen atoms in the γ-position in the alcohol. These correlations yield information on the influence of *ortho*-substituents on the relative importance of specific and non-specific solvent effects. In analyses of type (*b*) the correlation equations are established with a limited set of substituents (up to 18), whose characteristic parameters σ_I, σ_R, and υ (determined by Charton) are well established, and are unlikely to show effects due to hydrogen-bonding or substituent conformation. The results for other substituents are then interpreted by comparing log *k*(calc). from a correlation expression with log *k*(obs.).

In Part 1,[2] we discussed the kinetics of the reactions of *o*-alkyl- and *o*-halogeno-benzoic acids with diazodiphenylmethane (DDM) in ethanol. The influence of an *o*-alkyl group on the rate coefficient was attributed mainly to a secondary steric effect and that of an *o*-halogen to a strong polar effect. In Part 5 [3] the work was extended to a few further *ortho*-substituted benzoic acids and related acids. A favourable influence of hydrogen-bonding on reactivity was indicated for *o*-hydroxybenzoic acid. Part 9 [4] dealt with the kinetics of the reactions of *o*-alkyl- and *o*-halogeno-benzoic acids with DDM in 2-methoxyethanol or in certain aprotic solvents, *e.g.* dioxan or ethyl acetate. The secondary steric effects of *o*-alkyl groups varied only slightly with the solvent, but polar effects of *o*-halogeno-substituents varied considerably. In Part 12 [5] and elsewhere [6-8] the influence of the solvent on the kinetics of the reaction between DDM and benzoic acid was extensively investigated. The main kinetic results we now present are for the reactions of DDM with benzoic and 32 *ortho*-substituted benzoic acids in 11 alcohols including 2-methoxyethanol.

ortho-Substituted benzene derivatives, as is well known, often behave differently from the corresponding *meta*- or *para*-substituted compounds.[9,10] This peculiarity of *ortho*-substituted compounds is sometimes named the '*ortho*-effect'.[11] At one time most attempts to explain the *ortho*-effect involved the concept of 'steric hindrance'.[10] Later the intervention of hydrogen-bonding was often postulated.[11] It is now clear that several kinds of structural influence may all play a part: the problem is to identify and to assess the relative importance of the various contributory factors. Until recently there had been little progress in this, compared with the understanding achieved for the influence of *meta*- and *para*-substituents on reactivity. The methods of linear free-energy relationships (correlation analysis) which have been so successful for *meta*- and *para*-substituents in the form of the Hammett equation and its extensions,[12] have now been adapted with some success to analysing the *ortho*-effect, *e.g.* Charton's work, which is based on the multiple regression analysis of reactivity data in terms of *substituent parameters* which measure the electronic or steric effects of substituents.[13,14] This approach is essentially an extension of the dual substituent-parameter treatment of the effects of *meta*- and *para*-substituents, as applied by Taft, Ehrenson, and others.[12] Charton has analysed a vast amount of data from the literature, with many interesting findings, but correlation analysis is often limited because the reaction series involve rather few or not very well chosen substituents, and there has been little systematic study of the influence of the solvent on the *ortho*-effect. The present work contributes to remedying these limitations, for one particular reaction.

Earlier papers [3,5,15] and those of other authors [16] showed that in the reaction between DDM and carboxylic acids in alcohols, the rate-determining step involves a proton transfer from the carboxylic acid to DDM to form a diphenylmethanediazonium–carboxylate ion-pair. Subsequent fast product-governing stages have been variously formulated.[3,16-18] The intervention of a diphenylmethyl–carboxylate ion-pair seems most likely; this may then either 'collapse' to give the ester or react with the solvent to give an ether.

DISCUSSION

Dependence of the Rate Coefficients on the Properties of the Solvent Alcohol for the Reactions of Benzoic Acid with Diazodiphenylmethane at 30 °C.—In Part 12 [5] we presented correlation analysis of second-order rate coefficients for the reactions in 19 alcohols at 30.0 °C. We concluded that the solvent effect was best expressed through multiple regression of log *k* on f(ε) [the Kirkwood function $(\varepsilon - 1)/(2\varepsilon + 1)$ of dielectric constant[19]], σ^* (the Taft polar constant for the alkyl group of the alcohol[20]), and $n_{\gamma H}$ (the number of γ-hydrogen atoms in the alcohol). The regression equation was (1) with

$$\log k = -1.799 + 4.645\mathrm{f}(\varepsilon) + 2.967\sigma^* + 0.0301n_{\gamma H} \quad (1)$$

multiple correlation coefficient, R 0.991 and standard deviation of the estimate, s 0.062. The terms of the equation are interpreted as follows. A favourable influence of dielectric constant is expected for a reaction in which passage from initial to transition state involves charge separation, but stepwise regression showed that the σ^* term is the more important. This was held to indicate the dominant role of the solvating properties of the alcohol, *i.e.* Lewis basicity or acidity of the solvent. The term in $n_{\gamma H}$, which is of minor importance overall, was interpreted in terms of a steric effect that moderates the basic properties of the alcohol oxygen. For certain alcohols it has a strong effect, *e.g.* the reaction is considerably faster in 2-methylbutan-1-ol than in ethanol, even though the former has the lower dielectric constant and the more negative value of σ^*, because for 2-methylbutan-1-ol, $n_{\gamma H} = 6$ whereas for ethanol $n_{\gamma H} = 0$. The acceleratory effect of γ-hydrogen atoms was confirmed by a study of 2,2-dimethylbutan-1-ol ($n_{\gamma H} = 8$).

In the present work the rate coefficients at 30.0 °C for the reactions in the original 19 alcohols have been redetermined (Table 1), with particular attention to purity of solvent and to constancy of initial concentrations of reactants (0.035M-benzoic acid, 0.0035M-DDM, except for the reaction in benzyl alcohol, for which the rate coefficient was determined by the second-order procedure; see Experimental section). In addition, rate coefficients were determined for the reactions in hexan-1-ol, octan-1-ol, and cyclohexanol.

