The Influence of the Solvent on Organic Reactivity. Part 3.[1] The Kinetics of the Reactions of Diazodiphenylmethane with Benzoic Acid or 2,4-Dinitrophenol in Aprotic Solvents

By **Alan G. Burden, Norman B. Chapman,* Hilary F. Duggua,** and **John Shorter,** Department of Chemistry, The University, Hull HU6 7RX

The kinetics of the reactions between diazodiphenylmethane and benzoic acid at 37 °C have been studied in a further 13 aprotic solvents. Values of k_0, the limiting second-order rate coefficient at [acid] = 0 are tabulated. log k_0 values were subjected to multiple correlation with solvent parameters, results from this and earlier work being combined for 43 solvents in all. In addition to updating the analysis of the type advocated by Koppel and Palm, we also examined possible improvements in this and the application of alternative solvent parameters. We conclude that the B parameter is still the most useful available measure of solvent basicity in the correlation analysis of the present reactions, but there is a case for using the E_T parameter rather than separate solvent electrophilicity (E) and dielectric $[(\varepsilon - 1)/(2\varepsilon + 1)]$ parameters. The kinetics of the reactions between diazodiphenylmethane and 2,4-dinitrophenol in 38 aprotic solvents at 30 °C have also been studied. In contrast to the reaction with benzoic acid, observed second-order rate coefficients always showed little dependence on concentration. The spread of values of rate coefficients over the range of solvents studied was only 180-fold, compared with 3 200-fold for benzoic acid. An analysis of the Koppel–Palm type is presented for the reaction in 31 solvents in which 2,4-dinitrophenol is believed to be present in the chelated form, but this analysis does not apply to the highly basic solvents in which the chelate ring is broken. In contrast to the reaction with benzoic acid, the dielectric properties of the reaction medium are more important than solvent basicity in governing log k. However, simple regression of log k on E_T is remarkably successful.

Two of our previous papers [2,3] on the kinetics of the reactions of carboxylic acids with diazodiphenylmethane in aprotic solvents dealt with values of k_0, the limiting second-order rate coefficient at [acid] = 0 for the reactions of benzoic acid in 31 aprotic solvents. We have also presented detailed results for reactions in solvents in which the acid is believed to be largely monomeric [3] or mainly in the form of a dimer.[1] We now present results for the reactions in a further 13 aprotic solvents.

We have also extended our studies of solvent effects to the kinetics of the reaction of diazodiphenylmethane with 2,4-dinitrophenol. This reaction has previously been studied only in ethanol (by Roberts *et al.*[4]), whereas the analogous reaction between diazodiphenylmethane and *p*-nitrophenol has been studied in several aprotic solvents by Isaacs and Rannala.[5] As pointed out by the latter authors, the reactions of a nitro-substituted phenol with diazodiphenylmethane should be largely free of complications due to dimerisation.[6] 2,4-Dinitrophenol has an acid dissociation constant comparable with that of benzoic acid (pK_a *ca.* 4.0 in water) and gives convenient rates in a wide range of aprotic solvents.†

DISCUSSION

Kinetics of the Reactions between Benzoic Acid and Diazodiphenylmethane in Aprotic Solvents at 37 °C.—We showed previously [3] that the reaction in many donor aprotic solvents conforms to equation (1). Here k(obs) is the observed second-order rate coefficient when [acid] = c, and k_0 and k' are constants characteristic of the carboxylic acid and the solvent, k_0 being the rate coefficient for $c = 0$, while k' refers to a component of the overall reaction which is of the second order in carboxylic acid and first order in diazodiphenylmethane.

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

We have shown [3] that equation (1) is best interpreted in terms of Scheme 1. [D represents diazodiphenylmethane, HA monomeric acid, and $(HA)_2$ dimeric acid,

$$\text{D} + \text{HA} \overset{K}{\rightleftharpoons} \text{DHA}$$

$$\text{DHA} \xrightarrow{k_3} \text{products}$$

$$2\text{HA} \overset{K_{12}}{\rightleftharpoons} (\text{HA})_2$$

$$\text{D} + (\text{HA})_2 \xrightarrow{k_2} \text{products} + \text{HA}$$

SCHEME 1

this being present to only a minute extent in donor aprotic solvents. DHA is an intermediate complex. The products are the diphenylmethyl ester and N_2.] The total rate coefficient is then given by equation (2).

$$k(\text{obs}) = k_3K + k_2K_{12}[\text{HA}] \qquad (2)$$

This is equivalent to equation (1) with $k_0 = k_3K$, $k' = k_2K_{12}$, and c = [HA].

For solvents in which the carboxylic acid is considerably dimerised, k(obs) commonly varies with c curvilinearly, and may either increase or (more rarely) decrease as the concentration is increased.[1] There are occasional

---

† We have also carried out a limited study in a series of 10 alcohols, but the results are somewhat inconclusive, as the rate coefficients cover only a three-fold range, *cf.* the 60-fold range shown by the reactions of benzoic acid.[2] We defer publication of these results pending further work.

[1] Part 2, N. B. Chapman, M. R. J. Dack, D. J. Newman, J. Shorter, and R. Wilkinson, *J.C.S. Perkin II*, 1974, 971.

[2] N. B. Chapman, M. R. J. Dack, and J. Shorter, *J. Chem. Soc.* (*B*), 1971, 834.

[3] Part 1, N. B. Chapman, M. R. J. Dack, D. J. Newman, J. Shorter, and R. Wilkinson, *J.C.S. Perkin II*, 1974, 962.

[4] J. D. Roberts, W. Watanabe, and R. E. McMahon, *J. Amer. Chem. Soc.*, 1951, **73**, 2521.

[5] N. S. Isaacs and E. Rannala, *J.C.S. Perkin II*, 1974, 902.

