Kinetic Isotope Effects and Aliphatic Diazo-compounds. Part VI.† The Values of α and the Marcus Theory

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The collected data for proton transfer to three diazo-compounds, namely diazoacetate anion, 3-diazobutan-2-one, and ethyl diazopropionate, show that although the rates of the reactions are different the details of the proton-transfer part of the reaction are very similar. This qualitative conclusion is reinforced by quantitative analysis according to the Marcus theory. The Brønsted α changes if the catalyst is changed but not if the diazo-compound is changed. This difference is connected with the difference between C bases and O and N bases. A model in which the acid strengths of the C base varies continuously with the solvation co-ordinate is examined and rejected. An extended version of the Marcus expression is developed and it is shown that the diazo-systems and the protonation of nitro-compounds, for which α_S is negative, can be successfully described by the extended theory. The data for the nucleophilic attack in the second step of the decomposition of the three diazo-compounds are compared and the suggested differences in mechanism between diazoacetate anion and 3-diazobutan-2-one are shown to be reasonable.

THE reactions involved in the acid-catalysed decomposition of the three diazo-compounds, ethyl diazopropionate $N_2{:}CMe{\cdot}CO_2Et$, 3-diazobutan-2-one,[1-3] $N_2{:}CMe{\cdot}CO{\cdot}Me$, and diazoacetate anion[4] $N_2{:}CH{\cdot}CO_2^-$, may be written as in Scheme 1. H_3O^+ and H_2O are treated as special cases because if H_2O is a reactant or a product then the reaction cannot be limited by diffusion together of the reactants or diffusion away of the products. Table 1 compares the kinetic parameters found for these reactions.[1-7] The forward rate constants for the first step contain both the diffusion pre-equilibrium and the proton transfer (1); k_2 and k'_{H_2O} refer to

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† Part V, W. J. Albery, J. R. Bridgeland, and J. S. Curran, preceding paper.

[1] W. J. Albery, A. N. Campbell-Crawford, and K. S. Hobbs, *J.C.S. Perkin II*, 1972, 2180.

[2] W. J. Albery, J. S. Curran, and A. N. Campbell-Crawford, *J.C.S. Perkin II*, 1972, 2185.

[3] W. J. Albery, A. N. Campbell-Crawford, and R. W. Stevenson, *J.C.S. Perkin II*, 1972, 2198.

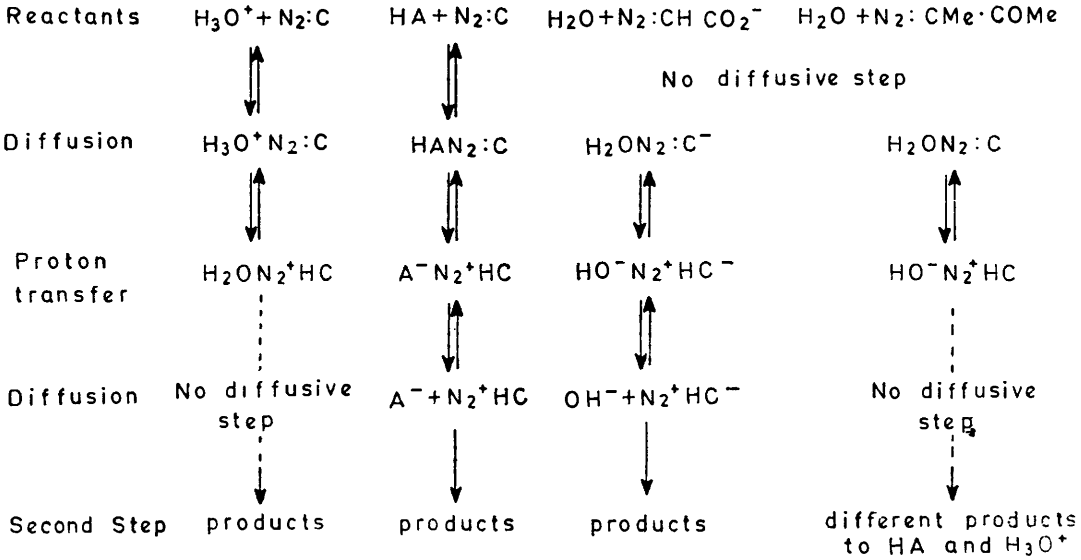
[4] M. M. Kreevoy and D. E. Konaeswich, *J. Phys. Chem.*, 1970, **74**, 4464.

