

Proton Transfer from Disulphonyl-activated Carbon Acids

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Rates of the water catalysed detritiation of six disulphonyl-activated carbon acids, with acidities in the range $11 < \text{p}K^0 < 15$, have been measured in aqueous solution. A Brønsted exponent $\alpha = 1.1 \pm 0.1$ has been calculated. The rates of recombination of the carbanions with hydronium ion have values close to $2 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$. It is shown that the association step included in Marcus' theory of proton transfer is necessary to explain the results. The transition state for proton transfer from disulphones to weak bases resembles an encounter complex between the carbanion and conjugate acid of the base catalyst. A comparison is made with other carbon acids and it appears that the behaviour of disulphones approaches more closely to the 'normal' proton transfer of oxygen acids.

UNTIL recently¹ the proton transfer behaviour of carbon acids in aqueous solution was thought to differ considerably from the *normal* behaviour of oxygen acids. For the ionisation of a *normal* acid,² proton transfer in a thermodynamically favourable direction is diffusion controlled and therefore occurs at a rate which is independent of the $\text{p}K^0$ values of the acids and bases involved. In a thermodynamically unfavourable direction, the rate varies linearly with the equilibrium constant of the reaction. For proton transfer from an oxygen acid (HA) to a series of bases (B) these two situations correspond to β exponents in the Brønsted catalysis law of zero and unity respectively. The Brønsted exponents only deviate from these limiting values for a small region around $-3 < \Delta \text{p}K^0 < +3$, where $\Delta \text{p}K^0 = \text{p}K^0_{\text{HA}} - \text{p}K^0_{\text{BH}^+}$. For most carbon acids, in contrast, intermediate values for Brønsted exponents are observed over large ranges of $\Delta \text{p}K^0$ and the rates only approach the diffusion limit when $\Delta \text{p}K^0 > 20$. This behaviour is typical of carbon acids activated with keto,³ nitro,³ and ester³ groups and of aromatic carbon acids.⁴

It was discovered recently¹ that cyanocarbon acids exhibit many of the properties of normal acids. For malononitriles a value $\beta = 0.98$ was observed for proton transfer to a number of bases over the range $2 < \Delta \text{p}K^0 < 14$. In the reverse direction the rates and activation energies were close to those expected for a diffusion controlled reaction; $k = 1 \times 10^8$ and $3 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ for reaction of the carbanions with several general acids and with hydronium ion respectively. In addition, a very low primary kinetic isotope effect ($k^{\text{H}}/k^{\text{T}} = 1.6$) was observed which is compatible with a transition state having a fully transferred proton.⁵

We now report a study of proton transfer from disulphonyl-activated carbon acids and show that these carbon acids also exhibit almost normal proton transfer behaviour. Apart from the recent study by Bell and Cox,⁶ little information on the rate of proton transfer in aqueous solution is available.

¹ E. A. Walters and F. A. Long, *J. Amer. Chem. Soc.*, 1969, **91**, 3733; F. Hibbert, F. A. Long, and E. A. Walters, *ibid.*, 1971, **93**, 2829; F. Hibbert and F. A. Long, *ibid.*, 1972, **94**, 2647.

² M. Eigen, *Angew. Chem. Internat. Edn.*, 1964, **3**, 1.

³ (a) R. P. Bell, 'Proton in Chemistry,' Methuen, London, 1959, p. 161; (b) R. P. Bell and J. E. Crookes, *Proc. Roy. Soc.*, 1965, *A*, **286**, 285.

⁴ F. A. Long and J. L. Longridge, *J. Amer. Chem. Soc.*, 1967, **89**, 1292.

