The Influence of the Solvent on Organic Reactivity. Part II.[1] Kinetics and Mechanism of the Reactions of Carboxylic Acids with Diazodiphenylmethane in Aprotic Solvents in which the Acids may be Dimeric

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Apparent second-order rate coefficients have been determined for the reactions at 37 °C of diazodiphenylmethane with benzoic acid in 11 aprotic solvents in which the dimeric form of the acid predominates. Depending on the solvent chosen, k(obs) shows one of several forms of dependence upon the initial concentration of acid, c. The mechanism previously developed for the reaction in donor aprotic solvents is applied and adapted to the situation in which the acid is largely dimeric. Besides processes involving reactions of monomer and dimer, the kinetics suggest the participation of a reactive multimer, probably a trimer and possibly a tetramer. Established or inferred approximate values for K_{21}, the dissociation constant of dimer in the various solvents, are used to analyse the kinetics in terms of the equation $k(\text{obs}) = \alpha[\text{HA}]/c + \beta[\text{HA}]^2/c + \gamma[\text{HA}]^3/c + \delta[\text{HA}]^4/c$, where the coefficient of $[\text{HA}]^n$ characterises the reaction of $(\text{HA})_n$ (the cubic and/or quartic terms are not always needed). The variety of ways in which k(obs) may vary with concentration arises from the different solvent, structural, and isotopic effects on the coefficients.

Two of our previous papers[1,2] on the kinetics of the reactions of carboxylic acids with diazodiphenylmethane in aprotic solvents have dealt with values of k_0, the limiting second-order rate coefficient at [acid] = 0, for the reactions of benzoic acid in 22 aprotic solvents,[2] and with detailed results for reactions in solvents in which the carboxylic acid is believed to be largely monomeric.[1] We now present similar results for the reactions of benzoic acid in 11 solvents in which the carboxylic acid is mainly in the form of a dimer. These are various aromatic solvents, chloroform, and carbon tetrachloride. Reactions of acetic acid and of deuteriated benzoic and acetic acid ($PhCO_2D$ and $MeCO_2D$) have also been studied.

DISCUSSION

The Kinetics of the Reaction between Carboxylic Acids and Diazodiphenylmethane in 'Dimerising' Aprotic Solvents at 37 °C.—In Part I[1] it was shown that the reaction in various donor aprotic solvents conformed to equation (1) (the symbols are explained in ref. 1).

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

Figures 1—5 show that the behaviour of the reaction in aromatic solvents, carbon tetrachloride, and chloroform is much more varied. Throughout this paper values of c are molar concentrations calculated by

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[1] Part I, N. B. Chapman, M. R. J. Dack, D. J. Newman, J. Shorter, and R. Wilkinson, preceding paper.

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

employing the molecular weight of the monomeric carboxylic acid. Thus while a few systems show a rectilinear rise in *k*(obs) with *c*, for others *k*(obs) shows various types of curvilinear dependence on *c*, and may either rise or fall. In several examples *k*(obs) did not vary significantly over the concentration range examined. The tendency of *k*(obs) to increase with *c* seems to be increased by using acetic rather than benzoic acid, and protio-acid rather than deuterio-acid. The marked difference in behaviour between $PhCO_2H$ and $PhCO_2D$ for the reaction in toluene has been observed previously.[3]

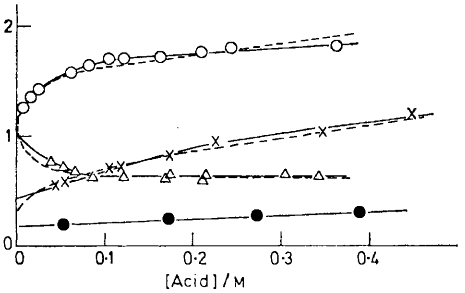

FIGURE 1 Reactions of carboxylic acids in toluene: ○, $PhCO_2H$; ×, $MeCO_2H$; △, $PhCO_2D$; ●, $MeCO_2D$. Broken lines indicate values calculated from Table 2, toluene model