[6] M. M. Davis, 'Acid–Base Behavior in Aprotic Organic Solvents,' National Bureau of Standards Monograph 105, Washington, 1968, p. 25.

examples of rectilinear behaviour or of k(obs) being almost independent of concentration. (The latter behaviour is also shown in certain donor aprotic solvents.) The above mechanistic scheme may be adapted to the situation in the ' dimerising ' solvents,[1] but these details need not concern us in the present paper.

The detailed results for the 13 new solvents are either summarised in Table 1 in terms of k_0 and k', or are shown graphically in Figures, 1 and 2, with the k_0 values recorded in Table 2.

TABLE 1

Kinetics of the reactions between benzoic acid and diazodiphenylmethane in various aprotic solvents at 37 °C (least-squares analysis)

Solvent	k_0/l mol^{-1} min^{-1}	% Error [a]	k'/l^2 mol^{-2} min^{-1}	% Error [a]	Number of points	r [b]	s [c]
Bromobenzene	3.72	2.4	−2.69 [d]		5	0.734	0.089
Tetrahydrofuran	0.030 1	4.5	0.126	4.3	7	0.995	0.002
Di-isopropyl ether	0.015 8	19.8	0.51	5.2	6	0.995	0.004
Diphenyl ether	3.83	0.8	2.42	15.8	6	0.953	0.041

[a] Standard deviation. [b] Correlation coefficient. [c] Standard deviation of the estimate. [d] Not to be interpreted as in equation (2).

TABLE 2

Kinetics of the reactions between benzoic acid and diazodiphenylmethane in various aprotic solvents at 37 °C (graphical treatment)

Solvent	k_0/ l mol^{-1} min^{-1}	Number of points [a]	Sign of slope (Figures 1 or 2)
Dichloromethane	14.4	5	−ve
1,2-Dichloroethane	11.8	8	−ve
o-Dichlorobenzene	4.75	7	−ve
m-Dichlorobenzene	2.12	7	−ve (v. small)
Phenetole	1.30	8	+ve
o-Xylene	1.20	8	+ve (v. small)
m-Xylene	0.40	7	+ve
p-Xylene	0.57	7	+ve
NN-Dimethylformamide	0.089	4	*ca.* 0

c = 0.02—0.14M

[a] Not all plotted in Figures 1 and 2.

The concentration dependence observed for bromobenzene and for the two dichlorobenzenes is small, as was observed previously for other halogenobenzenes,[1] although the rate coefficient for the reaction in *o*-dichlorobenzene depends considerably more on concentration than the others. The concentration dependence for the ethers in Table 1 is comparable with that found previously for analogous compounds.[3] Phenetole, however, (Figure 2), like anisole,[1] gives a strongly curved plot of k(obs) against [acid] and k_0 cannot be determined very precisely. The aliphatic chloro-compounds give strongly curved plots of negative slope (Figure 1), as found previously for chloroform,[1] and k_0 can be estimated only approximately. The behaviour of the xylenes (Figure 2) is similar to that found previously for toluene and mesitylene (although the concentration dependence for *o*-xylene is small, like that for benzene [1]). Finally, for the reaction in *NN*-dimethylformamide k(obs) is virtually independent of concentration (Table 2); this is similar to the observations for *NN*-dimethylacetamide and dimethyl sulphoxide.[3]

We also tried to measure rate coefficients for the reactions in several highly basic solvents. Piperidine and triethylamine gave no results which could be distinguished from the spontaneous decomposition of diazodiphenylmethane, while *N*-methylaniline absorbed too strongly at the wavelength (525 nm) used in the kinetic study. Pyridine gave measurable reaction rates, but the first-order plots showed marked curvature. Aniline gave satisfactory kinetics, but the rate coefficients were surprisingly high: 7.1 l mol^{-1} min^{-1} at 0.036M-benzoic acid, and 3.4 at 0.106M. An experiment in which anilinium chloride was used instead of benzoic acid gave second-order rate coefficients of about the same magnitude. We infer, therefore, that in aniline, benzoic acid forms anilinium benzoate; the reaction then involves the transfer of a proton from the anilinium ion to diazodiphenylmethane, and so is not comparable with the reactions in the other solvents.

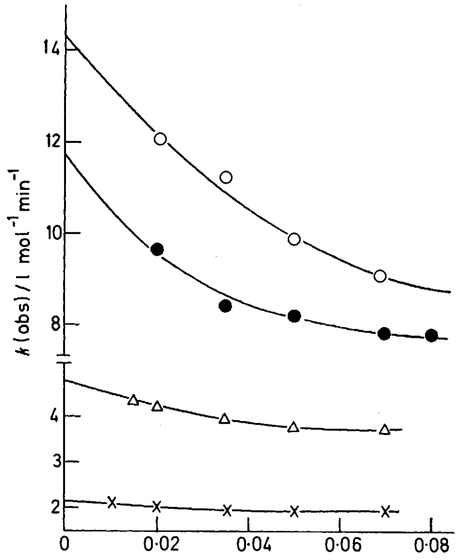


FIGURE 1 Dependence of k(obs) on [acid] for the reactions of benzoic acid with diazodiphenylmethane in various chloro-compounds at 37 °C: ○ dichloromethane; △ *o*-dichlorobenzene; ● 1,2-dichloroethane; × *m*-dichlorobenzene

