The Separation of Polar and Steric Effects. Part XIII.[1] Kinetics of the Reactions of Cinnamic Acid and *meta*-Substituted Cinnamic Acids with Diazodiphenylmethane in Various Alcohols and in Aprotic Solvents

By **Norman B. Chapman,* David J. Newman, John Shorter,** and **H. Michael Wall,** Chemistry Department, The University, Hull HU6 7RX

Rate coefficients have been determined for the reactions at 30 °C of diazodiphenylmethane with cinnamic acid and *meta*-substituted cinnamic acids (substituents: Me, Cl, or NO_2) in 12 alcohols, in ethyl acetate, and in acetone.

The reactions of cinnamic acid with diazodiphenylmethane in alcohols show a good linear free-energy relationship with the corresponding reactions of benzoic acid. The solvent effect can be interpreted in terms of the dielectric constant and the influence of hydrogen bonding. Multiple linear correlation with three suitable solvent parameters is quite successful. Comparisons are made with the benzoic and the phenylacetic acid system.

The Hammett ρ-values (ρ_3) for the reactions of cinnamic acids are correlated with solvent parameters and comparisons are made with ρ-values for the benzoic (ρ_1) and the phenylacetic (ρ_2) acid system. The expressions $\rho_3 = 0.39\rho_1$, and $\rho_2 = 0.60\ (\rho_1 - 0.25)$ hold, and are interpreted in terms of Bowden, Chapman, and Shorter's treatment of the transmission of polar effects through side-chains.

IN Part VIII [2] and XII,[1] and also in Part I [3] and II [4] of a new series, we reported the kinetics of the reactions of diazodiphenylmethane with benzoic acid [1-4] and *meta*- or *para*-substituted benzoic acids [2,3] in both protic [1,2] and

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

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

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

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

aprotic[1-4] solvents. In Part X[5] we dealt with *meta*- or *para*-substituted phenylacetic acids, mainly with alcohols as solvents. We now report work on *meta*-substituted cinnamic acids, in a wide range of alcohols as solvents, and in a few donor aprotic solvents. Our object was to investigate further the influence of the solvent on the rate coefficients for the parent acid and on the Hammett ρ-constant,[6] in order to compare the cinnamic, the phenylacetic, and the benzoic acid system in these respects, and to apply multiple linear correlations involving combinations of solvent parameters[7] in the interpretation of solvent effects.

Earlier papers[1,2,8] and those of other authors[9] have dealt with the reaction mechanism in alcohols. The rate-determining step involves a proton transfer from the carboxylic acid to form a diphenylmethyldiazonium–carboxylate ion-pair. (Subsequent fast product-governing stages have been variously formulated.[8-11] The intervention of a benzhydryl–carboxylate ion-pair seems most likely; this may either ' collapse ' to give the ester or react with the solvent to give an ether.[9-11]) In donor aprotic solvents the reaction mechanism probably involves the reversible formation of a complex between monomeric acid and diazodiphenylmethane, and its subsequent rate-limiting breakdown to products.[3] There may also be a substantial contribution from the reaction of a small amount of highly reactive acid in the form of open-chain dimer.[3]

DISCUSSION

The Variation of the Rate Coefficients with Solvent for the Reactions of Cinnamic Acid with Diazodiphenylmethane at 30 °C.—Values of the rate coefficients for the reactions in 12 alcohols are in Table 1. When the values of log k are correlated with the corresponding values for the reactions of benzoic acid with diazodiphenylmethane at 30 °C,[1] the results conform to the linear free-energy relationship (1).

$$\log k\ (\text{cinnamic}) = 0.909\,5 \log k\ (\text{benzoic}) + 0.1447 \quad (1)$$

(Correlation coefficient, r, 0.997, and standard deviation of the estimate, s, 0.0339.) The second-order rate coefficients (extrapolated to [acid] = 0) for reactions in ethyl acetate or acetone (Table 1 and Part XII[1]) show large deviations from the relationship, indicating that it holds only for alcohols as solvents (*cf.* Part X[5]).