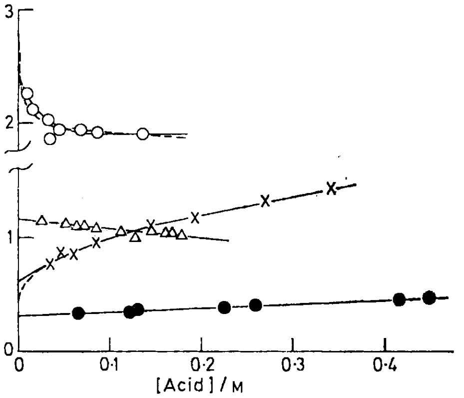

FIGURE 2 Reactions of carboxylic acids in benzene: key as in Figure 1. Broken lines indicate values calculated from Table 2, benzene model

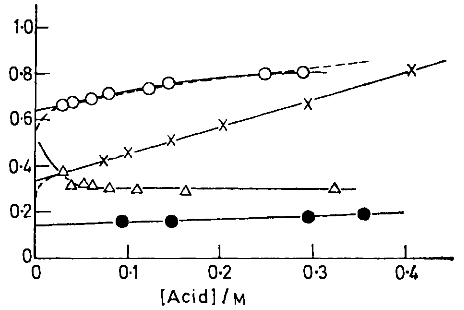

FIGURE 3 Reactions of carboxylic acids in carbon tetrachloride: key as in Figure 1. Broken lines indicate values calculated from Table 2, carbon tetrachloride model

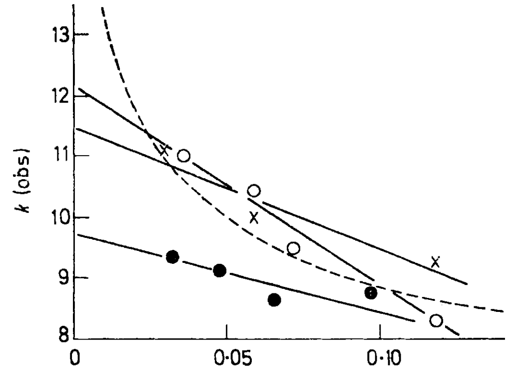

FIGURE 4 Reactions of benzoic acid in chloroform: ○, 1% ethanol; ×, 1·5% ethanol; ●, 2·5% ethanol. The broken line indicates values calculated from Table 2, chloroform model

The Mechanism of the Reaction between Carboxylic Acids and Diazodiphenylmethane in 'Dimerising' Aprotic Solvents.—In Part I[1] it was assumed that carboxylic acids exist largely as monomer in donor aprotic solvents. The situation is different for the solvents now considered. Dimerisation constants, K_{12}, for benzoic or acetic acid dissolved in several of the solvents are in Table 1 and the situation for other solvents may be assessed qualitatively. Values of K_{12} determined for a given acid and solvent by various authors by using different methods often do not agree well.[4] Further, for certain solvents it is possible that the problem is complicated by the formation of small amounts of trimer or larger aggregates,[5,6] leading to a concentration dependence of the observed values of K_{12}.

For log K_{12} = 2·3, the fraction of carboxylic acid in the form of monomer is *ca.* 15% at *c* 0·1M and 30% at *c* 0·02M. For log K_{12} = 3·0, the corresponding values are 7 and 16% respectively. In our experiments involving

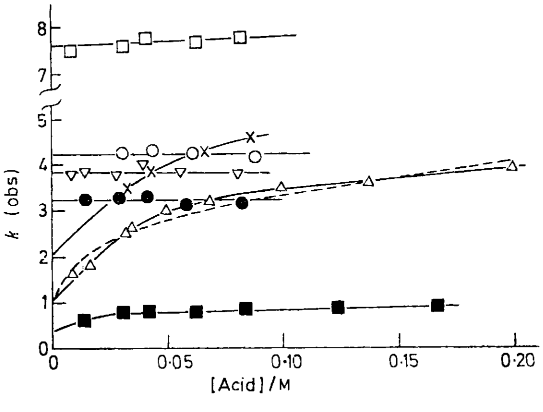

FIGURE 5 Reactions of benzoic acid in aromatic solvents: ○, fluorobenzene; ×, benzonitrile; ●, chlorobenzene; △, anisole; ■, mesitylene; ▽, iodobenzene; □, nitrobenzene. The broken line indicates values calculated from Table 2, anisole model. The calculated line for the chlorobenzene model coincides with the observed line