Correlation Analysis of the Influence of Aprotic Solvents on the Reaction of Diazodiphenylmethane with Benzoic Acid.—We have previously examined [3] the multiple correlation of log k_0 with f(ε), f(n^2), B, and E as advocated by Koppel and Palm.[7] The symbols have the following meanings: f(ε) is the Kirkwood function of dielectric constant, $(\varepsilon - 1)/(2\varepsilon + 1)$, while $f(n^2)$ is the corresponding function of the square of the refractive index (sodium D line);[8] B is the Lewis basicity parameter based on the wavenumber shift on transfer of CH_3OD from the gas phase to solution in a given solvent,[7,9,10] while E measures the Lewis acidity of the solvent and is derived from the E_T scale (Dimroth and Reichardt),[11] corrected for non-specific (mainly dielectric) effects.[7] The correlation equation developed by stepwise regression for 24 solvents was (3), with R 0.975 and s 0.209.[3]

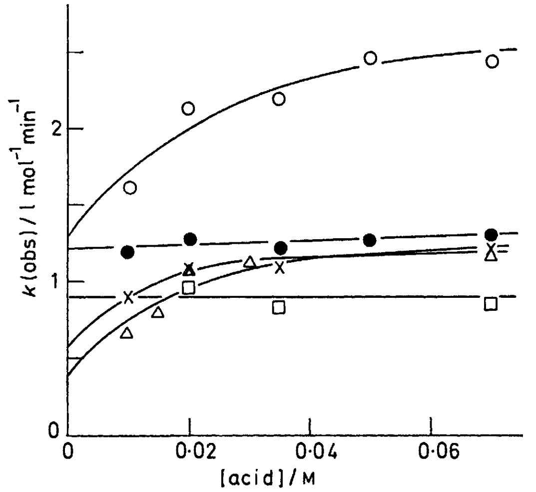


FIGURE 2 Dependence of k(obs) on [acid] for the reactions of benzoic acid with diazodiphenylmethane in various aprotic solvents at 37 °C: ○ phenetole; × *p*-xylene; ● *o*-xylene; □ *NN*-dimethylformamide [10k(obs)]; △ *m*-xylene

$$\log k_0 = -1.94 + 4.185f(\varepsilon) + 8.391f(n^2) + 0.224E - 0.021\,2B \quad (3)$$

We have now repeated the correlation analysis for 43 aprotic solvents. [Of the 44 for which results are now available, we have omitted only di-isopropyl ketone, for which a satisfactory E_T (and hence E) value has not been determined.] Detailed Tables of the variables employed in this correlation and the other correlations below and other statistical material are given in Supplementary Publication No. SUP 22188 (7 pp.).* There are, however, a few matters which should be recorded here. We have re-examined the literature to ascertain the most reliable values of ε, as far as possible for 20 °C, but in a few cases we have had to accept values for 25 °C. The values of B employed are those we determined in a recent study.[10] The values of E are mainly from the recent tabulation of Koppel and Paju;[12] a few values have been determined by us. The correlation equation is (4), with R 0.979 and s 0.176. A plot of log k_0(calc) versus log k_0(obs) is in Figure 3. Stepwise regression †

$$\log k_0 = \underset{}{-3.190} + \underset{(\pm 0.346)}{4.463f(\varepsilon)} + \underset{(\pm 1.544)}{12.330f(n^2)} + \underset{(\pm 0.020)}{0.210\,E} - \underset{(\pm 0.000\,8)}{0.018\,1\,B} \quad (4)$$

shows (as before[3]) that the order of decreasing significance of the terms is B, f(ε), E, and $f(n^2)$, R for the successive one-, two-, and three-parameter equations being 0.810, 0.907, and 0.944 respectively.‡

The value of R for equation (4) is slightly higher than that for (3), so that (4) explains 95.8% of the variance, compared with 95.0% for (3). Also, as a summary of the data (as indicated by s) (4) is also slightly superior. These improvements are to some extent due to eliminating the large deviations previously shown by 1,8-epoxy-*p*-menthane (cineole) and diethyl carbonate by using experimentally determined E values instead of values fixed by analogy with other solvents. (Compare also Figure 3 with Figure 1 in Part 1[3] in this respect.) When the greatly increased number of degrees of freedom for

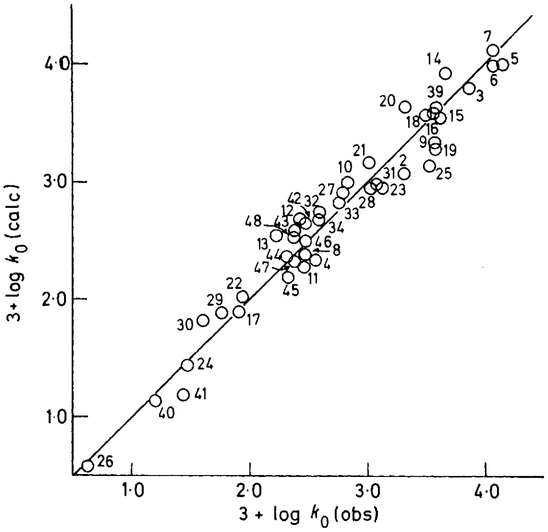


FIGURE 3 Plot of log k_0(calc) according to equation (4) against log k_0(obs). For some point numbers, see Table 3; also **39**, iodobenzene; **40**, di-isopropyl ether; **41**, di-n-butyl ether; **42**, ethyl methyl ketone; **43**, isopropyl methyl ketone; **44**, methyl t-butyl ketone; **45**, cyclohexanone; **46**, methyl n-propyl ketone; **47**, methyl n-butyl ketone; **48**, diethyl carbonate

---

* Details of Supplementary Publications are given in *J.C.S. Perkin II*, 1977, Index issue.

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

‡ As also may be seen from SUP 22188, collinearities between the several explanatory variables are sufficiently small in magnitude to warrant the treatment we have adopted. After B the next most successful parameter in a one-parameter equation is (n^2), with ± 0.484, *cf.* 0.810.

[7] 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.

[8] E. M. Kosower, 'Physical Organic Chemistry,' Wiley, New York, 1968, p. 272.