TABLE 1

Rate coefficients (l mol^{-1} min^{-1}) for the reactions between benzoic (BA) or salicylic acid (SA) and diazodiphenylmethane in alcohols at 30.0 °C

Solvent	k (BA)	k (SA)	ε [a]	σ^* [b]	$n_{\gamma H}$ [c]
1 Methanol	2.47	17.6 [d]	32.7	0.00	0
2 Ethanol	0.995	7.49	24.55	−0.10	0
3 Propan-1-ol	1.06	7.87	20.33	−0.115	3
4 Propan-2-ol	0.677	6.13	19.41	−0.19	0
5 Butan-1-ol	0.982	7.21	17.51	−0.13	2
6 Butan-2-ol	0.643	6.33	16.56	−0.21	3
7 2-Methylpropan-1-ol	1.62	11.1	17.93	−0.125	6
8 2-Methylpropan-2-ol	0.261	4.20	12.47	−0.30	0
9 Pentan-1-ol	0.830	5.92	13.9	−0.135	2
10 Pentan-3-ol	0.547	6.17	12.4	−0.225	6
11 2-Methylbutan-2-ol	0.142	2.80	5.82	−0.31	3
12 Hexan-1-ol	0.708	5.39	13.3	−0.14	2
13 Heptan-1-ol	0.622	4.76	10.8	−0.145	2
14 Octan-1-ol	0.547	4.40	9.8	−0.15	2
15 Decan-1-ol	0.477	3.97	7.2	−0.155	2
16 Dodecan-1-ol	0.454	3.69	6.3	−0.16	2
17 Cyclopentanol	0.741	6.50	15.8	−0.15	0 [f]
18 Cyclohexanol	0.750	6.47	15.0	−0.15	0 [f]
19 Benzyl alcohol	9.15 [d]	69.6 [d]	12.8	+0.215	0
20 1-Phenylethanol	3.42	39.5 [e]	8.7	+0.105	0
21 2-Phenylethanol	2.87	30.2 [e]	12.5	+0.08	0
22 3-Phenylpropan-1-ol	2.60	26.8 [e]	11.4	+0.02	2

[a] Dielectric constant at 30 °C (see text). [b] Polar substituent constant of alkyl group. See refs. 5, 20, 21, and text. [c] Number of γ-hydrogen atoms. [d] Rate coefficients determined by second-order procedure (see Experimental section). [e] Rate coefficients determined by first-order procedure [acid] 0.007M, [DDM] 0.0007M, (see Experimental section). [f] Because of the ring structure the effective value is taken to be zero.

The new values of k usually agree with the old[5] to within 3—4%. The one exception is for the reaction in cyclopentanol, where there is a discrepancy of *ca.* 11%, the earlier value being 0.83 l mol^{-1} min^{-1}. The discrepancy was traced to a marked concentration-dependence of the second-order rate coefficient for the reaction in cyclopentanol (see Experimental section).

Correlation analysis of log k in terms of f(ε), σ^*, and $n_{\gamma H}$ has been extended to the results for 22 alcohols. The σ^* values for the unbranched alkyl groups have been modified on the basis of spectroscopic studies[21] (the values are rounded off to the nearest 0.005 unit) whereas previously it was assumed[12,20] that the σ^* values come to a limit at Bu^n. The values of dielectric constants have been up-dated by re-examining the literature to ascertain the most reliable values of ε, as far as possible for 30 °C. Experimental values were not always available for this temperature; a value at 30 °C was then estimated from values at other temperatures.

The correlation expression is equation (2). In spite of the inclusion of three more data-points, the correlation

$$\begin{array}{l} \log k = -1.484 + 3.957\mathrm{f}(\varepsilon) + 3.055\sigma^* + 0.029n_{\gamma H} \\ \qquad\qquad\qquad\qquad (\pm 0.474) \quad (\pm 0.099) \quad (\pm 0.0069) \quad (2) \\ \qquad\qquad\qquad R = 0.993, \; s = 0.0525 \end{array}$$

coefficient has improved slightly and the standard deviation has decreased, compared with equation (1). The coefficient of the f(ε) term has changed slightly, but the coefficients of the other terms remain virtually unchanged. The standard errors of the regression coefficients are small, in accord with low collinearities between the several explanatory variables. [Statistical details are in Supplementary Publication No. SUP 22975 (18 pp.).* All regression analyses in this work were carried out with the ICL Statistical Analysis Package Mark 2 XDS3.]

The Dependence of the Rate Coefficients on the Properties of the Solvent Alcohol for the Reactions of Salicylic Acid with Diazodiphenylmethane at 30 °C.—Rate coefficients for the reactions of salicylic acid with DDM have also been determined in the 22 alcohols (Table 1). Regression analysis of log k on f(ε), σ^*, and $n_{\gamma H}$ gave equation (3).

$$\begin{array}{l} \log k = 0.453 + 1.707\mathrm{f}(\varepsilon) + 2.744\sigma^* + 0.0157n_{\gamma H} \\ \qquad\qquad\qquad (\pm 1.148) \quad (\pm 0.240) \quad (\pm 0.0167) \quad (3) \\ \qquad\qquad\qquad R = 0.947, \; s = 0.127 \end{array}$$

The regression coefficients are rather lower than those for benzoic acid [equation (2)]; the correlation coefficient is poor, the standard deviation is high, and there are relatively large standard errors for the regression coefficients of the f(ε) and the $n_{\gamma H}$ term. In fact, the

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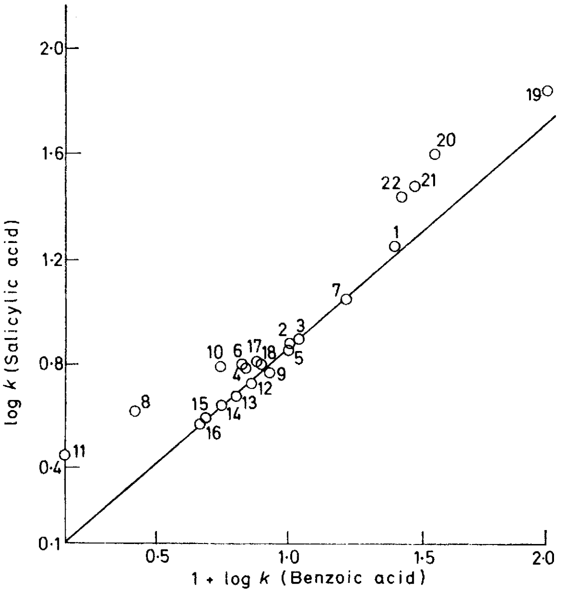
* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc., Perkin Trans. 2*, 1979, Index issue.

contributions of the f(ε) and the $n_{\gamma\mathrm{H}}$ terms do not reach an acceptable level of significance, and meaningful correlation analysis stops at simple regression on σ^*, with $r = 0.938$ and $s = 0.130$.