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

[4] M. M. Davis, 'Acid–Base Behavior in Aprotic Organic Solvents,' NBS Monograph 105, Washington, DC, 1968, pp. 31—37.

[5] K. R. Harris and P. J. Dunlop, *J. Phys. Chem.*, 1967, **71**, 483.

[6] H. Buchowski, *J. Phys. Chem.*, 1969, **73**, 3520.

the solvents listed in Table 1, the proportion of acid present as dimer was thus always substantial and in many experiments the proportion of monomer was small, say 10% or less. Dimerisation is probably promoted primarily by low Lewis basicity and acidity of the solvent. For most of the solvents listed in Table 1 solvent basicity is probably the main factor. As a measure of solvent basicity we use the $\Delta\nu_D$ value,[2,7] *i.e.* the frequency shift relative to that for benzene as solvent, for the O–D vibration of CH_3OD dissolved in the given solvent. Values of K_{12} are greatest in carbon tetrachloride, the least basic solvent ($\Delta\nu_D = -21$) and are rather lower in benzene, which has π-donor properties ($\Delta\nu_D = 0$). These are weakened by the introduction of the chloro-substituent, so that K_{12} for benzoic acid in chlorobenzene ($\Delta\nu_D = -2$) is greater than that for benzene. The π-donor properties are enhanced by methyl groups[8] so we expect K_{12} for toluene ($\Delta\nu_D = 2$) to be lower than for benzene. Table 1 shows a small difference in the opposite sense, but the experimental method concerned is not very accurate. The relatively low values of K_{12} in chloroform are not due to its Lewis basicity ($\Delta\nu_D = -17$) but to its feeble protic character.

TABLE 1

Dimerisation constants of carboxylic acids

Solvent	log K_{12}/l mol^{-1} [a] Benzoic acid [b]	Acetic acid
Carbon tetrachloride	4·17 [c]	3·24 [f]
Chlorobenzene	3·26	
Toluene	2·93	
Benzene	2·80 [d]	2·70 [g]
Chloroform	2·64 [e]	2·11 [h]

[a] At 25 °C. [b] Based on ΔH and ΔS values from W. Maier, *J. chim. Phys.*, 1964, **61**, 239 (ultrasonic absorption), as recalculated by M. M. Davis, ref. 4, p. 37. [c] Y. I'Haya and T. Shibuya, *Bull. Chem. Soc. Japan*, 1965, **38**, 1144 give 3·37 (i.r. spectroscopy) at *ca.* 25 °C. [d] Several experimental methods give values lying between 2·75 and 2·84. See ref. 4, p. 33. [e] I'Haya and Shibuya, *op. cit.*, give 2·60 at *ca.* 25 °C. [f] J. J. Lindberg and C. Majani, *Suomen. Kem.*, 1964, **B37**, 21 (i.r. spectroscopy). Ref. 4, p. 32 quotes earlier values of 3·30, 3·38, and 3·60. [g] D. P. N. Satchell and J. L. Wardell, *Trans. Faraday Soc.*, 1965, **61**, 1199 (i.r. spectroscopy) for 28 °C. Values determined by other authors are also available; see A. I. Popov, in ' The Chemistry of Non-aqueous Solvents,' ed. J. J. Lagowski, Academic Press, New York, 1970, vol. III, ch. 5. [h] G. M. Barrow and E. A. Yerger, *J. Amer. Chem. Soc.*, 1954, **76**, 5248 (i.r. spectroscopy) for ambient temperature.