[9] T. Kagiya, Y. Sumida, and T. Inoue, *Bull. Chem. Soc. Japan*, 1968, **41**, 767.

[10] A. G. Burden, G. Collier, and J. Shorter, *J.C.S. Perkin II*, 1976, 1627.

[11] C. Reichardt, *Angew. Chem. Internat. Edn.*, 1965, **4**, 29.

[12] I. A. Koppel and A. I. Paju, *Org. Reactivity*, 1974, **11**, 137.

(4) is taken into account (38 compared with 19), (4) is certainly the more meritorious correlation. The regression coefficients in (4) (standard deviations are given in parentheses) are little different from those in (3) except for the f(n^2) term, the one of least importance. An increase in the value of this coefficient compared with the value in equation (3) is linked to a rather more negative value of the intercept term in (4).

Limitations of the correlation equation (4). Equation (4) still has the deficiencies of equation (3) with regard to placing some solvents wrongly in the pattern,[3] *e.g.* for log k_0(obs), benzene $\gg$ carbon tetrachloride, but the log k_0(calc) values are very close together. (However, as noted above, certain major deviations have now been eliminated.) As we have remarked previously,[3] doubtless there are special effects of which our correlation takes no account. We now consider what such effects might be and whether it is possible to express them by suitable parameters.

Two possible factors come readily to mind. First, there is the occurrence of steric effects on nucleophilic solvation which are not included in B because B is based on interaction with the rather small molecule CH_3OD. Secondly, the solvents vary quite considerably in viscosity and this could conceivably influence the rate at which diazodiphenylmethane and benzoic acid molecules come together. We have tried parametrising the former by molar refraction as a measure of molecular volume, and the latter by the logarithm of the fluidity. Molar refraction turns out to be detectably collinear with both E and f(n^2) (r *ca.* 0.68), but in stepwise regression E and f(n^2) are marginally preferred, and once they are in the regression, no significant role is left for molar refraction. This comment applied also to log(fluidity), for which the principal collinearity is with f(n^2) (r *ca.* 0.63).

It therefore seems unlikely that the ' special effects ' not incorporated in our present correlation equation can be quantified by means of parameters. If it be accepted that the best approach to understanding the solvent effect in this reaction is primarily in terms of the nucleophilicity of the solvent (B) and after that in terms of its dielectric properties [f(ε)], which together explain *ca.* 82% of the variance, then the best additional parameters are the electrophilicity of the solvent (E) and its polarisability [f(n^2)], and there is nothing further to be done.

Alternative solvent parameters. We have examined possible alternative sets of solvent parameters, particularly with regard to measures of solvent basicity.

Koppel and Paju [13] have developed a new B scale in terms of the wavenumber shift of the OH stretching vibration of phenol produced by addition of a given Lewis base to a solution of phenol in carbon tetrachloride, dilute solutions being used. They tabulate values for almost 200 Lewis bases. However, the new B scale shows strong collinearity with the original (r 0.987 for 54 compounds [13]), in spite of the new scale being based on interactions in dilute solutions and the original scale being based on interactions in bulk solvent. There seemed little advantage in the new B scale for the present work, particularly as, for the solvents we have employed, we have B values on the original scale determined very carefully by us, with one i.r. spectrometer,[10] *cf.* the variety of sources involved in the new B scale.[13]

We have also examined the use, as measures of solvent basicity, of parameters related to the interaction of *p*-fluorophenol and bases, developed by Taft, Arnett, and their co-workers.[14] These are the formation constants of the hydrogen-bonded complexes in carbon tetrachloride (used as log K_f) and their enthalpies of formation, ΔH_f. Values of the former are unfortunately available for only 14 of the solvents used in the present work, and of the latter for only 18 of the solvents. For the appropriate solvents we have carried out multiple regressions of log k_0 on f(ε), f(n^2), E, and either log K_f or ΔH_f, and, for comparison, the normal regression using B for the same solvents: log K_f was significantly less useful than B in this respect. Correlation with ΔH_f, f(ε), and E gave R 0.922, compared with 0.921 when B was used, but f(n^2) then produced no significant improvement, while for the correlation involving B, an f(n^2) term raised R to 0.951. Thus neither log K_f nor ΔH_f appears to have any advantage over B as a measure of solvent basicity in the correlation analysis of the reactions between diazodiphenylmethane and benzoic acid.

Gutmann [15] has developed other parameters for solvent nucleophilicity and electrophilicity known as the donor number (DN) and acceptor number (AN) respectively. The DN is defined as $-\Delta H$/kcal mol^{-1} for the formation of a complex between the donor and antimony(v) chloride in 1,2-dichloroethane. The AN is defined in terms of the ^{31}P n.m.r. shifts produced in triethylphosphine oxide by electrophilic solvent actions, which lower the electron density at P by co-ordination with the oxygen atom. The shifts are related to that for the $Et_3PO\rightarrow SbCl_5$ adduct in 1,2-dichloroethane, which is arbitrarily assigned a value of 100. Values of DN are known for *ca.* 50 solvents and of AN for *ca.* 30, but unfortunately both DN *and* AN are known for only 10 of the aprotic solvents used in the present work.

For these solvents stepwise regression of log k_0 on DN, AN, and f(ε) has been performed, and a normal regression has been done for comparison. DN is taken in first (r 0.806), then AN (R 0.970), and finally f(ε), giving R 0.987 for the final three-parameter correlation. The preference for AN rather than f(ε) (R 0.940) is only marginal, and is possibly an artefact of the particular limited number of solvents involved. In the normal stepwise regression for these solvents the terms are taken in the usual order B, f(ε), E, and f(n^2) and the corresponding correlation coefficients are 0.867, 0.948, 0.975,

---

[13] I. A. Koppel and A. I. Paju, *Org. Reactivity*, 1974, **11**, 121.