EXPERIMENTAL

Materials.—Bisethylsulphonylmethane,⁷ 1,1-bisethylsulphonylethane,⁷ bismethylsulphonylmethane,⁸ and $\alpha\alpha$ -bisethylsulphonyltoluene⁹ were prepared by reacting the corresponding thiol and aldehyde, followed by oxidation of the thioacetal produced. In the preparation of $\alpha\alpha$ -bisethylsulphonyltoluene, ethanethiol was generated *in situ* from the Bunte salt. For bisphenylsulphonylmethane, reaction of thiophenol with methylene bromide in ethanolic sodium ethoxide gave the thioacetal which was then oxidised to the disulphone. This was converted to 1,1-bisphenylsulphonylethane.¹⁰ The solids were purified by recrystallisation and then gave satisfactory m.p.s and n.m.r. spectra. Tritiated sulphones were prepared by dissolving the solids (0.05 g) in tritiated water (10 ml, 25 mCi) at ca. 350 K. After 2 h, crystals of the labelled sulphones were obtained by cooling.

Kinetics.—Detritiation of the disulphones in 0.100M-HCl at 298.2 K was measured. The disulphones were introduced into the thermostatted HCl (100 ml) as a solution in dioxan (0.05 ml) and after rapid shaking, samples of the reaction mixture were withdrawn at intervals. The partially exchanged sulphone was extracted by running each sample into toluene and its activity was measured on a Packard Tricarb liquid scintillation counter, model 3320. Extraction was completed within 15 s. For 1,1-bisethylsulphonylethane, using 5 ml aqueous samples and 15 ml toluene, 91% of the disulphone was extracted. The reactions were accurately first order in tritiated sulphone for at least three half-lives. Rate coefficients were calculated from the slopes of plots of $\log(C_t - C_\infty)$ against time, where C_t and C_∞ are the activities of toluene extracts taken t seconds and at least ten half-lives respectively after the start of the reaction. Rate coefficients were always reproducible to $\pm 2\%$. The effect of dioxan on the rate was negligible. Rate coefficients determined in 0.010M-HCl containing 0.090M-NaCl were identical to the measurements in 0.100M-HCl.

Measurement of $\text{p}K$.—The $\text{p}K^0$ value of 1,1-bisphenylsulphonylethane was determined at 298.2 K using a spectrophotometric method. At 300 nm the undissociated carbon acid has negligible absorbance compared with its carbanion ($\epsilon = 4.4 \times 10^3$). A solution of the carbon acid in dioxan (0.05 ml) was introduced into a sodium hydroxide

⁵ F. Hibbert and F. A. Long, *J. Amer. Chem. Soc.*, 1971, **93**, 2836.

⁶ R. P. Bell and B. G. Cox, *J. Chem. Soc. (B)*, 1971, 652.

⁷ M. W. Cronyn, *J. Amer. Chem. Soc.*, 1952, **74**, 1225.

⁸ H. J. Backer, *Rec. Trav. chim.*, 1946, **65**, 53.

⁹ H. E. Westlake, jun., and G. Dougherty, *J. Amer. Chem. Soc.*, 1941, **63**, 658.

¹⁰ R. L. Schriner, H. C. Struck, and W. J. Jorison, *J. Amer. Chem. Soc.*, 1930, **52**, 2060.

solution (100 ml) at 298.2 K, and the optical density was measured. The apparent extinction coefficients (ϵ_{app}) in sodium hydroxide solutions of different molarities were determined as the slopes of plots of optical density against total carbon acid concentration (carbanion and undissociated acid). The results are shown in Table 1. Since the undissociated carbon acid has negligible absorbance, it can be shown that $\epsilon_{\text{app}} = \epsilon_{\text{RC}^-} - (\epsilon_{\text{app}} \times h_-)/K^0_{\text{RCH}}$ where K^0_{RCH} is the thermodynamic dissociation constant of the carbon acid, ϵ_{RC^-} is the extinction coefficient of its anion, and h_- is the acidity function in concentrated sodium hydroxide solution. A plot of ϵ_{app} against $\epsilon_{\text{app}} \times h_-$ was linear and gave $\text{p}K^0 = 13.76 \pm 0.04$. In sodium hydroxide solutions more concentrated than 3M, the apparent extinction coefficient begins to decrease. This was not investigated further since the results up to this point provide sufficient evidence of a straightforward ionisation.