The above relationship shows that the same solvent properties act on the reactions of the two acids in the various alcohols, and that the influence of a given property in one reaction is proportional to its influence in the other. Earlier work[1,2,5] has established that the solvent effect is best interpreted in terms of the following properties: (*a*) the behaviour of the solvent as a dielectric in facilitating the separation of opposite charges in the formation of the activated complex, (*b*) the ability of the medium to solvate the carboxylic proton, and (*c*) the ability of protic solvents to form a hydrogen bond with the negative end of an ion-pair. Both (*b*) † and (*c*) stabilise the transition state relative to the initial state. The Kirkwood function[12,13] of the dielectric constant ε, $f(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1)$, is a suitable measure of (*a*), while (*b*) and (*c*) together are governed mainly by the polar effect of the alkyl group of the alcohol, appropriately measured by the Taft polar substituent constant,[14] σ^*.[1] Steric moderation of (*b*) also occurs, and this is suitably measured by $n_{\gamma\text{H}}$, the number of γ-hydrogen atoms in the alcohol. Our general approach is similar to that adopted by Koppel and Palm[7] for the solvolysis of t-butyl chloride in various protic solvents.

TABLE 1

Rate coefficients (l mol^{-1} min^{-1}) for the reactions of cinnamic acid and *meta*-substituted cinnamic acids with diazodiphenylmethane in alcohols and certain aprotic solvents at 30.0 °C

	Substituent			
Solvent	*m*-Me	H	*m*-Cl	*m*-NO_2
(1) Benzyl alcohol	8.5	9.2	12.0	14.7
(2) 2-Phenylethanol	2.50	2.65	3.26	4.24
(3) Methanol	2.18	2.34	2.82	3.34
(4) 2-Methylpropan-1-ol	1.73	1.98	2.55	3.59
(5) Propan-1-ol	1.16	1.17	1.79	2.20
(6) Ethanol	1.00	1.02	1.46	1.80
(7) Butan-1-ol	1.01	1.14	1.53	1.97
(8) Propan-2-ol	0.780	0.810	1.14	1.45
(9) Butan-2-ol	0.730	0.790	1.16	1.55
(10) Decan-1-ol	0.492	0.590	0.782	—[a]
(11) 2-Methylpropan-2-ol	0.318	0.363	0.543	0.821
(12) 2-Methylbutan-2-ol	0.176	0.196	0.315	0.504
Ethyl acetate *	0.030 5	0.035 6	0.071	0.136
Acetone *	0.053 8	0.061 1	0.117	0.180

Values of rate coefficients were reproducible to ±2% or better.

* Values of second-order rate coefficient extrapolated to [acid] = 0. See refs. 1 and 3.

[a] Acid insufficiently soluble.

Solvent parameters are shown in Table 2. Multiple linear regression of log k for cinnamic acid with $f(\varepsilon)$, σ^*, and $n_{\gamma\text{H}}$ gives expression (2), with the multiple correlation

$$\log k = -1.368 + 3.712 f(\varepsilon) + 2.667\sigma^* + 0.0387 n_{\gamma\text{H}} \quad (2)$$

coefficient $R = 0.986$ and $s = 0.0849$. The corresponding expression for benzoic acid reacting with diazodiphenylmethane in the same series of alcohols is (3), with

$$\log k = -1.653 + 4.297 f(\varepsilon) + 2.910\sigma^* + 0.0363 n_{\gamma\text{H}} \quad (3)$$

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† *cf.* Footnote on p. 966 of ref. 3.

[5] Part X, N. B. Chapman, J. R. Lee, and J. Shorter, *J. Chem. Soc.* (*B*), 1969, 769.

[6] L. P. Hammett, ' Physical Organic Chemistry,' McGraw-Hill, New York, 1970, 2nd edn., ch. 11.

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

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

[10] A. F. Diaz and S. Winstein, *J. Amer. Chem. Soc.*, 1966, **88**, 1318.

[11] D. Bethell and R. D. Howard, *Chem. Comm.*, 1966, 94.

[12] J. G. Kirkwood, *J. Chem. Phys.*, 1934, **2**, 351.

[13] K. J. Laidler and H. Eyring, *Ann. New York Acad. Sci.*, 1940, **39**, 303.

[14] R. W. Taft, in ' Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, ch. 13.

$R = 0.994$ and $s = 0.0605$. [The coefficients in the various terms of (3) differ slightly from those in the corresponding expression for the series of 19 alcohols in Part XII.[1]] In both systems the influence of the alcohol structure on log k is exerted mainly through the σ^* term, simple linear regression of log k on σ^* giving $r \sim 0.95$. The $f(\varepsilon)$ term is next in importance. The $n_{\gamma H}$ term is needed to account for the observed rate-enhancing effect of branching at the β-carbon atom of the alcohol.[1]