[5] W. J. Albery and A. N. Campbell-Crawford, *J.C.S. Perkin II*, 1972, 2190.

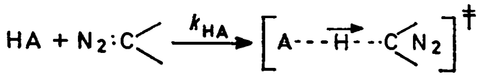
[6] W. J. Albery, J. R. Bridgeland, and J. S. Curran, preceding paper.

[7] M. M. Kreevoy and D. E. Konasewich, *Adv. Chem. Phys.*, 1971, **21**, 243.

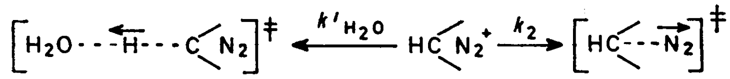
the rate constants describing the fates of the protonated intermediate (2). The second step probably involves nucleophilic participation by H_2O in the case of 3-diazobutan-2-one and ethyl diazopropionate.[2] For the former k_{L_2O} refers to the attack of water with the second step, the nucleophilic attack of OH^- being rate-determining; for diazoacetate anion k_{L_2O} refers to the first step, the proton transfer from H_2O to the diazo-compound. The rate constants [1-7] in Table 1 have been ' normalised ' by dividing them by k_{H^+}. When this is done it is striking how similar is the behaviour of the three different diazo-compounds despite the fact that diazoacetate anion reacts 10^5 times more rapidly than 3-diazobutan-2-one; the relative rates for the different catalysts, the values of α_L, ϕ_1, and k_2/k'_{H_2O} are all very similar.



Scheme 1



(1)



(2)

Kreevoy and Konasewich[7] have discussed the data for diazoacetate anion in terms of the Marcus theory[8] of proton transfer. The theory states equation (3) where

$$\Delta G_{\ddagger}^{\circ} = w_{\mathrm{R}} + \tfrac{1}{4}\lambda\left(1 + \frac{\Delta G_{\mathrm{R}}^{\circ}}{\lambda}\right)^2 \qquad (3)$$

$\Delta G_R^\circ = \Delta G_{TD}^\circ - w_R - w_P$, $\Delta G_\ddagger^\circ$ is the free energy of activation, w_R is a term describing solvation changes on bringing the reactants together, w_P is a similar term for separating the products, ΔG_{TD}° is the thermodynamic change in free energy for the proton transfer, ΔG_R° is that part of ΔG_{TD}° concerned with driving the proton transfer, and $\lambda/4$ is the free-energy barrier for the symmetrical proton transfer when $\Delta G_R^\circ = 0$.

Depending on one's faith the theory can be derived, justified, or suggested from or by the successful Marcus theory of electron transfer by use of a bond-order argument. Even if one is agnostic, equation (3) is at least a convenient algebraic expression. The Brønsted α_B can be expressed in Marcus parameters by differentiating it to give equation (4). Kreevoy and Konasewich[7]

$$\alpha_B = \left(\frac{\partial \Delta G_{\ddagger}^{\circ}}{\partial \Delta G_{\mathrm{TD}}^{\circ}}\right)_{\lambda, w_{\mathrm{R}}, w_{\mathrm{P}}} = \tfrac{1}{2}\left(1 + \frac{\Delta G_{\mathrm{R}}^{\circ}}{\lambda}\right) \qquad (4)$$

discussed the conditions under which λ, w_R, and w_P may be expected to be constant; in particular for a family of similar acids (*e.g.*, carboxylic) the assumptions are likely to hold. In equation (4) for a symmetrical transfer, $\Delta G_R^\circ = 0$ and $\alpha = \frac{1}{2}$; for a downhill transfer $\Delta G_R^\circ < 0$, $\alpha_B < \frac{1}{2}$ and the transition state is reactant-like, while for an uphill transfer $\Delta G_R^\circ > 0$, $\alpha_B > \frac{1}{2}$ and the transition state is product-like. These changes are in accordance with the Hammond postulate. Thus for an acid-catalysed reaction α becomes less the lower the pK of the acid catalyst. This is the behaviour found in the