Because the kinetic results obtained for $\alpha\alpha$ -bisethylsulphonyltoluene are unusual (see later), the literature $\text{p}K^0$ value for this compound was checked using the above method. Measurements of the apparent extinction coefficient in 0.005, 0.01, and 0.2M-sodium hydroxide agreed with the published values⁶ and gave the same $\text{p}K^0$.

TABLE 1

Dissociation of $(\text{PhSO}_2)_2\text{CHMe}$ at 298.2 K in aqueous solution

	$\text{p}K^0 = 13.76 \pm 0.04$					
$[\text{NaOH}]/M^a$	0.05	0.100	0.150	0.200	0.300	0.500
$10^{14}h_-$	19.5	9.77	6.46	4.90	3.24	1.95
$10^3\epsilon_{\text{app}}$	0.350	0.675	0.948	1.11	1.63	2.06
$[\text{NaOH}]/M$	0.750	1.00	1.25	1.50	2.00	3.00
$10^{14}h_-$	1.29	0.977	0.740	0.600	0.398	0.219
$10^3\epsilon_{\text{app}}$	2.65	2.79	3.13	3.49	3.52	3.80

^a J. T. Edward and I. C. Wang, *Canad. J. Chem.*, 1962, **40**, 399.

TABLE 2

Detritiation of disulphones in 0.1M-HCl at 298.2 K

	$\text{p}K^0$	$10^6k^{\text{T}}/\text{s}^{-1}$	$10^6k^{\text{H}}/\text{s}^{-1}$	$10^{-10}k^{\text{D}}/\text{s}^{-1}$
$(\text{PhSO}_2)_2\text{CH}_2$	11.21 ^a	365	408	2.1
$(\text{EtSO}_2)_2\text{CHPh}$	12.12 ^b	1.90	1.06	0.045
$(\text{EtSO}_2)_2\text{CH}_2$	12.20 ^b	27.5	30.7	1.6
$(\text{MeSO}_2)_2\text{CH}_2$	12.55 ^b	18.4	20.6	2.3
$(\text{PhSO}_2)_2\text{CHMe}$	13.76 ^c	2.05	1.15	2.1
$(\text{EtSO}_2)_2\text{CHMe}$	14.56	0.113	0.063	0.73

^a E. J. Corey, H. König, and T. H. Lowry, *Tetrahedron Letters*, 1962, 515. ^b Mean of values from ref. 6, note a, and J. Hine, J. C. Philips, and J. I. Maxwell, *J. Org. Chem.*, 1970, **35**, 3943. ^c This work.

TABLE 3

Activation parameters for detritiation of $(\text{PhSO}_2)_2\text{CH}_2$ in 0.1M-HCl at 298.2 K. Rate coefficients $k^{\text{T}}/\text{s}^{-1}$

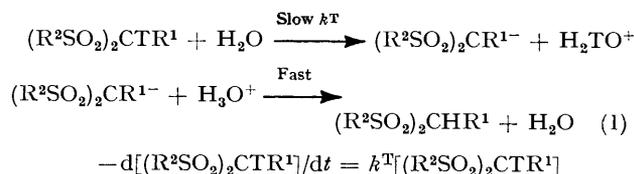
$\Delta G^\ddagger/\text{kJ mol}^{-1}$	81.5
$\Delta H^\ddagger/\text{kJ mol}^{-1}$	48.1
$E_a/\text{kJ mol}^{-1}$	50.6
$\Delta S^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$	-112

RESULTS

Since the rates of detritiation are independent of acid concentration the only reasonable mechanism is a water catalysed slow triton transfer in which the carbanion is