[14] D. Gurka and R. W. Taft, *J. Amer. Chem. Soc.*, 1969, **91**, 4794; E. M. Arnett, L. Joris, E. Mitchell, T. S. S. R. Murty, T. M. Gorrie, and P. v. R. Schleyer, *ibid.*, 1970, **92**, 2365; E. M. Arnett, E. J. Mitchell, and T. S. S. R. Murty, *ibid.*, 1974, **96**, 3875.

[15] V. Gutmann, *Co-ord. Chem. Rev.*, 1976, **18**, 225 and references therein.

and 0.993. Thus B by itself is more successful than DN alone, but the addition of AN effects an improvement considerably greater than that produced by f(ε) in the Koppel–Palm type regression. Possibly AN will be very valuable as a parameter of solvent electrophilicity when values are available for many more solvents.

Fawcett and Krygowski[16] have suggested the correlation analysis of solvent effects in terms of DN and E_T (see also ref. 5). They used our earlier results[2] on the reaction of diazodiphenylmethane with benzoic acid in such a multiple regression (8 solvents), giving R as 0.989. This was stated to be a better correlation than our equation (3), but this unfavourable comparison ignored the much greater number of data points involved in establishing (3). However Fawcett and Krygowski's remarks directed our attention to the possibility of using E_T directly as a parameter to supplement B, rather than following Koppel and Palm's[7] procedure of using f(ε) and the electrophilicity parameter E.

Multiple regression on B and E_T of results for the 43 solvents on which equation (4) is based, yielded equation (5), with R 0.954 and s 0.255. Although R is somewhat

$$\log k_0 = -3.396 - \underset{(\pm\,0.001\,0)}{0.020\,6}\,B + \underset{(\pm\,0.012\,2)}{0.130\,0}\,E_T \qquad (5)$$

smaller and s somewhat greater than for equation (4), (5) must be regarded as quite successful since it involves only two solvent parameters, whereas (4) involves four. Further, (5) is much more successful than regression on B and f(ε), which gives R as 0.907.

E_T is highly correlated with f(ε) (r *ca.* 0.9), so that after E_T is taken into the correlation there is no role for f(ε). However E_T shows only a low degree of collinearity with f(n^2), (r *ca.* 0.29), so a possible contribution from a f(n^2) (polarisability) term is worth exploring. Equation (6) is found, with R 0.970 and s 0.210 [*cf.* R 0.944 for regression on B, f(ε), and E].

$$\log k_0 = -5.379 - \underset{(\pm\,0.000\,9)}{0.018\,9}\,B + \underset{(\pm\,0.010\,1)}{0.135\,1}\,E_T + \underset{(\pm\,1.707)}{7.659}\,f(n^2) \qquad (6)$$

It thus appears that for the influence of the solvent on the reactions between diazodiphenylmethane and benzoic acid it is simpler and reasonably successful to use E_T directly rather than E and f(ε). This calls in question the value and reality of Koppel and Palm's analysis of E_T into 'pure' electrophilicity effects and non-specific effects, and the general validity of applying 'bulk' dielectric constant to molecular phenomena. These matters merit some discussion.

Parametrisation of solvent electrophilicity. We have already remarked that E_T is highly correlated with f(ε) (r *ca.* 0.9) for the solvents with which we are particularly concerned. These include many solvents which would, on structural grounds, be expected to show appreciable electrophilicity and which do indeed receive significant E values in Koppel and Palm's[7] analysis. When attention is focused on solvents which would, on structural grounds, not be expected to show appreciable electrophilicity, the relationship between E_T and f(ε) becomes even clearer. This is, of course, essentially the basis of Koppel and Palm's derivation of E values. In the latest form of the derivation (Koppel and Paju[13]), the E_T values of 26 solvents of assumed zero electrophilicity are correlated with $Y = (\varepsilon - 1)/(\varepsilon + 2)$ and $P = (n^2 - 1)/(n^2 + 2)$ * to give equation (7), with R 0.974 and s 0.78. The principal relationship embodied in this equation is between E_T and Y. E values for other solvents are then calculated from equation (8).

At first sight it is difficult not to concede that Koppel and Palm are right *in principle* in seeking to remove from E_T the contributions of non-specific solvent effects as expressed through Y and P. However, their procedure for doing this obviously has its limitations. The regression coefficients and intercept term in equation (8) have quite appreciable standard errors [see equation (7)], which in turn means that the calculation of an E value involves subtracting from E_T a somewhat uncertain number. For aprotic solvents this number is never much less than E_T itself, the values of E being mainly in the range 0—5.2, so the calculation of E values is subject to considerable uncertainty. Further it must be admitted that the E values of aprotic solvents are not always easily interpretable in terms of molecular structure (*cf.* the B values[10]).

If Koppel and Palm are right in principle, even if the practice is deficient, it then follows that a correlation involving E_T directly must be to some extent *superficial*, *i.e.* it mixes up non-specific polarisation and polarisability effects on the process in question with those on the solvatochromic process used to define E_T. If one wishes to regard correlation with E_T as *fundamental*, then it is necessary also to regard as invalid the use of bulk dielectric constant in the correlation analysis of solvent effects. This is necessary on practical as well as on logical grounds because of the high degree of collinearity between E_T and functions of dielectric constant (see above). The limitations of applying bulk dielectric constant to interactions on a molecular scale have often been pointed out.[17] Nevertheless it has usually been accepted that bulk dielectric constant does have some meaning in relation to phenomena on the molecular scale and should be retained failing anything better.

$$E_T = \underset{(\pm\,1.06)}{25.10} + \underset{(\pm\,0.74)}{14.84}\,Y + \underset{(\pm\,3.70)}{9.59}\,P \qquad (7)$$

$$E = E_T - 25.10 - 14.84\,Y - 9.59\,P \qquad (8)$$

It is widely accepted that E_T largely relates to Lewis

---

* For this purpose Koppel and Palm prefer ε and n^2 in the form of the molar polarisation and refraction functions rather than the Kirkwood functions of ε and n^2.