We now consider the other solvents used in the rate measurements. We assume that a carboxylic acid is less dimerised in mesitylene ($\Delta\nu_D = 10$) than in benzene, and that in spite of the values of K_{12} in Table 1, the extent of dimerisation in toluene ($\Delta\nu = 2$) is slightly less than in benzene. Dimerisation in fluorobenzene ($\Delta\nu_D = -18$) may well be considerably greater than in benzene, but iodobenzene and benzene will probably be similar in this respect. [As measured by $\Delta\nu_D$ ($= 3$), iodobenzene is a slightly stronger base than benzene.] Anisole ($\Delta\nu_D = 26$), benzonitrile ($\Delta\nu_D = 38$), and nitrobenzene ($\Delta\nu_D = 21$) have considerable basic properties by virtue of lone pairs, as well as through π-electrons. In these solvents dimerisation must be somewhat suppressed relative to that in benzene.

In Table 1 the K_{12} value for acetic acid in a given solvent tends to be lower than that for benzoic acid. This is contrary to the general rule that the acid which is weaker in water is more highly dimerised in an aprotic solvent.[4,9]

We have previously argued[1] that in donor aprotic solvents the most likely reaction mechanism involves (*a*) the reversible formation of a complex between monomeric acid and diazodiphenylmethane, which undergoes rate-limiting breakdown to products, and (*b*) the rate-determining reaction of diazodiphenylmethane with a low concentration of highly reactive, open-chain dimer. The main evidence was provided by the conformity to equation (1), with k_0 showing a small normal or possibly an inverse protium–deuterium isotope effect in certain solvents, and k' showing a large normal isotope effect. In view of our successful correlation of k_0 with solvent parameters for 24 solvents comprising the donor aprotic solvents and the solvents with which we are concerned in the present paper, we assume that the component of the mechanism corresponding to k_0 is the same in the latter solvents as in the former. Further we interpret the more complicated kinetics of the present paper in terms of extensive dimerisation of the carboxylic acid.

The isotope effects offer some support to the postulated role of the intermediate complex. For toluene (Figure 1) the ratio $k_0(\mathrm{H}) : k_0(\mathrm{D})$ ($= R_0$) is *ca.* 1·1 for benzoic and 2·0 for acetic acid. For benzene (Figure 2) the corresponding values of R_0 are 3·0 and 2·0 respectively, and for carbon tetrachloride (Figure 3), 1·3 and 2·4 respectively. The extrapolation to $c = 0$ is often difficult and some of these values of R_0 are subject to considerable uncertainty, but it is clear that the isotope effect on k_0 is usually small, as for the donor aprotic solvents.

We cannot present a complementary discussion of $k'(\mathrm{H}) : k'(\mathrm{D})$ ($= R'$) as in the previous paper, for such a quantity cannot here be defined. However Figures 1—3 show that the isotope effect on the way in which k(obs) varies with c is usually considerably greater than that on k_0. This is particularly clear for acetic acid, and conforms with the view that the component of reaction in which the dimer is involved is characterised by a normal isotope effect, the protio-acid being several times more reactive than the deuterio-acid.

The reaction mechanism developed previously,[1] with small changes in presentation convenient in the present situation, is given in the Scheme, where D represents diazodiphenylmethane, HA monomeric acid, $(HA)_2$ dimeric acid, and DHA represents a 1 : 1 complex of D and HA. It is convenient now to use the constant K_{21} for the dissociation of the dimer to monomer, rather than K_{12} for the association of the monomer; $K_{21} = 1/K_{12}$.

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

[8] L. J. Andrews and R. M. Keefer, *J. Amer. Chem. Soc.*, 1952, **74**, 4500; N. Ogimachi, L. J. Andrews, and R. M. Keefer, *ibid.*, 1955, **77**, 4202.

[9] G. Allen and E. F. Caldin, *Quart. Rev.*, 1953, **7**, 255.