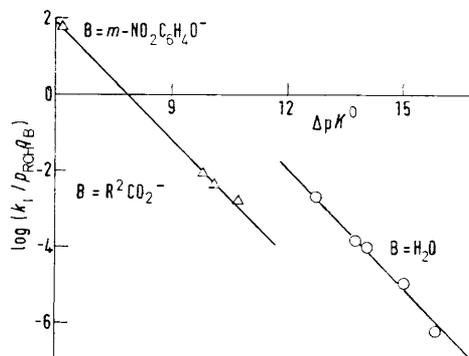
¹¹ C. G. Swain, E. C. Stivers, J. F. Reuwer, jun., and J. L. Schaad, *J. Amer. Chem. Soc.*, 1958, **80**, 5885.

produced in steady state concentrations (1). The rate



coefficients for detritiation (k^{T}) are shown in Table 2. For bisphenylsulphonylmethane, the reaction is too rapid to follow at 298.2 K. Rate coefficients were therefore determined at eight temperatures from 274 to 287 K and a value at 298.2 K was obtained by extrapolation. Activation parameters calculated from these results are shown in Table 3.

Isotope Effects.—Primary kinetic isotope effects for 1,1-bis(ethylsulphonyl)ethane were calculated by comparison of the present data with earlier results. A value $k^{\text{H}}/k^{\text{T}} = 3.1 \pm 0.1$ (298.2 K; ionic strength $I = 0.1M$) was calculated from the rates of triton and proton⁶ transfer. According to the Swain relation,¹¹ this corresponds to $k^{\text{H}}/k^{\text{D}} = 2.2 \pm 0.1$.



Plot of $\log(k_1/p_{\text{RCH}}q_{\text{B}})$ against $\Delta\text{p}K^0 = \text{p}K^0_{\text{RCH}} - \text{p}K^0_{\text{BH}^+} + \log(q_{\text{B}}/p_{\text{RCH}}/p_{\text{BH}^+}q_{\text{RC}^-})$ where p_{RCH} and p_{BH^+} are the number of dissociating protons in the carbon acid and conjugate acid of the base catalyst respectively and q_{RC^-} and q_{B} are the number of equivalent basic sites in RC^- and B . The data are taken from ref. 6 ($\text{B} = \text{R}^2\text{CO}_2^-$), ref. 12 ($\text{B} = m\text{-NO}_2\text{C}_6\text{H}_4\text{O}^-$), and the present work ($\text{B} = \text{H}_2\text{O}$). The final lower point on the $\text{B} = \text{H}_2\text{O}$ line is taken from ref. 6 and the present work.

The rate of deuterium transfer $k^{\text{D}} = 1.84 \times 10^{-5} \text{ s}^{-1}$ (298.2 K; $I = 0.02M$) was calculated from a value¹² at 299 K using the activation parameters in Table 3. When compared with k^{H} this gives $k^{\text{H}}/k^{\text{D}} = 1.9 \pm 0.1$.

The solvent catalysed detritiation of 1,1-bisphenylsulphonylthane in deuterium oxide occurs at a rate $k^{\text{T}}(\text{D}_2\text{O}) = 5.9 \times 10^{-5} \text{ s}^{-1}$, giving a solvent isotope effect $k^{\text{T}}(\text{H}_2\text{O})/k^{\text{T}}(\text{D}_2\text{O}) = 3.5$.

Brønsted Catalysis.—The rate coefficients (k^{T}) were plotted in the form of the Brønsted equation: $\log k^{\text{T}} = \alpha \log(K^0/p) + \text{constant}$, where p is the number of acidic protons and K^0 the dissociation constant of the disulphone. A good straight line treated by a least squares analysis gave a Brønsted exponent $\alpha = 1.1 \pm 0.1$. The point for $\alpha\alpha$ -bisethylsulphonyltoluene was excluded.