TABLE 2

Solvent parameters for alcohols

Solvent	ε [a]	σ^* [b]	$n_{\gamma H}$ [c]
(1) Benzyl alcohol	13.1	+0.215	0
(2) 2-Phenylethanol	13.0	+0.08	0
(3) Methanol	32.6	0.00	0
(4) 2-Methylpropan-1-ol	17.7	−0.125	6
(5) Propan-1-ol	20.1	−0.115	3
(6) Ethanol	24.3	−0.10	0
(7) Butan-1-ol	17.1	−0.13	2
(8) Propan-2-ol	18.3	−0.19	0
(9) Butan-2-ol	15.8	−0.21	3
(10) Decan-1-ol	7.4	−0.16 [d]	2
(11) 2-Methylpropan-2-ol	12.2	−0.30	0
(12) 2-Methylbutan-2-ol	5.8	−0.31 [e]	3

[a] Dielectric constant, usually at 25 °C. See Part XII [1] for references and other details. [b] Polar substituent constant of the alkyl group, mainly from Taft.[14] [c] Number of γ-hydrogen atoms. [d] G. Geiseler, J. Fruwert, and F. Gyalogh, *Spectrochim. Acta*, 1966, **22**, 1165. [e] Part X.[5]

Expression (1) shows that the cinnamic acid system is less sensitive to solvent changes than the benzoic acid system. This is confirmed by the smaller coefficients of $f(\varepsilon)$ and σ^* in expression (2). (The phenylacetic acid system was also less sensitive than the benzoic acid system.[5]) For the cinnamic acid system, however, there is a general increment in log k, as indicated by the intercept term in expression (1) and the difference between the intercept term in expressions (2) and (3). The latter observation may be due to the extent of conjugation of the carboxy-group with the rest of the molecule being less in cinnamic acid than in benzoic acid.[15,16] Thus cinnamic acid appears to be inherently more reactive than benzoic acid towards diazodiphenylmethane. The easier proton transfer will be less susceptible to influence by the solvent and thus the lower sensitivity of the cinnamic acid system to solvent changes is explained on the basis of a ' selectivity–reactivity ' relationship.[5,17]

The Variation of the Hammett ρ-Constant with the Solvent for the Reactions of Substituted Cinnamic Acids with Diazodiphenylmethane at 30 °C.—Hammett ρ-values [6] and associated statistical quantities are given in Table 3 for the reactions in 12 alcohols, ethyl acetate, and acetone. The substituents chosen (see Table 1) are in accord with the views of van Bekkum, Verkade, and Wepster.[18]

We have previously [2,5] detailed several factors which may contribute to the variation of ρ with the solvent. First, ρ decreases as the dielectric constant of the medium increases,[19,20] because the transmission of polar effects through the medium is suppressed. Secondly, at high dielectric constant the energy necessary to bring about the charge separation in the transition state is relatively small, and this gives rise to a low susceptibility to the polar effects of substituents (a selectivity–reactivity relationship [17]). Thirdly, besides the above general electrostatic effects, there are specific interactions which influence ρ, as they influence log k for the parent acid (see above): stabilisation of the initial state will increase ρ, while stabilisation of the activated complex will decrease ρ (again a selectivity–reactivity relationship [17]). It is thus reasonable to correlate ρ with $f(\varepsilon)$ and σ^* as for log k; this was previously done for substituted phenylacetic and benzoic acids.[5] (We omit $n_{\gamma H}$ since the peculiarity which requires its introduction in the case of log k is not clearly discerned in ρ.)

TABLE 3

Hammett polar susceptibility constants, ρ, for the reactions of substituted cinnamic acids with diazodiphenylmethane in alcohols and certain aprotic solvents at 30.0 °C

Solvent	ρ [a]	log k^0 [b]	r [c]	s [d]
(1) Benzyl alcohol	0.30	0.959	0.997	0.010
(2) 2-Phenylethanol	0.29	0.418	0.997	0.009
(3) Methanol	0.23 [e]	0.362	0.997	0.008
(4) 2-Methylpropan-1-ol	0.38	0.277	0.994	0.019
(5) Propan-1-ol	0.38	0.086	0.989	0.025
(6) Ethanol	0.34 [f]	0.021	0.994	0.016
(7) Butan-1-ol	0.36	0.044	0.996	0.015
(8) Propan-2-ol	0.35	−0.083	0.999	0.008
(9) Butan-2-ol	0.42	−0.102	0.999	0.010
(10) Decan-1-ol [g]	0.42	−0.257	0.966	0.037
(11) 2-Methylpropan-2-ol	0.51 [h]	−0.453	0.999	0.009
(12) 2-Methylbutan-2-ol	0.58	−0.712	1.000	0.005
Ethyl acetate [i]	0.83	−1.454	1.000	0.005
Acetone [i]	0.68	−1.212	0.997	0.024