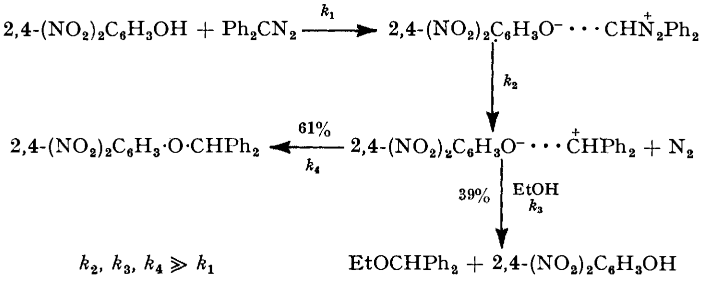
[16] W. R. Fawcett and T. M. Krygowski, *Austral. J. Chem.*, 1975, **28**, 2115.

[17] *e.g.* J. Shorter, 'Correlation Analysis in Organic Chemistry,' Clarendon Press, Oxford, 1973, p. 68.

acidity because the *N*-phenol–pyridinium betaine dyestuffs used to define the scale have an exposed O^-, whereas the N^+ is buried in the molecule.[18] This interpretation of E_T seems particularly appropriate for protic solvents, for which hydrogen-bonding to the betaine O^- may be envisaged, and the values all lie at the top of the E_T scale, *viz.* 44—63. The situation for the aprotic solvents, whose E_T values lie in the range 31—46 is much less clear and it may well be that E_T measures various aspects of intermolecular interactions, *e.g.* dipole–dipole, donor–acceptor, dispersion forces, *etc.* Viewed in this way it is perhaps not unreasonable to regard E_T as a kind of substitute for dielectric and refractive index parameters, perhaps remedying to some extent the deficiencies of these ' bulk ' properties when applied to phenomena on the molecular scale.

Kinetics of the Reaction between 2,4-*Dinitrophenol and Diazodiphenylmethane in Aprotic Solvents at* 30 °C.—Roberts *et al.*[4] studied in detail the kinetics of the reaction of 2,4-dinitrophenol with diazodiphenylmethane in ethanol. They found that the reaction had much in common with that between benzoic acid and diazodiphenylmethane. Two products were formed: *ca.* 61% of 2,4-dinitrophenyl diphenylmethyl ether and 39% of diphenylmethyl ethyl ether, *i.e.* the products were analogous to and formed in much the same proportions as those of the benzoic acid reaction.[19,20] The reaction was accurately first order in each reactant.

It seems appropriate to write the mechanism in a way similar to that used for the reactions of carboxylic acids with diazodiphenylmethane,[20-22] as in Scheme 2.



SCHEME 2

We have studied the kinetics of the reaction of 2,4-dinitrophenol with diazodiphenylmethane under the usual first-order conditions in 38 aprotic solvents. In view of the widely observed dependence of apparent second-order rate coefficient on concentration in the benzoic acid reaction, we usually determined the rate coefficient at two values of [DNP] differing by a factor of about two. The results are presented in Table 3.

For most of the solvents for which measurements were carried out at two or three different concentrations of 2,4-dinitrophenol, there appears to be no appreciable concentration dependence of *k*. This fact is particularly striking for dichloromethane, 1,2-dichloroethane, ethyl acetate, and dioxan (for example), for which the concentration dependence in the reaction of benzoic acid with diazodiphenylmethane is very marked (see above and ref. 3). For several other solvents there are slight signs of a concentration dependence, which is the most marked for chloroform, but still much smaller than that observed for the benzoic acid reaction.[3] Thus the complications arising from dimerisation or acid catalysis[1,3] are clearly much less important with 2,4-dinitrophenol than they are with benzoic acid.[5] In Table 3, when values of *k* at two or more concentrations are available, the ' accepted *k* ' is either the mean value, or, if there are indications of concentration dependence, the value of *k* at [DNP] *ca.* 0.03M.

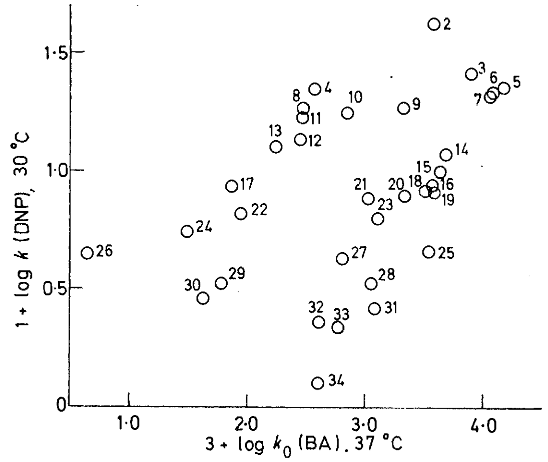


FIGURE 4 Lack of relationship between rate coefficients of the reaction of diazodiphenylmethane with benzoic acid (37 °C) and those of the reaction with 2,4-dinitrophenol (30 °C) in the same aprotic solvents

In discussing the rate coefficients we shall assume that *k* relates to a rate-determining proton transfer from 2,4-dinitrophenol to diazodiphenylmethane as in Scheme 2, but without the opportunity of the later reaction with the solvent. We cannot, however, at present exclude the possibility that *k* is really a product of the equilibrium

---

[18] Ref. 17, pp. 73—75.

[19] J. D. Roberts, W. Watanabe, and R. E. McMahon, *J. Amer. Chem. Soc.*, 1951, **73**, 760.