Rate coefficients for proton transfer were calculated by multiplying the rates of detritiation by the kinetic isotope effect ($k^{\text{H}}/k^{\text{T}}$), assumed to apply to all the disulphones, and by a factor of two for those acids with two dissociating protons. The values, converted to second-order units by dividing by 55.5, are shown in Table 2. These data are plotted in the Figure together with data which will be dis-

cussed later, for proton transfer from 1,1-bisethylsulphonyl-ethane to a series of bases. The logarithm of the rate coefficient for proton transfer is plotted against the difference in pK^0 between the disulphone and base catalyst, both functions being statistically corrected. The line in the Figure for water catalysis and the Brønsted plot of the detritiation rates are similar. This form, however, allows a better comparison with the other data shown.

Reverse Rate Calculations.—The rate coefficients for recombination of the carbanions with hydronium ion (k_{-1} ; 298.2 K; $I = 0.1M$) were calculated by dividing the rate coefficients for proton transfer (k_1) by the dissociation constants of the disulphones. The dis-



sociation constant at $I = 0.1M$ was used; it was calculated from the thermodynamic value using the expression $\log \gamma_{\pm} = -0.51 \sqrt{I}/(1 + \sqrt{I})$. For bisethylsulphonyl-methane, using $pK^0 = 12.20 \pm 0.04$, $k^T = 2.75 \pm 0.06 \times 10^{-3} \text{ s}^{-1}$, and $k^H/k^T = 3.1 \pm 0.1$, a value of $k_{-1} = 1.6 \pm 0.3 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$ is obtained. The pK^0 values for the two weakest acids are least precise since calculation of their values assumes cancellation of the activity coefficient ratios for the carbon acid and h_- indicator. Therefore, except for α, α -bisethylsulphonyltoluene the reverse rate coefficients in Table 2 are the same, and the values are very close to those expected for a diffusion controlled reaction. The anomalous data for α, α -bisethylsulphonyltoluene will be the subject of a subsequent publication.*

DISCUSSION

The value of the Brønsted exponent ($\alpha = 1.1 \pm 0.1$) for the reaction of disulphones with water and the magnitude of the rate coefficients for recombination of the carbanions with hydronium ion ($2 \times 10^{10} \text{ l mol}^{-1} \text{ s}^{-1}$) are precisely the results expected for the normal ionisation of a weak acid. This behaviour contrasts with other carbon acids of similar acidity.^{3a}

Before discussing the unusual behaviour of disulphones, further relevant information can be obtained by comparing the present results with Bell and Cox's study⁶

* The effect relative to hydrogen of introducing an α -phenyl substituent into bisethylsulphonylmethane is to *reduce* the rate of carbanion formation despite an *increase* in the thermodynamic acidity. The rate coefficient for reaction between α, α -bisethylsulphonyltoluene and hydronium ion is about a factor of 40 below the other reverse rates and below the diffusion limit. However, those derivatives with phenyl attached only indirectly to the α -carbon atom, through sulphonyl groups, show normal reverse rates. The expected effect of an α -phenyl substituent is to stabilise the carbanion and transition state by inductive and mesomeric electron withdrawal into the aromatic ring. There are at least two possible explanations for the unusual observed effect. The first notes that, of all these compounds, α, α -bisethylsulphonyltoluene contains the most bulky groups around the acidic site. The second possibility depends upon the fact that sp^2 carbon atom is more electronegative than sp^3 hybridised carbon atom. If we assume that in the transition state for the disulphone, carbon is approximately sp^2 hybridised and that this carbon is more electronegative than the sp^3 carbon atom of the carbon acid even though a negative charge is generated, then the normal inductive withdrawal by phenyl will destabilise the transition state compared with the reactants (see J. Hine, L. G. Mahone, and C. L. Liotta, *J. Amer. Chem. Soc.*, 1967, **89**, 5911). This effect will be overcome in the carbanion however by the mesomeric effect of phenyl which is more fully operative than in the transition state.