The total rate of reaction, v_t, is given by $v_t = k_3K[\mathrm{D}][\mathrm{HA}] + k_2[\mathrm{D}][(\mathrm{HA})_2]$ leading to equation (2)

$$\begin{gathered}
(\mathrm{HA})_2 \xrightleftharpoons{K_{21}} 2\mathrm{HA} \\
\mathrm{D} + \mathrm{HA} \xrightleftharpoons{K} \mathrm{DHA} \\
\mathrm{DHA} \xrightarrow{k_3} \text{products} \\
\mathrm{D} + (\mathrm{HA})_2 \xrightarrow{k_2} \text{products} + \mathrm{HA}
\end{gathered}$$

SCHEME

where c is the total concentration of carboxylic acid calculated by employing the molecular weight of the monomer.

$$k(\mathrm{obs}) = k_3K[\mathrm{HA}]/c + k_2[\mathrm{HA}]^2/K_{21}c \qquad (2)$$

Equation (2) is of the form (3) where $\alpha = k_3K(= k_0)$ and $\beta = k_2/K_{21}$. The values of [HA] and c are interrelated through equation (4). Equation (3) is clearly able to account qualitatively for the observed forms of dependence of k(obs) on c. Depending on the relative magnitudes of α and β, k(obs) may either increase with c, decrease with c, or be little affected by c. However, when we try to fit equation (3) to the values of k(obs) for a given acid and solvent by taking trial values of α and β, the shapes of the theoretical and experimental curves often seem incompatible. The inclusion of higher order terms, *viz.* $[\mathrm{HA}]^n/c$ where $n > 2$ is helpful. Usually a term with $n = 3$ is sufficient, but once a term with $n = 4$ seemed more appropriate. We therefore enlarge equation (3) to give equation (5).[10] The third term

$$k(\mathrm{obs}) = \alpha[\mathrm{HA}]/c + \beta[\mathrm{HA}]^2/c \qquad (3)$$

$$[\mathrm{HA}] = \{-K_{21} + \sqrt{(K_{21}^2 + 8K_{21}c)}\}/4 \qquad (4)$$

$$k(\mathrm{obs}) = \alpha[\mathrm{HA}]/c + \beta[\mathrm{HA}]^2/c + \gamma[\mathrm{HA}]^3/c + \delta[\mathrm{HA}]^4/c \qquad (5)$$

corresponds to the participation of a reactive trimer, and the fourth term to that of a reactive tetramer.* The possibility that carboxylic acids in certain aprotic solvents may form a small proportion of multimeric molecules, $(\mathrm{RCO_2H})_n$ $(n > 2)$, has been increasingly recognised.[5,6]

In examining the applicability of equation (5), we calculate the terms $[\mathrm{HA}]^n/c$ $(n = 1$—$4)$ by means of equation (4), *i.e.* we assume that although a trimer or a tetramer may make a significant contribution to the reaction rate, the concentrations of such species will be so low that the concentrations of monomer and dimer will be essentially unaffected. In using equation (4) we have employed appropriate conveniently-rounded values of K_{21} calculated for 37 °C. These are based on values of K_{21} at 25 °C [experimental (see Table 1), or inferred], together with approximate values for the enthalpy of dissociation of the dimer.[4] The form of the curves of k(obs) *versus* c is not very sensitive to changes in K_{21}. Further we have not attempted to distinguish between benzoic and acetic acid, or between protio- and deuterio-acid in respect of K_{21}. (Differences between benzoic and acetic acid are relatively small. The protium–deuterium isotope effect on K_{21} has not been much investigated but seems to be small.[11]) The analysis below is in terms of a series of ' models ' which we consider to correspond approximately to the solvents in question. The values used for K_{21} and the coefficients obtained by trial for equation (5) are in Table 2, and the corresponding relationships between k(obs) and c are shown by broken lines in Figures 1—5.