[20] K. Bowden, A. Buckley, N. B. Chapman, and J. Shorter, *J. Chem. Soc.*, 1964, 3380.

[21] A. Buckley, N. B. Chapman, M. R. J. Dack, J. Shorter, and H. M. Wall, *J. Chem. Soc.* (*B*), 1968, 631.

[22] R. A. More O'Ferrall, W. K. Kwok, and S. I. Miller, *J. Amer. Chem. Soc.*, 1964, **86**, 5553.

constant for a pre-equilibrium proton transfer, followed by a rate-limiting completion step, as in part of Scheme 1.

The rate coefficients in Table 3 cover a *ca.* 180-fold range, compared with a 3200-fold range for the reaction with benzoic acid. We are therefore now dealing with a greatly reduced solvent influence. Further, the arrangement of the solvents in the order of decreasing *k* in Table 3 differs very greatly in detail from a corresponding Table for the benzoic acid reaction, and this is shown graphically in Figure 4. It is clear that the relative importance of the various aspects of solvent–solute interaction is quite different as between the two reactions.*

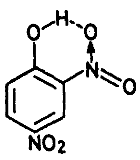
TABLE 3

Kinetics of the reaction between 2,4-dinitrophenol and diazodiphenylmethane in various aprotic solvents at 30 °C

	Solvent	k/l mol^{-1} min^{-1} (10^2[DNP]/mol l^{-1})				Accepted [a] k
1	Nitromethane	5.88	(3.09)			5.88
2	Acetonitrile	4.24	(2.98)	3.97	(1.99)	4.24
3	Nitrobenzene	2.61	(4.48)	2.64	(2.91)	2.63
4	Acetone	2.27	(4.55)	2.22	(3.02)	2.24
5	Dichloromethane	2.27	(14.0)	2.30	(7.01)	2.28
6	Chloroform	1.94	(12.0)	2.09	(6.03)	
		2.21	(2.99)			2.21
7	1,2-Dichloroethane	2.15	(6.95)	2.15	(3.52)	2.15
8	Diethyl ketone	1.84	(4.54)	1.88	(2.97)	1.86
9	Benzonitrile	2.02	(6.01)	1.88	(3.00)	1.88
10	Acetophenone	1.90	(5.48)	1.79	(3.02)	1.79
11	Cyclopentanone	1.72	(3.06)			1.72
12	Methyl acetate	1.36	(7.04)	1.36	(3.52)	1.36
13	Ethyl acetate	1.27	(11.9)	1.27	(5.94)	
		1.26	(2.96)			1.27
14	*o*-Dichlorobenzene	1.19	(6.99)	1.19	(3.52)	1.19
15	Fluorobenzene	1.03	(6.02)	0.987	(3.03)	1.01
16	Bromobenzene	0.90	(6.06)	0.86	(3.03)	0.88
17	Dimethyl sulphoxide	0.86	(7.03)			0.86
18	Chlorobenzene	0.83	(12.0)	0.86	(6.02)	
		0.83	(2.97)			0.84
19	Diphenyl ether	0.85	(7.00)	0.83	(3.47)	0.84
20	*m*-Dichlorobenzene	0.76	(7.02)	0.77	(3.53)	0.77
21	Anisole	0.73	(7.05)	0.71	(3.50)	0.72
22	*NN*-Dimethylformamide	0.66	(7.03)	0.68	(3.48)	0.67
23	Phenetole	0.71	(6.82)	0.63	(3.48)	0.63
24	Tetrahydrofuran	0.55	(6.97)	0.54	(3.49)	0.55
25	Benzene	0.511	(7.02)	0.456	(3.11)	0.456
26	1,8-Epoxy-*p*-menthane	0.481	(6.00)	0.442	(3.17)	0.442
27	Carbon tetrachloride	0.430	(3.51)			0.430
28	Toluene	0.343	(6.73)	0.324	(3.54)	0.332
29	Dioxan	0.336	(6.05)	0.327	(2.87)	0.331
30	*NN*-Dimethylacetamide	0.293	(6.07)	0.282	(2.98)	0.287
31	*o*-Xylene	0.266	(7.03)	0.253	(3.51)	0.260
32	*m*-Xylene	0.234	(6.98)	0.221	(3.53)	0.227
33	*p*-Xylene	0.225	(7.02)	0.208	(3.50)	0.216
34	Mesitylene	0.138	(6.99)	0.126	(3.55)	0.126
35	Pyridine	0.104	(3.48)			0.104
36	α-Picoline	0.050 8	(3.51)			0.0508
37	β-Picoline	0.048 6	(3.49)			0.048 6
38	γ-Picoline	0.033 3	(3.51)			0.033 3

Values of k are reproducible to ± 2%. [a] See text.

This is perhaps not surprising in view of the fact that in many of the solvents used, 2,4-dinitrophenol has the internally hydrogen-bonded structure (I). For *o*-nitrophenol there is extensive i.r. and u.v. evidence for the persistence of the chelate structure in a wide variety of solvents,[23,24] including carbon tetrachloride, benzene, nitromethane, acetonitrile, diethyl ether, dioxan, and nitrobenzene. There is similar but less extensive evidence for 2,4-dinitrophenol,[25,26] including its solution in dioxan.[26] It is to be expected that sufficiently basic solvents will break open the chelate structure by solvating the phenolic hydrogen, but it seems that even dioxan (*B* 128) is not sufficiently basic to do this. However we



(I)

---

* This appears to confirm, what we have always supposed,[21] that the influence of the solvent in the reaction of diazodiphenylmethane with Brönsted acids is not exerted through specific interactions with the diazodiphenylmethane molecule.

[23] L. J. Bellamy and H. E. Hallam, *Trans. Faraday Soc.*, 1959, **55**, 220.