Thus the reactions of benzoic and salicylic acid do not respond in a comparable manner towards all the various alcohols used as solvents. This is shown very simply when log *k* for salicylic acid is plotted against log *k* for benzoic acid (Figure). The points for primary aliphatic alcohols lie reasonably close to the straight line drawn, and the deviations for all the remaining alcohols are then positive in the direction of the vertical axis. This may be due to internal hydrogen-bonding, which stabilises the nascent salicylate ion (see below), being of more pronounced effect in such alcohols, than in the primary aliphatic alcohols, for which it seems to be approximately constant. The deviation is greatest in tertiary alcohols (lowest Lewis acidity) and is less in secondary alcohols (lying between primary and tertiary alcohols in Lewis acidity). Deviations are also fairly pronounced for alcohols containing a benzene ring. These may be connected with the presence of an intramolecular hydrogen bond between the hydrogen of the alcoholic OH and the electrons of the benzene ring, as suggested by Oki and Iwamura.[22]



Plot of log *k* for salicylic acid *versus* log *k* for benzoic acid. 1, Methanol; 2, ethanol; 3, propan-1-ol; 4, propan-2-ol; 5, butan-1-ol; 6, butan-2-ol; 7 2-methylpropan-1-ol; 8, 2-methylpropan-2-ol; 9, pentan-1-ol; 10, pentan-3-ol; 11, 2-methylbutan-2-ol; 12, hexan-1-ol; 13, heptan-1-ol; 14, octan-1-ol; 15, decan-1-ol; 16, dodecan-1-ol; 17, cyclopentanol; 18, cyclohexanol; 19, benzyl alcohol; 20, 1-phenylethanol; 21, 2-phenylethanol; 22, 3-phenylpropan-1-ol

The Influence of Alcohols as Solvent on the Reactions of ortho-*Substituted Benzoic Acids with Diazodiphenylmethane at* 30 °C.—For the *ortho*-substituted benzoic acids (with the exception of salicylic acid, see above) rate coefficients were determined in only 11 alcohols (Table 2), which however constitute a reasonably representative selection of the larger number (22) used for benzoic acid and salicylic acid. In the more limited correlation analysis of log *k* in terms of f(ε), σ^*, and $n_{\gamma\mathrm{H}}$ which is possible for the *ortho*-substituted acids, the greatly reduced number of degrees of freedom might be expected to lead to difficulties. The procedure was therefore tested on benzoic acid itself. The correlation expression obtained by using results for only the 10 alcohols, was equation (4).

$$\log k = -1.555 + \underset{(\pm 0.520)}{4.075\mathrm{f}(\varepsilon)} + \underset{(\pm 0.101)}{3.185\sigma^*} + \underset{(\pm 0.007)}{0.050n_{\gamma\mathrm{H}}} \quad (4)$$
$$R = 0.998,\ s = 0.038$$

The regression coefficients of the f(ε) and σ^* terms are close to their values in equation (2) for 22 alcohols. The coefficient for the $n_{\gamma\mathrm{H}}$ term is somewhat enhanced, doubtless due to 2-methylbutan-1-ol being more prominent in the 10 alcohols than in the 22. Thus correlation analysis for the *ortho*-substituted acids in the 10 alcohols should be reasonably reliable, particularly in a comparative way.† Full statistical details of the multiple regressions are in SUP 22975. In the main text we comment only on illustrative examples.

For all the *ortho*-substituted systems except those involving NHCOMe, SO_2Me, NO_2, or OH, the 10 data-point regressions of log *k* on f(ε), σ^*, and $n_{\gamma\mathrm{H}}$ are satisfactory, with $R \geqslant 0.990$ (confidence level $>99.9\%$), *s* between 0.074 and 0.027 (usually $s < 0.055$), and acceptable standard errors in the regression coefficients. For the systems involving the above mentioned substituents, correlation analysis involving three solvent parameters gives an unacceptably high relative standard error for the regression coefficient of the f(ε) term, and regression on σ^* and $n_{\gamma\mathrm{H}}$ alone is to be preferred. Thus for the *o*-NO_2 system we have equation (5) but equation (6) is preferable.

$$\log k = 1.098 + \underset{(\pm 0.678)}{0.997\mathrm{f}(\varepsilon)} + \underset{(\pm 0.132)}{2.832\sigma^*} + \underset{(\pm 0.0096)}{0.048n_{\gamma\mathrm{H}}} \quad (5)$$
$$R = 0.995,\ s = 0.050$$

$$\log k = 1.549 + \underset{(\pm 0.137)}{2.883\sigma^*} + \underset{(\pm 0.010)}{0.047n_{\gamma\mathrm{H}}} \quad (6)$$
$$R = 0.993,\ s = 0.054$$

For most systems the regression coefficient of $n_{\gamma\mathrm{H}}$ lies in the range 0.045—0.057, and, considering its standard error (0.007—0.010), must be regarded as effectively constant. (See the comment above regarding the value of this coefficient for benzoic acid in the 10 data-point and in the 22 data-point case.) When the coefficient of

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† It is not possible to include the results for 2-methoxyethanol (Table 2) in regressions of this type. σ^* for $MeO(CH_2)_2$ is +0.19, and accordingly the rate coefficient for a reaction in 2-methoxyethanol would be expected to lie between the values for benzyl alcohol and methanol. In fact it is always comparable with the values for secondary alcohols, as if σ^* were effectively *ca.* −0.2. This anomaly is probably connected with the special possibilities of hydrogen-bonding involving Me*O* and *H*O which this solvent presents. The behaviour of electronegatively substituted alcohols in general, XCH_2OH, will be discussed in a later paper.

$n_{\gamma H}$ lies outside this range, it is usually associated with a high standard error, *e.g.* for the *o*-OH acid (regression on σ^* and $n_{\gamma H}$) the value is 0.036 ± 0.014.

The coefficient of σ^* in almost all the correlations lies in the range 2.8—3.2, and, with a standard error of *ca.* 0.1, must be regarded as virtually constant. There are some exceptions to this, *e.g.* *o*-SO_2Me (regression on σ^* and $n_{\gamma H}$) 2.298 ± 0.152, but no clear structural influence is discernible. *Thus the* ortho-*substituent seems to exert little influence on the way the solvating properties of the alcohol affect the reactivity of the acid towards DDM.*

TABLE 2

Rate coefficients (l mol^{-1} min^{-1}) for the reactions between diazodiphenylmethane and *ortho*-substituted benzoic acids in various alcohols at 30.0 °C