[a] Calculated by the method of least squares from σ values based on the ionisation of benzoic acid. Number of data sets = 4, except as noted. [b] log k for parent acid, as calculated by least-squares treatment. [c] Correlation coefficient. [d] Standard deviation of the estimate. [e] By D. J. Newman; independent determination by H. M. Wall found 0.29. [f] By D. J. Newman; independent determination by H. M. Wall found 0.35, *cf.* the value (*ca.* 0.42) obtained by us in earlier work,[21] and by Ritter and Miller.[22] [g] Three data sets only (see Table 1). [h] Independent determination by M. R. J. Dack found 0.53. [i] For second-order rate coefficients extrapolated to [acid] = 0.

For the purpose of the correlations we denote the ρ values for substituted cinnamic acids by ρ_3 (*cf.* ρ_2 for phenylacetic acids and ρ_1 for benzoic acids in Part X [5]). For the cinnamic acids in the 12 alcohols, expression (4) holds, with $R = 0.929$ and $s = 0.039$.

$$\rho_3 = 1.086 - 1.682f(\varepsilon) - 0.405\sigma^* \qquad (4)$$

For a direct comparison with benzoic acids and phenylacetic acids we also give expressions (5), (6), and (7) for the reactions of all three sets of acids in the eight common alcohols (see Table 4).

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[15] Part I, N. B. Chapman, J. Shorter, and J. H. P. Utley, *J. Chem. Soc.*, 1962, 1824.

[16] Part IX, A. Buckley, N. B. Chapman, and J. Shorter, *J. Chem. Soc.* (*B*), 1969, 195.

[17] H. C. Brown and K. L. Nelson, *J. Amer. Chem. Soc.*, 1953, **75**, 6292.

[18] H. van Bekkum, P. E. Verkade, and B. M. Wepster, *Rec. Trav. chim.*, 1959, **78**, 815.

[19] L. P. Hammett, *J. Amer. Chem. Soc.*, 1937, **59**, 96.

[20] H. H. Jaffé, *Chem. Rev.*, 1953, **53**, 191.

[Expressions (5) and (6) differ slightly from those given in Part X.[5]]

$$\rho_1 = 2.365 - 3.177f(\varepsilon) - 0.860\sigma^* \quad (R = 0.982,\ s = 0.047) \qquad (5)$$

$$\rho_2 = 1.661 - 2.779f(\varepsilon) - 0.503\sigma^* \quad (R = 0.987,\ s = 0.027) \qquad (6)$$

$$\rho_3 = 1.341 - 2.216f(\varepsilon) - 0.350\sigma^* \quad (R = 0.953,\ s = 0.040) \qquad (7)$$

All the above correlations are significant at above the 99.9% confidence level, except for (7) which is significant between the 99% and 99.9% confidence levels. The ρ values for cinnamic acids are not as well correlated with $f(\varepsilon)$ and σ^* as those for benzoic and phenylacetic acids. However, the overall situation is quite clear: the sensitivity of ρ to changes in both dielectric constant and the Lewis acid–base behaviour of the alcohols shows the order $\rho_1 > \rho_2 > \rho_3$. Further the relative values of the coefficients of $f(\varepsilon)$ and σ^* in expressions (4)—(7) compared with the corresponding values in (2) and (3) show that the dielectric term plays a relatively more important role in governing ρ than it does in governing log *k* for the parent acid. Thus a selectivity–reactivity relationship between ρ and log *k* (see above) will be only qualitative in character, and indeed ρ and log *k* do not show a simple rectilinear relationship for any of the acids (see discussion and Figure 4 in Part X for phenylacetic acid [5]).

TABLE 4

Hammett polar susceptibility constants, ρ, for the reactions of substituted cinnamic, benzoic, and phenylacetic acids in alcohols and certain aprotic solvents at 30.0 °C

	Solvent	Cinnanic acid [a] ρ_3	Benzoic acid [b] ρ_1	Phenylacetic acid [c] ρ_2	ρ_3/ρ_1	ρ_2/ρ_1	$\frac{\rho_2}{\rho_1 - 0.25}$
(1)	Benzyl alcohol	0.30	0.78	0.33	0.38	0.42	0.62
(3)	Methanol	0.23	0.88	0.34	0.26 [d]	0.39	0.54
(4)	2-Methylpropan-1-ol	0.38	0.94	0.42	0.40	0.45	0.61
(5)	Propan-1-ol	0.38	0.99	0.42	0.38	0.42	0.57
(6)	Ethanol	0.34	0.94	0.40	0.36	0.43	0.58
(8)	Propan-2-ol	0.35	1.07	0.47	0.33	0.44	0.57
(11)	2-Methylpropan-2-ol	0.51	1.28	0.63	0.40	0.49	0.61
(12)	2-Methylbutan-2-ol	0.58	1.41	0.74	0.41	0.53	0.64
	Ethyl acetate [e]	0.83	2.06 [f]		0.40		
	Acetone [e]	0.68	1.85 [f]		0.37		