[24] J. C. Dearden and W. F. Forbes, *Canad. J. Chem.*, 1960, **38**, 1837.

[25] A. W. Baker and A. T. Shulgin, *J. Amer. Chem. Soc.*, 1958, **80**, 5358.

[26] J. H. Richards and S. Walker, *Trans. Faraday Soc.*, 1961, **57**, 406.

have observed that solutions of 2,4-dinitrophenol in *NN*-dimethylacetamide (*B* 178), dimethyl sulphoxide (*B* 192), and other very highly basic solvents have a much deeper yellow colour than the solutions in the less basic solvents, corresponding to a prominent absorption peak at *ca* 430 nm. We infer that in such solutions the chelate ring is broken and the phenolic hydrogen is heavily solvated. This is fully confirmed by the correlation analysis of the solvent effect on the reaction between 2,4-dinitrophenol and diazodiphenylmethane.

Correlation Analysis of the Influence of Aprotic Solvents on the Reaction of Diazodiphenylmethane with 2,4-*Dinitrophenol*.—We have been unable to devise any correlation equation which will deal adequately with the results for all 38 solvents. It is necessary to consider separately the very highly basic solvents, nos. 17, 22, 30, and 35—38 in Table 3. We have applied the Koppel–Palm [7] treatment to the results for the remaining 31 solvents, in which we presume the reaction to involve the chelated form (I). The equation obtained was (9), with *R* 0.960 and *s* 0.120. [The $f(n^2)$ term was insignificant.]

$$\log k = -1.486 + \underset{(\pm 0.256)}{4.165}\, f(\varepsilon) + \underset{(\pm 0.013\,2)}{0.066\,6}\, E - \underset{(\pm 0.000\,7)}{0.002\,0}\, B. \qquad (9)$$

The order of decreasing significance of the terms is f(ε), *E*, and *B*, *R* for the successive one- and two-parameter equations being 0.900 and 0.946 respectively. The equation explains 92% of the variance and the correlation is therefore highly successful.

The most striking contrast with the benzoic acid reaction is the relatively high importance of the dielectric term, with solvent basicity being less important than electrophilicity. It is interesting to note that the regression coefficient of f(ε) in equation (9) is fairly close to the corresponding value in equation (4). Presumably the minor role of solvent basicity is connected with the involvement of the phenolic hydrogen in the chelate ring, but solvent electrophilicity is able to assist by stabilising the nascent anion after there has been some degree of proton transfer to the diazodiphenylmethane (*cf.* the benzoic acid reaction [2,3]).

When equation (9) was applied to the very highly basic solvents excluded in establishing it, log *k*(calc) was always very much greater than log *k*(obs), *e.g.* for *NN*-dimethylacetamide, log *k*(calc) was 0.317 compared with −0.542, while for α-picoline log *k*(calc) was −0.290 and log *k*(obs) was −1.294. The breaking of the chelate structure by the very highly basic solvents presumably enhances the unfavourable effect of solvent basicity on the rate of reaction.

Our success above in the direct use of E_T in correlation analysis of the benzoic acid reaction prompted the examination of this procedure here. Regression on E_T alone in fact produced equation (10), with *r* 0.939 and *s* 0.142. This simple equation explains 88% of the variance. It is interesting to note that the coefficient of E_T (0.103 5) is fairly similar to that of E_T (0.130 0) for the benzoic acid reaction [equation (5)]. Isaacs and Rannala [5] did not find such a simple relationship with E_T for the reaction of *p*-nitrophenol with diazodiphenylmethane. This confirms the importance of the chelate ring in the reactions of 2,4-dinitrophenol.

$$\log k = -3.975 + \underset{(\pm 0.007\,1)}{0.103\,5}\, E_T \qquad (10)$$

In stepwise regression with *B* or f(ε) as additional explanatory variables, f(ε) was marginally preferred, giving *R* 0.948, compared with *R* 0.944 when *B* was introduced. In view of the high degree of collinearity between E_T and f(ε) (*r ca.* 0.9), the introduction of the latter after the former cannot be considered meaningful, while the introduction of *B* explains only an additional 1% of the variance. The overall situation is that as a single solvent parameter for this reaction, E_T is very successful but as a first step in a multiple regression, f(ε) is to be preferred.

As for the reaction with benzoic acid, there are clear features of the pattern of results which cannot be parametrised. For instance the log *k*(obs) values for carbon tetrachloride and mesitylene differ by 0.534 but their log *k*(calc) values, from any of the correlation equations, are almost the same. Thus the explanations of the role of the solvent through correlation analysis can reach *ca.* 92% of the variance for these reactions; the rest of the variance is concerned with highly specific features of each solvent.

EXPERIMENTAL

The experimental procedures for the preparation and/or purification, and assay of reactants and solvents for the kinetic studies of the reaction between diazodiphenylmethane and carboxylic acids have been described in previous papers [1—3,27] (see also ref. 10 in connection with solvents).

2,4-Dinitrophenol was recrystallised from ethanol. Its equivalent weight by titration agreed with the theoretical value to within 1%.

The procedure for following the reaction of 2,4-dinitrophenol with diazodiphenylmethane was very similar to that used for the benzoic acid reaction.[1—3,27] In most solvents the absorption of DNP at the wavelength used for following the reaction (525 nm) was negligible, but in the very highly basic solvents the shift of the absorption to longer wavelengths produced a contribution of DNP to the optical density at 525 nm and appropriate allowance was made for this in calculating rate coefficients.

We are grateful to Mr. G. Collier for assistance with spectroscopic and g.l.c. work.

[7/868 *Received*, 18*th May*, 1977]

---

[27] N. B. Chapman, D. J. Newman, J. Shorter, and H. M. Wall, *J.C.S. Perkin II*, 1976, 847.