Sub- stituent	Methanol	Ethanol	Pentan- 1-ol	2-Methyl- propan- 1-ol	2-Phenyl- ethanol	3-Phenyl- propan- 3-ol	Benzyl alcohol [a]	Butan- 2-ol	2-Methyl- butan- 2-ol	Cyclo- pentanol	2- Methoxy- ethanol
H	2.47 [a]	0.99_5	0.830	1.62	2.87	2.60	9.15	0.643	0.142	0.741	0.653
Me	2.39	0.898	0.673	1.44	2.35	1.97	7.16	0.542	0.097	0.567	0.433
Et	2.87	1.03	0.741	1.56	2.55	2.09	8.17	0.597	0.110	0.599	0.479
Pr^i	4.30 [a]	1.45	1.02	2.21	3.39	2.84	10.1	0.83	0.164	0.783	0.639
Bu^t	7.56 [a]	2.67	2.12	4.20	6.40	5.34	19.5	1.50	0.252	1.47	1.04
F	6.59 [a]	2.58	2.21	4.23	7.96	6.93	23.1	1.81	0.419	1.95	1.52
Cl	13.0 [a]	4.89	3.87	8.16	14.5 [b]	11.9	41.6	3.54	0.865	3.35	2.74
Br	15.7 [a]	5.90	4.61	9.54	17.3 [b]	13.5	45.2	4.21	1.07	4.07	3.22
I	16.4 [a]	6.20	4.74	9.94	16.9 [b]	13.7	46.3	4.45	1.09	4.04	3.06
CF_3	17.1 [a]	6.70	5.85	10.9	20.4 [b]	18.5 [c]	64.6	5.07	1.29	4.99	4.17
OMe	3.31	1.28	1.03	2.09	2.73	2.38	7.43	0.812	0.181	0.810	0.490
OEt	3.43	1.37	1.05	2.15	2.55	2.21	5.83	0.820	0.187	0.721	0.574
OPh	7.64	3.18	2.60	5.13	6.77	6.08	21.6	2.04	0.397	1.90	1.30
NH_2	1.20	0.466	0.370	0.726	1.48	1.21	3.88	0.299	0.069	0.333	0.230
NHMe	1.26	0.493	0.380	0.743	1.28	1.12	3.52	0.332	0.068	0.357	0.266
NHPh	2.68	1.29	0.951	1.95	3.25	2.87	8.55	0.858	0.225	0.900	0.946
NHCOMe	10.7 [a]	4.64	3.57	6.38	12.9 [c]	10.4	32.1	3.56	1.48	3.49	4.99
OH	17.6 [a]	7.49	5.92	11.1	30.2 [b]	26.8 [b]	69.6	6.33	2.80	6.50	9.83
SH	5.61	2.50	2.21	4.00	7.40	6.67	22.6	1.81	0.546	1.91	1.86
SMe	4.86	2.04	1.60	3.27	5.27	4.49	15.5	1.36	0.255	1.29	1.06
SO_2Me	46.2	26.6	23.7 [c]	45.6_5 [b]	56.2 [b]	51.3 [b]	147.0	23.4 [b]	10.1	21.0	17.2
NO_2	37.8 [a]	17.0	16.1 [c]	29.0 [b]	57.0 [b]	49.7 [b]	148.0	15.4 [b]	5.42	14.2	9.87
CN	17.3 [a]	8.72	8.25	14.4	23.9_5 [c]	22.7 [b]	64.7	7.64	2.56	7.20	6.83
$CONH_2$	6.42	3.13	2.95 [b]	5.63 [c]	8.31	7.77 [b]	22.4	2.69 [b]	0.971 [a]	1.48 [b] (2.48)	1.60
OCOMe	6.86	2.66	2.29	4.17	6.66	5.67	19.4	1.84	0.422	1.86	1.39
CO_2Me	14.3 [a]	5.79	5.29	9.88	15.6 [c]	12.8 [c]	44.6	4.22	1.24	3.98	2.76
CO_2H [d]	13.9 [a]	6.46	6.74 [c]	13.0 [c]	23.5 [b]	22.7 [b]	70.3	5.48	1.30	5.40	3.01
CH_2CO_2Me	4.38	1.84	1.53	2.76	3.65	3.28	11.5	1.16	0.238	1.14	0.891
Ph	10.1 [a]	3.71	3.00	5.85	7.59	6.60	25.9	2.16	0.336	1.99	1.45
CH_2Ph	4.83 [a]	1.77	1.36	2.91	3.72	3.33	12.0	1.15	0.213	1.07	0.796
$(CH_2)_2Ph$	3.62	1.36	0.99	2.10	3.07	2.84	9.89	0.853	0.153	0.783	0.648
COPh	18.3 [a]	7.74	6.60	11.8	16.8 [b]	14.9	47.3	5.54	1.17	5.02	3.75
2,3-$(CH)_4$ [e]	4.31	1.61	1.20	2.67	4.14	3.64	12.5	1.09	0.208	1.03	0.833

[a] Determined by the second-order method. [b] Determined at [acid] 0.0070M (the value in parentheses for $CONH_2$ is the adjusted value for [acid] 0.035M. [c] Determined at 0.0175M. [d] Corrected by a statistical factor of 2. [e] 1-Naphthoic acid.

In contrast, the variation in regression coefficient is very marked for the f(ε) term. This coefficient is effectively zero for the *o*-NO_2 acid, it is *ca.* 4 for benzoic acid itself, and sometimes rises to above 6 as shown by equation (7) for the *o*-Bu^t acid.

$$\log k = 2.246 + \underset{(\pm 0.482)}{6.416}f(\varepsilon) + \underset{(\pm 0.093)}{3.161}\sigma^* + \underset{(\pm 0.007)}{0.055}n_{\gamma H} \quad (7)$$

$$R = 0.998, s = 0.036$$

The detailed statistical information indicates that electron-donating groups often give a high regression coefficient of the f(ε) term, while markedly electron-attracting substituents tend to give a lower value. The clearest structural relationship is to the 'external aspect' of the substituent, *i.e.* the nature of what is presented towards the surrounding solvent molecules. Thus some groups are essentially of 'hydrocarbon-like' aspect; the coefficient of f(ε) then tends to be enhanced compared with that for *o*-H, *e.g.* Me (5.608), Bu^t (6.416), OEt (6.029), OPh (5.527), SMe (5.032), Ph (6.943).

Other groups are essentially of 'electronegative' aspect, *i.e.* in the main they present electron clouds towards the solvent; the coefficient of f(ε) then tends to be reduced compared with that for *o*-H, and in extreme cases is zero, *e.g.* Hal (*ca.* 3.7), OH (0.0), SH (1.605), SO_2Me (0.0), NO_2 (0.0), CN (1.610), CO_2H (2.412). *We suggest that the 'electronegative' groups orientate the solvent molecules so strongly that it matters little which alcohol is there and the dielectric constant, as measured normally as a bulk property, becomes less important or even irrelevant.* When there is a 'hydrocarbon-like' group present, the role of the solvent as a dielectric is more distinctive, *i.e.* solvent molecules can move more freely and be orientated in a way which is related to bulk dielectric constant. Thus, with these groups the f(ε) term becomes important.