Toluene Model.—The value $K_{21} = 4 \times 10^{-3}$ was chosen to be slightly greater than that for benzene. For both protio-acids the continued rise in k(obs) above c *ca.* 0·1M requires a considerable contribution from the cubic term, particularly for acetic acid.[10] The well-established[3] fall in k(obs) as c is increased for deuteriated benzoic acid is adequately expressed by contributions from the linear and the quadratic term, as far as the available results go, but some contribution from a cubic term seems likely. The actual values of the coefficients should not be stressed, because these may be varied within quite wide limits but still produce an acceptable fit. However, the very different behaviour of protio- and deuterio-benzoic acid as to dependence of k(obs) on c is clearly due to α showing only a small and probably an inverse isotope effect, while β shows a substantial normal isotope effect. Figure 1 and some of the later Figures,

TABLE 2

Dependence of k(obs) upon c as expressed by equation (5)

Solvent model	$10^3\,K_{21}$/mol l^{-1}	Acid	α	β	γ	δ
Toluene	4·0	[H]Benzoic	0·90	760	8,500	
		[^{2}H]Benzoic	1·40	280		
		[H]Acetic	0·30	200	13,750	
Benzene	3·0	[H]Benzoic	4·0	1850		
		[H]Acetic	0·40	410	26,500	
Carbon tetrachloride	1·0	[H]Benzoic	0·55	1200	40,000	
		[H]Acetic	0·25	700		5×10^6
Chloroform	5·0	[H]Benzoic	(25)	(2450)		
Chlorobenzene	1·0	[H]Benzoic	3·20	6400		
Anisole	5·0	[H]Benzoic	0·50	950	40,000	

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* Insofar as dimerisation increases reactivity,[1] it is reasonable to suppose that multimerisation would increase it even more.

[10] *Cf.* N. B. Chapman, A. Ehsan, J. Shorter, and K. J. Toyne, *Tetrahedron Letters*, 1968, 1049.

[11] (*a*) Ref. 4, p. 40; (*b*) P. K. Glasoe, S. Hallock, M. Hove, and J. M. Duke, *Spectrochim. Acta* (*A*), 1971, **27**, 2309.

also indicate that some of the values of k_0 which we have determined by straightforward extrapolation may well be considerably in error, for k(obs) may change very markedly with c at values of c below those convenient for experiment. We have not presented an analysis for deuteriated acetic acid in terms of equation (5). The slight rise in k(obs) over the range $c = 0{\cdot}05$—$0{\cdot}6$M suggests the participation of a cubic or quartic term.

Benzene Model.—The kinetics for benzoic acid are adequately represented by an equation involving the linear and the quadratic term, while for acetic acid a cubic term is also needed. The quadratic term seems less sensitive than the linear to the change from benzoic to acetic acid, and this, combined with the importance of γ for acetic acid (*cf.* the toluene model) is responsible for k(obs) varying with c in opposite directions for the two acids. The results for the deuteriated acids are not amenable to detailed analysis, but as in toluene a higher term for acetic acid seems subject to a considerable protium–deuterium isotope effect.

Carbon Tetrachloride Model.—The log K_{12} value for benzoic acid given in Table 1 is probably much too high, and the alternative value (footnote *c*) of 3·37 which is close to that of 3·24 for acetic acid, is more probable. The value of $K_{21} = 1{\cdot}0 \times 10^{-3}$ at 37 °C is based on log $K_{12} = 3{\cdot}30$ at 25 °C. Of the various solvents we used, carbon tetrachloride probably promotes the most extensive dimerisation of the acids, and their further multimerisation is probable. For both benzoic and acetic acid the higher order terms of equation (5) emerge as very important, the cubic term for benzoic acid and the quartic term for acetic acid. This term is mainly responsible for the large and almost linear rise in k(obs), the linear and the quadratic term having attained their combined limiting value at $c = 0{\cdot}03$M. The higher order terms seem subject to a large isotope effect, leading to indications of deuteriated benzoic acid showing opposite behaviour to that of the protio-acid in the dependence of k(obs) upon c, while k(obs) for deuteriated acetic acid shows only a slight rise with c compared with the protio-acid.