of base catalysed proton transfer from 1,1-bisethylsulphonyl-ethane. Rate coefficients for proton transfer to three carboxylate ions, to hydroxide ion, and to water were calculated from rates of bromination and combined with a previous value for *m*-nitrophenolate ion.¹² A Brønsted plot for the different bases gave β ca. 0.8. We will show that a more likely value calculated from these results is $\beta = 1.0$, which is probably not outside the uncertainty set by β ca. 0.8. Bell's data, excluding the point for hydroxide ion, are given in the Figure for comparison with the present results. Our reason for omitting hydroxide ion is based on its frequently anomalous behaviour when compared with other bases in plots of this kind.^{1,13} The point for the water catalysed proton transfer of 1,1-bisethylsulphonyl-ethane is the final lower point on the $B = H_2O$ line. The Figure makes it clear that catalysis by the carboxylate and *m*-nitrophenolate ions is fitted by a different line from that which defines catalysis by water. Hence a more probable value for the Brønsted coefficient calculated from Bell's data neglects the water point and is given by the slope of this separate line, $\beta = 1.0$. Both sets of data, therefore, give Brønsted exponents which are close to the limiting values of unity. The different Brønsted lines mean that the rates of the reverse reactions are different. For recombination of the carbanions with general acids, the value ($1 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$) is more than two orders of magnitude below the rates for recombination with hydronium ion.

The Brønsted exponent for a reaction is often used as an approximate indication of the degree of proton transfer in the transition state.¹⁴ Recent criticisms¹⁵ of this concept have been based on a study of proton transfer from nitro-substituted carbon acids in which different exponents were generated by changing the carbon acid and base catalyst. In the present study, however, compatible values are obtained in these two ways. Therefore we tentatively conclude that the Brønsted coefficients for proton transfer from disulphones to weak bases indicate that the carbon-hydrogen bond is almost fully broken in the transition state. In a qualitative way, the very low primary isotope effect confirms this conclusion. In addition, the solvent isotope effect $k^T(\text{H}_2\text{O})/k^T(\text{D}_2\text{O}) = 3.5$ is consistent with a transition state having the structure $\text{RC}^- \cdots \text{H}_3\text{O}^+$. The detailed arguments which lead to this conclusion are presented in an earlier study of proton transfer from malononitriles in which a similar solvent isotope effect of 3.6 was observed.⁵

The above evidence shows that disulphones closely

¹² B. G. Cox, F. G. Riddell, and D. A. R. Williams, *J. Chem. Soc. (B)*, 1970, 859; see also footnote in ref. 6.

¹³ R. P. Bell, R. D. Smith, and L. A. Woodward, *Proc. Roy. Soc.*, 1948, **A**, 192, 479.

¹⁴ (a) Ref. 3 (a), ch. 10; (b) J. E. Leffler and E. Grunwald, 'Rates and Equilibria of Organic Reactions,' Wiley, New York, 1963, p. 157; (c) R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891; (d) W. J. Albery, A. N. Campbell-Crawford, and J. S. Curran, *J.C.S. Perkin II*, 1972, 2206.

¹⁵ F. G. Bordwell, W. J. Boyle, jun., and K. C. Yee, *J. Amer. Chem. Soc.*, 1970, **92**, 5926.

resemble cyanocarbon acids¹ and we can summarise the behaviour of both as follows: (a) Brønsted exponents are equal to the limiting values of unity; (b) recombination rates are near the diffusion limit for reaction with hydronium ion but at least an order of magnitude lower for reaction with general acids; (c) primary and solvent kinetic isotope effects are consistent with an ion-pair transition state. Both these classes of carbon acid approach *normal* proton transfer behaviour.