Correlation Analysis of the Influence of ortho-*Substituents on the Reactions of Benzoic Acid with Diazodiphenylmethane in Various Alcohols.*—The matrix of rate coefficients (30.0 °C) for the reactions of benzoic acid and

32 *ortho*-substituted benzoic acids with DDM in 11 alcohols including 2-methoxyethanol constitutes Table 2. The application of modern statistical techniques, such as principal components analysis, to this large and complete data matrix is now being examined in association with Professor S. Wold. In this paper we use the simpler form of correlation analysis by multiple regression: across the rows of the matrix for the solvent effect, as described above, and down the columns of the matrix for the *ortho*-effect.

The analysis employs the extended Hammett equation in form (8). σ_I and σ_R are respectively the inductive and

$$\log k = h + \alpha\sigma_I + \beta\sigma_R + \phi\upsilon \qquad (8)$$

resonance substituent constants of Taft's analysis of the ordinary composite Hammett constants.[12] We employ values obtained by Charton,[23] calculated by a consistent procedure for the substituents involved in the present work. υ is the steric substituent constant developed by Charton.[24] (The υ scale is based on a consideration of van der Waals radii and Taft's E_s values.[20]) The intercept term, h, notionally corresponds to log k for H as an *ortho*-substituent, but is not found in practice always to agree closely with the observed value of log k for the parent system. The values of σ_I, σ_R, and υ are in Table 3.

TABLE 3

Values of σ_I, σ_R, and υ

Substituents	σ_I	σ_R	υ
H	0	0	0
Me	−0.01	−0.16	0.52
Et	−0.01	−0.14	0.56
Pr^i	0.01	−0.16	0.76
Bu^t	−0.01	−0.18	1.24
F	0.54	−0.48	0.27
Cl	0.47	−0.25	0.55
Br	0.47	−0.25	0.65
I	0.40	−0.16	0.78
CF_3	0.40	0.12	0.91
OMe	0.30	−0.59	0.36
OEt	0.28	−0.58	0.48
OPh	0.40	−0.48	0.57
NH_2	0.17	−0.80	0.35
NHMe	0.13	[−0.84]	0.39
NHPh	0.30	−0.85	0.65
NHCOMe	0.28	−0.30	[0.75]
OH	0.24	−0.62	0.32
SH	0.27	[−0.30]	0.60
SMe	0.30	−0.35	0.64
SO_2Me	0.59	0.12	1.2
NO_2	0.67	0.10 (0.0)	1.39 (0.35)
CN	0.57	0.08	0.40
$CONH_2$	0.28	[0.08] (0.0)	1.4, (0.50)
OCOMe	0.38	−0.23	[0.70]
CO_2Me	0.32	0.10 (0.0)	1.51 (0.50)
CO_2H	0.30	0.08 (0.0)	1.48, (0.50)
CH_2CO_2Me	0.15	−0.11	[0.65]
Ph	0.12	−0.11 (0.0)	2.15 (0.57)
CH_2Ph	0.03	−0.13	0.70
$(CH_2)_2Ph$	0.02	−0.13	0.70
COPh	0.32	[0.1] (0.0)	1.4 (0.50)

Values in parentheses are for the orthogonal conformation.
Values in squares brackets are subject to some uncertainty.

Nine substituents (Set A: H, Me, Bu^t, F, Cl, Br, I, CF_3, and CN) were selected as a basic set for the following qualities: (i) symmetry and simplicity, (ii) freedom from conformational effects, (iii) lack of a large resonance effect, (iv) lack of any marked tendency to form hydrogen bonds with the reaction centre. Multiple regression of log k on σ_I, σ_R, and υ was carried out for Set A data for the 11 solvents. The correlations were always quite good, with R values between 0.973 and 0.985 (confidence level >99.9%), and values of s between 0.082 and 0.120. (Detailed statistics are in SUP 22975.)

The effect of extending the correlation analysis to a total of 18 substituents was then examined, by including some which might show conformational effects, but which can, however, be placed on the σ_R and υ scales on the basis of reasonable assumptions about conformation. Set B is Set A + Et, Pr^i, OMe, OEt, OPh, SMe, SO_2Me, CH_2Ph, and $(CH_2)_2Ph$. The correlations based on Set B are superior to those based on Set A. (See deposited material for details.) The values of R are 0.978—0.990, and the values of s 0.070—0.106, an improvement on Set A in spite of the inclusion of 9 additional data-points. The standard errors of the regression coefficients were always greatly reduced, sometimes by as much as 50% as between Set A and Set B.

To illustrate these correlations we show here expressions (9) and (10) for the reactions in methanol.

Methanol, Set A

$$\begin{gathered}\log k = 0.314 + 1.233\sigma_I + 0.453\sigma_R + 0.508\upsilon \\ (\pm 0.149) \quad (\pm 0.197) \quad (\pm 0.100) \qquad (9) \\ n = 9 \quad R = 0.973,\ s = 0.102\end{gathered}$$

Methanol, Set B

$$\begin{gathered}\log k = 0.313 + 1.248\sigma_I + 0.544\sigma_R + 0.492\upsilon \\ (\pm 0.086) \quad (\pm 0.095) \quad (\pm 0.070) \qquad (10) \\ n = 18 \quad R = 0.980,\ s = 0.081\end{gathered}$$

Changes in the regression coefficients of σ_I and υ as between Set A and Set B are relatively small, as exemplified in equations (9) and (10), but are more marked for σ_R, which is, however, a relatively unimportant term.

Our discussion henceforth will be on the basis of Set B correlations, of which we give two further examples, (11) and (12).