Chloroform Model.—Chloroform is an exceedingly difficult solvent for the study of the diazodiphenylmethane reaction. Decomposition of the chloroform (which produces acid) must be inhibited by small amounts of ethanol, and determination of k_0 involved extrapolation to zero concentration of ethanol as well as zero concentration of carboxylic acid.[2] Further, the rate coefficients are inconveniently high. Thus the results in Figure 4 allow only the determination of a very rough value of k_0 for benzoic acid, and demonstrate that k(obs) decreases as c is increased. The latter effect is the most pronounced for any solvent or acid we have used. Carboxylic acids have less tendency to dimerise in chloroform than in the other solvents we are discussing (Table 1) and a value of $K_{12} = 5 \times 10^{-3}$ is reasonable. With this value, the behaviour shown in Figure 4 would be compatible with α *ca.* 25 and β *ca.* 2500 for pure chloroform. Such a value of α, which is far higher than we should expect from our simple methods of extrapolation to obtain k_0, is very large compared with the value of α for any other solvent. The fall in k(obs) as c is increased is thus due to β being not unduly large.

Chlorobenzene Model.—Benzoic acid is probably dimerised to comparable extents in chlorobenzene and in carbon tetrachloride (Table 1) so we take a value of $K_{21} = 1 \times 10^{-3}$. The values of α and β given in Table 2 express well the constancy of k(obs) over the range $c = 0{\cdot}015$—$0{\cdot}08$M (Figure 5). More complicated expressions including higher order terms could be devised to fit the results, and the participation of multimers in the reaction seems as likely in chlorobenzene as in carbon tetrachloride, so no particular significance should be attached to the actual values of α and β. Figure 5 shows that k(obs) is also virtually independent of c for the reaction of benzoic acid in fluorobenzene (0·03—0·09M), iodobenzene (0·01—0·08M), and nitrobenzene (0·01—0·08M). Suitable values of K_{21} could be suggested, and α and β calculated appropriately, but the concentration ranges (limited by solubility) are too narrow for the coefficients to be of much significance.

Anisole Model.—The dimerisation of benzoic acid in this solvent should be somewhat suppressed relative to that in benzene, and we take $K_{21} = 5 \times 10^{-3}$ as for chloroform. The curvilinear dependence of k(obs) on c (0·01—0·20M; Figure 5) requires the first three terms of equation (5). The results for benzonitrile are too limited to merit detailed analysis but the situation is probably similar to that for anisole. Mesitylene is the one remaining solvent for which results are given in Figure 5. A value of $K_{21} = 5 \times 10^{-3}$ is also suitable for this solvent. Results are again somewhat limited, but the relatively weak dependence of k(obs) on c in the upper part of the experimental range suggests only a small participation of a cubic term, which is probably relatively less important than for toluene (see above).

Final Comments on the Mechanism of the Reaction between Carboxylic Acids and Diazodiphenylmethane in 'Dimerising' Aprotic Solvents.—The foregoing discussion shows that the various forms of dependence of k(obs) on c may be explained in terms of a mechanism involving primarily the reaction of monomer (*via* an intermediate complex) and dimer with diazodiphenylmethane, with participation of a multimer (trimer or tetramer) in certain solvents. The variety of forms essentially arises because the reactions of monomer, dimer, and multimer are influenced to different extents by the solvent and by the structure of, and isotopic substitution in, the acid. Thus for a series of solvents arranged in increasing order of monomer reactivity (α), the dimer reactivity (β) may also increase in the same order but not so markedly. This can produce the result that in the 'slower' solvents k(obs) increases with c, in the somewhat 'faster' solvents k(obs) is almost independent of c, while in the fastest solvents k(obs) decreases as c is increased. The actual observations may be complicated by the participation of multimer. Deuteriation has a greater effect on the reactions of dimer or multimer than on those of monomer, so that the tendency of k(obs) to increase with c is less with deuterio-acid than with protio-acid. The structural change from benzoic to acetic acid, while reducing the reactivity of monomer and dimer, appears to favour a contribution from multimer, and the greater tendency of k(obs) for acetic acid to increase with c is a consequence of this. (This behaviour contrasts with that in dipolar aprotic solvents, where k' for benzoic acid is always greater than for acetic acid.[1])