[a] Table 3. [b] Ref. 2. [c] Ref. 5. [d] Using Wall's ρ value for cinnamic acid (Table 3, footnote *e*), the ratio is 0.33. [e] For second-order rate coefficients extrapolated to [acid] = 0. [f] At 37 °C. Ref. 3.

Direct comparison of the ρ values for the reactions of the three acids in a given solvent is of interest in connection with our [21] simple treatment of the transmission of the polar effects of substituents through aromatic and arylaliphatic acids of the type $Ar{-}Y{-}CO_2H$ for reactions with diazodiphenylmethane in ethanol. If the assumptions of this treatment are valid for the series of solvents in Table 4, the ρ values for cinnamic and benzoic acids should be given by $\rho_3/\rho_1 = 0.39$, where 0.39 is the distance between C(1) and the carboxy-carbon atom of benzoic acid divided by the corresponding distance in cinnamic acid. For six of the eight alcohols in Table 4, as well as for ethyl acetate and acetone, ρ_3/ρ_1 lies in the range 0.39 ± 0.03, which we consider satisfactory within the limits of experimental error. The conformity of the two aprotic solvents to the same relationship as the alcohols contrasts with the deviations of the aprotic solvents from equation (1). For propan-2-ol and for methanol ρ_3/ρ_1 appears to be somewhat lower. It is sometimes difficult to determine small ρ values precisely (see footnotes in Table 3), and at present the extent to which methanol and propan-2-ol conform to or deviate from $\rho_3/\rho_1 = 0.39$ should remain open.

The conformity to the simple relationship $\rho_3/\rho_1 = 0.39$ contrasts with the failure of the reactions of phenylacetic acids to obey the corresponding relationship $\rho_2/\rho_1 = 0.60$, the observed ratio being in most cases *ca.* 0.43, but rising significantly in the less polar tertiary alcohols (Table 4). The more complicated relationship $\rho_2/(\rho_1 - 0.25) = 0.60$ is, however, well obeyed, where 0.25 is the contribution to ρ_1 of the C(1)-to-carboxy-carbon bond of benzoic acid, arising from the conjugation of this bond with the ring, and 0.60 is the length of this bond divided by the corresponding distance in phenylacetic acid. In Part X [5] 0.30 was accepted as the ' conjugation contribution ' but this quantity can only be assessed approximately.[21] The value 0.25 gives better overall agreement with theory for the phenylacetic acids, but as pointed out in Part X,[5] the conjugation contribution could itself be solvent-dependent. No such correction is needed in relating ρ_3 to ρ_1 because the side-chain is conjugated with the ring in both acids.[21]

EXPERIMENTAL

Materials.—The acids were commercial samples or were prepared by standard methods. They were variously recrystallised several times from acetic acid, ethanol, or benzene. They had m.p.s identical with or very close to those recorded in the literature. The equivalent weight of each acid, determined by titration, was well within 1% of the calculated value. The purity of each acid was examined by g.l.c. of the methyl ester; there were no detectable impurities. Diazodiphenylmethane, prepared by the method

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[21] K. Bowden, N. B. Chapman, and J. Shorter, *Canad. J. Chem.*, 1964, **42**, 1979.

[22] J. D. S. Ritter and S. I. Miller, *J. Amer. Chem. Soc.*, 1964, **86**, 1507.

of Schroeder and Katz[23] was stored over potassium hydroxide in a desiccator in a refrigerator.

Solvents were purified as described previously.[1,2] They had b.p.s and refractive indices identical with, or very close to, those recorded in the literature and were pure by g.l.c. Wherever possible water content was examined by the Karl Fischer method[24] and was always $\ngtr 0.02\%$ (w/v) and generally $\ngtr 0.01\%$ (w/v).

Measurements.—Values of k were determined spectrophotometrically; a Unicam SP 600 spectrometer was used.[5]

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[23] W. Schroeder and L. Katz, *J. Org. Chem.*, 1954, **19**, 718.

[24] W. Seaman, W. H. McComas, and G. A. Allen, *Analyt. Chem.*, 1949, **21**, 510.