2-Methylbutan-2-mol, Set B

$$\begin{gathered}\log k = -0.983 + 1.982\sigma_I + 0.955\sigma_R + 0.440\upsilon \\ (\pm 0.113) \quad (\pm 0.125) \quad (\pm 0.092) \qquad (11) \\ n = 18 \quad R = 0.984,\ s = 0.106\end{gathered}$$

2-Methoxyethanol, Set B

$$\begin{gathered}\log k = -0.305 + 1.624\sigma_I + 0.964\sigma_R + 0.346\upsilon \\ (\pm 0.074) \quad (\pm 0.082) \quad (\pm 0.060) \quad (12) \\ n = 18 \quad R = 0.990,\ s = 0.070\end{gathered}$$

We note first that the regression coefficients of σ_I, σ_R, and υ terms are all positive. For the electronic-effect terms, σ_I and σ_R, this is because electron-attracting groups accelerate the reaction and electron-releasing groups retard it, as found for *meta*- and *para*-substituents some 30 years ago.[25] This is readily explicable in terms of the reaction mechanism as described earlier. The positive regression coefficient for the υ (steric) term corresponds to the reaction being subject *to steric acceleration* by *ortho*-substituents. We showed this originally in Part 1,[2] when the rate coefficients for *o*-alkylbenzoic acids reacting with DDM in ethanol were found to lie in the order H $\approx$ Me $<$ Et $<$ Pr^i $<$ Bu^t. This is a secondary steric effect and is due to the bulky *ortho*-substituent twisting the carboxy-group out of the plane of the ring, thereby reducing the conjugation of the benzene ring with the carboxy-group.

In stepwise regression the σ_I term is always taken in first. The relatively high regression coefficient is 1.25—1.98. While the values for several alcohols lie close to 1.5, secondary and tertiary alcohols give values rather higher than this [*cf.* equation (11)] and the lowest primary alcohols give lower values [*cf.* equation (10)]. This corresponds approximately to the variation with solvent polarity of the Hammett ρ value for the reaction of benzoic acid with DDM.[15]

Depending on the solvent, either σ_R or υ can enter the regression next. With the less polar alcohols σ_R enters before ν, while with more polar alcohols the situation is reversed. The regression coefficient of σ_R varies from 0.54 to 0.995, and tends to increase with decrease in the polarity of the solvent.

The regression coefficient of υ varies from 0.35 to 0.49 and is thus relatively insensitive to solvent. *This confirms our earlier conclusion that the secondary steric effect varines oly slightly with the solvent.*[4]

Limitations of the Above Correlation Analysis.—Although overall the above correlations for Set B data are quite successful, whether judged by *R* or by *s*, the equations are seen to have certain limitations when values of log *k*(calc.) from the regressions are compared with log *k*(obs.) (details in deposited material). We now outline these limitations and try to account for them.

(i) The parent system does not conform well to the regressions: log *k*(calc.) is always lower than log *k*(obs.) by 1.0—1.5 times the standard deviation, *i.e.* in the regression the *ortho*-substituted acids ' pull ' the parent acid down towards lower reactivity. Thus there *appears to be a retardatory effect connected with the replacement of* o-*H by any substituent, whatever its polarity.* In applications of the extended Hammett equation (8) it often turns out that the intercept *h* does not correspond closely to the log *k* value for the parent system.

(ii) For CF_3 log *k*(calc.) is always higher than log *k*(obs.). This deviation may be due to the neglect of orientational effects in this type of treatment. A σ_I value measures a blend of through-bond and through-space (field) effects for a given substituent in the *meta*- or *para*-position. This blend will not be exactly the same for the substituent in the *ortho*-position, although the overall success of equation (8) for Set A or Set B indicates that σ_I, *and also* σ_R, *values are broadly applicable to the* ortho-*position*. Deviations seem particularly likely for substituents such as CF_3 involving several bond dipoles, whose orientations with respect to the reaction centre differ markedly as between the *ortho*-position on the one hand and the *meta*- or *para*-position on the other. Another possible cause of the deviations for *o*-CF_3 is hydrogen-bonding of the ' unfavourable ' kind between an F atom and H of CO_2H (see below).

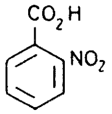
(iii) The regressions tend to compress the log *k* values for the *o*-alkyl systems, *e.g.* in methanol Δ log *k*(obs.) as between Me and Bu^t is 0.50, whereas Δ log *k*(calc.) is 0.34. For the reaction in benzyl alcohol the values are 0.43 and 0.26, respectively. For these groups the regression is dominated by the steric effect, the σ_I and σ_R values being almost constant. Thus *the* υ *scale*, based on van der Waals radii and E_s values (measured by a primary kinetic steric effect [20]), *does not fully express the spread of reactivity caused by a secondary steric effect.*

(iv) The regressions also tend to compress the log *k* values for the *o*-halogeno-substituents, *e.g.* in methanol Δ log *k*(obs.) as between F and I is 0.40, whereas Δ log *k*(calc.) is 0.25. For the reaction in 2-methylbutan-2-ol, the values are 0.415 and 0.265, respectively. As for *o*-CF_3, these discrepancies may well be due to the neglect of dipole orientation effects or to the occurrence of unfavourable hydrogen-bonding. The latter might be particularly important for *o*-F, and for this substituent log *k*(obs.) $<$ log *k*(calc.), except for the reaction in the phenyl-substituted alcohols.

(v) There are occasional apparently highly specific deviations, which we have confirmed by much repetition of the relevant experimental work, *e.g.* *o*-ethoxybenzoic acid shows marked deviations in the phenyl-substituted alcohols, while *o*-methylsulphonylbenzoic acid shows a considerable deviation in 2-methylbutan-2-ol.

Interpretation of the log k *Values for the Substituents not included in the Regressions*.—The Set B (18 point) correlations may be used to investigate the behaviour of the remaining 15 substituents. For substituents not included in the regressions there are two main sources of deviation.

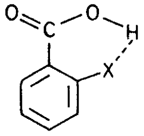
(*a*) Resonance and steric effects may show serious conformational dependence, *e.g.* *o*-nitrobenzoic acid.



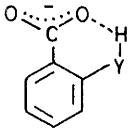
Coplanar NO_2: $\sigma_R = 0.10$, $\upsilon = 1.30$

Orthogonal NO_2: $\sigma_R = 0.00$, $\upsilon = 0.35$

(*b*) Hydrogen-bonding to the reaction centre may be possible. If *o*-X bonds to the H of CO_2H, the reaction will be retarded (' unfavourable ' hydrogen-bonding), while if *o*-YH bonds to a negatively charged O in the nascent carboxylate ion, the reaction will be accelerated (' favourable ' hydrogen-bonding).