In the previous paper [1] we concluded that the low concentration of reactive dimeric carboxylic acid present in solution in dipolar aprotic solvents is probably open-chain dimer rather than cyclic dimer.[4,12] It is commonly supposed that cyclic dimer predominates in solvents of the kind used in the present work,[4] although a small proportion of open-chain dimer would not be precluded. If the cyclic dimer is the reactive species then the rate coefficient for its reaction with diazodiphenylmethane is given by $K_{21}\beta$, as in equation (**3**). If, on the other hand, only a small proportion of the dimer, that present as open-chain dimer, is really reacting, then the true rate coefficient for the latter would be $\gg K_{21}\beta$. Table 2 shows that for benzoic [H]acid in the various solvents $K_{21}\beta$ is mainly in the range 1—6 l mol^{-1} min^{-1}. The corresponding quantity for the reactions in the donor aprotic solvents [1] is k'/K_{12}. The values of k' cover a wide range,[1] but many lie in the region 2 ± 1 l^2 mol^{-2} min^{-1}. In view of the inability of physical measurements to detect dimerisation in such solvents, K_{12} must be at the most *ca.* 0·1 l mol^{-1}. Hence many values of k'/K_{12} would lie in the region 20 ± 10 l mol^{-1} min^{-1}, and the use of smaller values of K_{12} would give even higher values of k'/K_{12}. This suggests that the dimer is inherently much less reactive in the 'dimerising' solvents than in the donor aprotic solvents. This may mean either that the bulk cyclic dimer is the reacting species, in contrast to the open-chain dimer in the donor aprotic solvents, or that in the dimerising solvents the reaction depends on a small proportion of open-chain dimer. As far as the multimers are concerned, the existence of these in open-chain forms seems very likely. As for the open-chain dimer,[1] we may suppose that these would be very reactive.

Finally we return briefly to an issue dealt with in the previous paper,[1] where we concluded that the dependence of k(obs) on c for the reaction in donor aprotic solvents was best understood in terms of a reactive dimer mechanism. The alternative catalysis by the monomer of the decomposition of the monomeric acid–diazodiphenylmethane complex [10] (DHA) was considered less likely, in view of the substantial isotope effect on k', and the difficulty of suggesting a mechanism whereby an additional molecule of acid might facilitate the decomposition of DHA. In the present paper we have so far regarded this issue as settled and have adapted and extended the mechanism to include reactive dimer and multimer for the dimerising solvents. Equation (**5**), however, permits an alternative explanation in terms of various kinds of catalysis, *e.g.* catalysis by monomer of reaction of monomer (quadratic term), catalysis by dimer of reaction of monomer (cubic term), *etc.* and indeed the real situation might be a combination of the reactive dimer and multimer and catalytic mechanisms. At one time [10] we were inclined to emphasise the role of catalysis but at present we consider that the reactive dimer and multimer mechanism is on balance more plausible. However we do not regard the issue as finally settled. Acid catalysis has been invoked by other authors in connection with related reactions, but satisfactory mechanisms for the catalysis have not been suggested. Thus Brønsted and Bell [13] interpreted the third-order kinetics of the reaction between ethyl diazoacetate and carboxylic acids in benzene in terms of dimeric molecules of acid catalysing their own reaction in some unspecified way. Also Hartman *et al.*[14] proposed for the reaction of ethyl diazoacetate and halogenoacetic acids that 'the reaction mechanism involves the formation of a reactive complex between acid and ester, followed by a decomposition of the ester through the reaction of the complex with another acid molecule'.

EXPERIMENTAL

Adequate accounts have been given previously.[1,2]

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