In comparing disulphones and cyanocarbons with other substituted carbon acids, it is apparent that a spectrum of proton transfer behaviour is observed depending upon the activating substituents in the molecule. Generally, groups which have a large acidifying effect on the carbon acid bring about the largest departure from normal behaviour. Recent results show that chloroform may be fully normal in its ionisation behaviour.¹⁶ Since ionisation of carbon acids depends upon the ability of the substituent to delocalise charge, the strongest activating groups result in large structural differences between the acid and its anion. Ionisation which is accompanied by electronic and geometrical rearrangement will occur with a higher activation energy than a process which takes place with little such rearrangement. Ionisation of cyano and sulphonyl carbon acids must occur with relatively minor structural modification. In the thermodynamically favourable direction, the main activation barrier is provided by the encounter of the reacting species and the actual proton transfer contributes little.

Marcus^{14c} has proposed a new theory for proton transfer reactions which successfully explains data for a number of carbon acids.^{14d,17} The results for disulphones and cyanocarbons provide a further test. The theory, as applied to these acids, is shown in equations (2) and (3), where $\Delta G_{\text{forward}}^{\ddagger}$ is the free energy of activation for proton transfer from RCH to B and ΔG_{TD}^0 is the standard free energy change for the overall reaction. The standard free energy change for the association of RC^- with BH^+ prior to proton transfer is $W_p(\text{RC}^- \cdots \text{BH}^+)$.

$$\Delta G_{\text{forward}}^{\ddagger} = \Delta G_{\text{TD}}^0 + W_p(\text{RC}^- \cdots \text{BH}^+) \quad (2)$$

$$\Delta G_{\text{reverse}}^{\ddagger} = W_p(\text{RC}^- \cdots \text{BH}^+) \quad (3)$$

Differentiation of (2) with respect to ΔG_{TD}^0 gives the Brønsted exponent, α or $\beta = 1.0$. The calculated free

¹⁶ F. A. Long and Z. Margolin, *J. Amer. Chem. Soc.*, 1972, **94**, 5108.

energy changes $W_p(\text{RC}^- \cdots \text{BH}^+)$ for association of disulphonyl carbanions with hydronium ion and carboxylic acids are respectively 14 and 27 kJ mol⁻¹. For cyanocarbanions, the corresponding values are 19 and 27 kJ mol⁻¹. For the disulphonyl carbanion and hydronium ion the value is only slightly larger than the value for diffusion together of the two species. In all the other cases, however, the association step has a substantial free energy and is therefore a necessary part of the Marcus theory. The results also confirm a recent prediction by Kreevoy^{17c} that, owing to the existence of an association step in proton transfer to carbon, even a reaction which is strongly favoured thermodynamically will have a rate well below the diffusion limit but will otherwise show the characteristics of a diffusion limited process. The association step involves locating the acid catalyst in the vicinity of the carbanion together with the accompanying solvent reorganisation. Hence we may expect similar W_p terms for different carbon acids. For proton transfer from carboxylic acids to diazoacetate ion a value for W_p is found,^{17c} which is very close to the values obtained here. The rates and general behaviour of this carbanion are otherwise very different from the present molecules.

The relative magnitude of the W_p values for reaction of the disulphonyl- and cyano-carbanions with hydronium ion compared with general acids is notable. The values correspond to enhanced rates for hydronium ion over general acids of 200- and 40-fold for disulphonyl- and cyano-carbanions respectively. These differences result in Brønsted plots for catalysis by water and by carboxylate ions which have the same slope but which are displaced by about two orders of magnitude. A partial explanation for this is the unique mechanism available to proton diffusion in aqueous solution. The major difference, however, probably results from the different energies involved in desolvating and locating the acid catalyst near the substrate.^{17c} The different charge types of the catalysts, hydronium ion and carboxylic acids, could account for this. For example, the carbanion of 1,4-dicyanobut-2-ene reacts with phenols at a rate which is ten times smaller than that for substituted ammonium ions.¹

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¹⁷ (a) A. O. Cohen and R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 4249; (b) R. A. Marcus, *J. Amer. Chem. Soc.*, 1969, **91**, 7224; (c) M. M. Kreevoy and D. E. Konasewich, *Adv. Chem. Phys.*, 1971, **21**, 243.