Unfavourable



Favourable

We shall show the occurrence of these effects for the various *ortho*-substituents through a comparison of log *k*(obs.) with log *k*(calc.) from the appropriate regression. Details are in SUP 22975, from which we draw illustrative material.

o-OH. log *k*(obs.) is much higher than log *k*(calc.) in all the solvents, *e.g.* in ethanol the values are 0.874 and −0.0096 respectively. This indicates the occurrence of a very favourable hydrogen-bonding effect,[3] apparently more pronounced in the less polar solvents, *e.g.* with 2-methylbutan-2-ol the discrepancy is 1.43, *cf.* 0.88 above.

o-NO_2. In all solvents log *k*(obs.) lies between the two extreme values of log *k*(calc.) calculated for the coplanar and for the orthogonal conformation, *e.g.* in ethanol log *k*(obs.) is 1.230, while log *k*(calc.) for coplanar NO_2 is 1.570 and for orthogonal NO_2 is 1.006. Probably both CO_2H and NO_2 groups are somewhat twisted out of the plane of the benzene ring, as has already been indicated for the molecular configuration of this acid.[26]

o-Ph. log *k*(obs.) is usually much closer to log *k*(calc.) for the orthogonal conformation than for the coplanar conformation, and in certain alcohols log *k*(obs.) virtually coincides with the orthogonal value, *e.g.* in 2-methylbutan-2-ol log *k*(obs.) is −0.474, while the calculated values for orthogonal and coplanar conformations are −0.494 and 0.091 respectively.

o-NH_2. Over the 11 solvents the agreement between log *k*(obs.) and log *k*(calc.) is sometimes not very good, but the discrepancies are not systematic. There is no clear indication of a favourable hydrogen-bonding effect; similarly for *o*-NHMe, but *o*-NHPh may have a contribution from a favourable effect.

o-NHCOMe. Although there is uncertainty in the υ value, there are indications of a small favourable hydrogen-bonding effect, even in the simple primary alcohols.

o-OCOMe. log *k*(obs.) values are always appreciably lower than log *k*(calc.) values, and the results suggest the possibility of unfavourable hydrogen bonding.

o-SH. The σ_R value for this substituent is a little uncertain, but the agreement between log *k*(obs.) and log *k*(calc.) is mainly good.

o-CO_2H. In most cases log *k*(obs.) lies between the log *k*(calc.) values for orthogonal and coplanar conformations, except for the phenyl-substituted alcohols, for which log *k*(obs.) is much closer to log *k*(calc.) for the coplanar conformation. Perhaps the phthalic acid molecule is ' buried ' between the molecules of the phenyl-substituted alcohols and this encourages the coplanarity of the acid molecule. There is no clear evidence for the favourable hydrogen-bonding effect which might be expected to occur.

o-CO_2Me. An intermediate conformation is indicated, perhaps closer to the orthogonal. No evidence of unfavourable hydrogen-bonding is apparent.

o-$CONH_2$. The log *k*(obs.) value is always near to the lower value of log *k*(calc.) (orthogonal conformation) and sometimes below log *k*(calc.).

o-CH_2CO_2Me. The log *k*(obs.) values are always below log *k*(calc.), probably indicating the occurrence of unfavourable hydrogen bonding.

o-COPh. This acid may be presumed to exist predominantly in an open-chain structure.[27] Although the value of σ_R is not well established for the coplanar conformation, log *k*(obs.) values are intermediate between the log *k*(calc.) values for the conformational extremes, and there is no evidence for any hydrogen-bonding effect.

2,3-$(CH)_4$. Substituent constants appropriate for the discussion of 1-naphthoic acid cannot at present be assigned. In reactivity towards DDM it always lies between the *o*-Pr^i and *o*-Bu^t acids.[28]

EXPERIMENTAL

Materials.—Many of the substituted benzoic acids were available from earlier work or commercially. Such samples were recrystallised from glacial acetic acid, then from aqueous ethanol, and finally from benzene or the light petroleum fraction appropriate to the m.p. Purity was checked by m.p., by g.l.c. of the corresponding methyl ester, and through titration equivalent.

Methylthiosalicylic acid was prepared from thiosalicylic acid by the method of Weygand *et al.*,[29] m.p. 169—171° (lit.,[29] 169—171°). *o*-Methylsulphonylbenzoic acid was made by the method of Arndt *et al.*[30] from methylthiosalicylic acid. A crude product (m.p. 135°) was recrystallised from water to give a monohydrate (m.p. 75°). This was dehydrated over P_2O_5 *in vacuo* at 77°, then at 100—105°, and after recrystallisation from dry toluene had m.p. 136—138° (lit.,[30] 138—140°). On being kept for some weeks the material gave an anomalously high rate constant for reaction with DDM in ethanol, so periodic recrystallisation from toluene was necessary.

o-Cyanobenzoic acid. 4M-Ammonia (50 ml) was added dropwise with continuous stirring to phthaloyl chloride (4 ml), cooled in an ice–water-bath. The mixture was stirred for a further 2 h and was then acidified with concentrated hydrochloric acid. The precipitate was filtered off and washed with cold water, until the filtrate gave no precipitate with silver nitrate solution. The acid had m.p. 178—183° (lit.,[31] 187—188°), and then resolidified as phthalimide. This acid was not recrystallised: when warmed in glacial acetic acid it gave phthalimide and in aqueous ethanol it formed phthalic acid. After 2—3 months, samples of *o*-cyanobenzoic acid showed diminished reactivity towards DDM and were discarded.

Phthalamic acid. Phthalimide of good quality from a freshly opened bottle (50 g) was dissolved in 25% aqueous KOH (150 g) in a closed vessel, and the solution was kept at room temperature for 1—2 h, until a sample no longer gave phthalimide as long needles on neutralisation with hydrochloric acid. This solution was then treated with a slight excess of hydrochloric acid. After a few minutes, crystals of phthalamic acid appeared and crystallisation was complete after a few hours. The crystals were filtered off and washed with cold water until the filtrate gave no precipitate with silver nitrate. The acid was used without recrystallisation (*cf.* *o*-cyanobenzoic acid), m.p. 148—149° (lit.,[32] 148—149°). See further below.

Monomethyl homophthalate was prepared by Wegscheider and Glogau's method;[33] it had m.p. 96—98° (lit.,[33] 96—98°).

Diazodiphenylmethane, prepared by the method of

Schroeder and Katz,[34] was stored over potassium hydroxide in a desiccator in a refrigerator.

Solvents which had been used in earlier work were in general purified by methods described in Part 12[5] or Part 8,[15] taking full advantage of the better quality commercial samples now available. Hexan-1-ol (puriss.) was kept over molecular sieve (Linde type 4A) for one week and was then used without further purification. Octan-1-ol, dried over K_2CO_3 and then molecular sieve, was fractionally distilled under nitrogen from fresh molecular sieve, and was finally passed through an alumina column. Cyclohexanol was purified by fractional freezing and was kept over molecular sieve for 1 week before use. All the purified solvents were examined for organic impurities by g.l.c. (impurities always found to be negligible) and were subjected to water analysis by Karl Fischer titration,[35] except when the Karl Fischer reagent reacted with the solvent (2-methylbutan-2-ol). The water content was always $<0.02\%$ (w/v) and generally $<0.01\%$ (w/v). All solvents were stored and manipulated under dry nitrogen.

Measurements.—Values of k were determined spectrophotometrically by mixing equal volumes of acid and of DDM solutions in the spectrometer cell, placed in a controlled-temperature block, and monitoring the disappearance of the DDM at 525 nm.

The standard procedure involved initial concentrations of acid and DDM of *ca.* 0.035M and 0.0035M (optical density *ca.* 0.35 at 525 nm in a 1 cm cell, Unicam SP 600 spectrometer) respectively, the excess of acid being sufficient to maintain first-order behaviour throughout the two half-life periods during which observations of optical density were made. Most acids gave a very low optical density after 10 half-lives but faintly coloured solutions of certain acids, *e.g.* thiosalicylic acid or *N*-phenylanthranilic acid, required a correction.

For very slow reactions the automatic recording facilities of a Unicam SP 8000 intrument were used. For rather reactive acids the standard first-order procedure was modified to use 4 cm cells with initial concentrations of acid 0.0175M and DDM 0.000875M, or acid 0.007M and DDM 0.0007M. For highly reactive acids the second-order procedure as described by O'Ferrall *et al.*[16] was used. The initial concentrations of both acid and DDM were 0.0035M.

The procedures involving the use of low concentrations of acid were also employed when the acid was only sparingly soluble in the particular solvent or to investigate any concentration dependence of the observed second-order rate coefficient.

Rate coefficients were reproducible to within ±2% and usually to within ±1% for the first-order methods, and to within ±3% for the second-order procedure. When k for a given reaction was determined by both first- and second-order procedures, agreement was normally good, *e.g.* for reactions in methanol, values of k (l mol^{-1} min^{-1}; 30.0 °C) respectively for first- and second-order procedures: benzoic acid, 2.42, 2.47; *o*-fluorobenzoic acid, 6.46, 6.59; *o*-benzylbenzoic acid, 4.73, 4.78.

Further details of the experimental procedures and their application are in ref. 36.

Rate Coefficients for the Reactions of Benzoic Acid at Various Initial Concentrations with Diazodiphenylmethane at 30.0 °C. —Possible dependence of rate coefficient on concentration of benzoic acid was examined for the higher alcohols involved in this work and for 2-methoxyethanol. Table 4 shows that usually there was no important change for a 3—5-fold variation in the initial concentration of acid. The second-order rate coefficient for the reaction in cyclopentanol, however, increased markedly with initial concentration, while that for cyclohexanol changed in the opposite direction. The rate coefficient for the reaction of acetic acid with DDM in cyclopentanol also increased markedly with initial concentration of acid (Table 4). (Similar results were also obtained for *m*-nitrobenzoic acid and for salicylic acid.)

TABLE 4

Rate coefficients (l mol^{-1} min^{-1}) for the reactions between benzoic acid (or certain other acids) and diazodiphenylmethane in alcohols at 30.0 °C, with various initial concentrations of acid

	Initial concentration of acid		
Solvent	0.035M	0.0175M	0.007M
Hexan-1-ol	0.708	0.714	0.715
Heptan-1-ol	0.622	0.597	0.588
Octan-1-ol	0.547	0.546	0.532
Decan-1-ol	0.477	0.471	0.475
Dodecan-1-ol	0.454	0.450	0.455
Cyclopentanol [a]	0.741	0.677	0.450
Cyclohexanol	0.750	0.841	0.923
2-Phenylethan-1-ol	2.87	2.91	2.90
3-Phenylpropan-1-ol	2.60	2.62	2.61
2-Methylbutan-2-ol [d]	5.24	5.42	5.32
Cyclopentanol	0.525 [e]	0.459 [e]	0.317 [e]
	6.50 [f]		2.90 [f]
	4.39 [g]		2.08 [g]
2-Methoxyethanol	0.635	0.631 [b]	0.635 [c]

[a] 0.231 at 0.0035M, second-order procedure. [b] At 0.07M. [c] At 0.105M. [d] Reactions of *o*-nitrobenzoic acid. [e] Reactions of acetic acid. [f] Reactions of salicylic acid. [g] Reactions of *m*-nitrobenzoic acid.

Variation of second-order rate coefficient with concentration is characteristic of the reaction of carboxylic acids with DDM in many aprotic solvents,[6,7] in which the acids tend to dimerise to a greater or less extent. The peculiar behaviour of cyclopentanol and cyclohexanol in the DDM reaction might be attributed to these cyclic alcohols being exceptionally associated, and therefore having a reduced tendency to solvate the acid through hydrogen bonding and thereby prevent dimerisation. The b.p., density, dielectric constant, surface tension, and viscosity of cyclopentanol are considerably higher than those of the open-chain secondary alcohols with the same number of carbon atoms. Comparison of the properties of cycloalkanes with normal alkanes, however, shows a similar pattern, so the peculiar physical properties of cyclopentanol may be due simply to its cyclic structure. Thus while its behaviour in the DDM reaction may be explained by cyclopentanol being an extremely associated liquid, the physical properties give no clear support to this idea. It may be significant, however, that a glass electrode in pure cyclopentanol showed an apparent pH of 9.6, whereas various primary and secondary aliphatic alcohols gave values ranging from 4 to 7. This does indeed suggest that some kind of association exists in cyclopentanol in which the H of the hydroxy-group is less free than the other alcohols.

Whatever the degree of association of cyclopentanol may be compared with that of other alcohols, the liquid presumably contains a considerable amount of dimer. In its extended conformation this bears some resemblance to the cyclic dimeric structure of benzoic acid. Possibly this resemblance encourages the dimerisation of benzoic acid in this solvent. This perhaps leads to the abnormal kinetic behaviour of benzoic acid and DDM in cyclopentanol, in so far as deviations from strict second-order kinetics in this reaction may be connected with the dimerisation of the carboxylic acid.[6,7]

The Behaviour of Phthalamic Acid.—This acid was difficult to study (see above for difficulties in its preparation). In several of the solvents the measured rate coefficient for reaction with DDM decreased quite rapidly as the stock solution of acid aged, *e.g.* for methanol the rate coefficient decreased by 30% when the solution was kept at 30.0° overnight and by *ca.* 80% after one week. Solutions of the acid in ethanol actually gave a precipitate on being kept. This appeared to be the ammonium salt of phthalamic acid.[37] It was therefore essential to determine rate coefficients for phthalmic acid with freshly prepared solutions.

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