[8] R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891.

diazo-systems, with α changing from 0·6 for $R{\cdot}CO_2H$ to 0·3 for H_3O^+. It should be pointed out that the Marcus curvature of the Brønsted plot is quite different from the curvature discussed by Eigen.[9] In the Marcus case the rate-determining process is always the actual proton transfer while in the Eigen case the curvature is caused by a shift in the rate-determining process from the proton transfer to the diffusion of reactants or products.

TABLE 1

Kinetic parameters for diazo-compounds from references 1—7

	3-Diazobutan-2-one	Ethyl diazopropionate	Diazoacetate anion
k_{H^+}/l mol^{-1} s^{-1}	0·74	19·2	$6{\cdot}5 \times 10^4$
k_{HA}/k_{H^+} for HA=			
$CCl_2H{\cdot}CO_2H$	1·0	0·9	0·25
$CClH_2{\cdot}CO_2H$	$1{\cdot}4 \times 10^{-1}$	$1{\cdot}5 \times 10^{-1}$	$0{\cdot}4 \times 10^{-1}$
$NCCH_2{\cdot}CO_2H$			$0{\cdot}9 \times 10^{-1}$
$HOCH_2{\cdot}CO_2H$	$3{\cdot}3 \times 10^{-2}$	$3{\cdot}4 \times 10^{-2}$	
AcOH	7×10^{-3}	8×10^{-3}	4×10^{-3}
α_B	0·61	0·59	0·51
Isotopic α_S			
$\alpha_{L_3O^+}$	0·27	0·29	0·30
$\alpha_{L_2C{\cdot}CO_2H}$	0·64		
α_{LCO_2H}	0·64		
Primary fractionation factors ϕ_1			
L_3O^+	0·22	0·22	0·24
AcOL		0·26	0·18
$C_6H_5NL^+$	0·26		
k_2/k_{H_2O}'	9×10^{-3}	10×10^{-3}	5×10^{-3}
$\Pi\phi_{2.\ddagger}$	0·76		1·2
$k_{H_2O}/k_{H^+}[H_2O]$		7×10^{-10}	$1{\cdot}1 \times 10^{-11}$
k_{D_2O}/k_{H_2O}		1·2	0·27

Besides predicting a change in α, equation (3) also splits the activation process into the solvation term, w_R, and the proton-transfer term. We first argue qualitatively from the data in Table 1, which show that the proton-transfer characteristics for the three diazo-compounds are very similar, that the main change in $\Delta G_{\ddagger}^{\circ}$ when one changes the diazo-compound does not lie in the λ term but in w_R. This conclusion does not depend upon a detailed quantitative analysis of the data according to equation (3). However such an analysis can be carried out in two ways. The first method is to analyse the curvature on the Brønsted plot. We fit the rate data to equation (5) where $z = \log (qK_{HA}/p)$ and for

$$\log (k_{HA}/p) = A + Bz + Cz^2 \qquad (5)$$

carboxylic acids $p = 1$ and $q = 2$. Then we obtain equations (6) and (7), for which values are given in Table 2.

$$\lambda = -2{\cdot}3RT/4C \qquad (6)$$

$$w_R = 2{\cdot}3RT\,[\log (kT/h) - A + B^2/4C] \qquad (7)$$

The second method compares the data for the carboxylic acids with those for H_3O^+. The points for H_3O^+ and $C_5H_5NH^+$ do not lie on the Brønsted plot for the carboxylic acids.[1,3] The primary fractionation factor ϕ_1 for $C_5H_5N^+H$ however is similar to that for AcOH,[3] and it seems reasonable to assume that the difference between the positively charged catalysts and the carboxylic acids lies in the w_R term. As we have shown[5] the transfers from H_3O^+ and $C_5H_5NH^+$ do not take place through solvent bridges and so to reach the transition state desolvation of the catalyst must take place, for instance from $H_9O_4^+ + S$ to $H_7O_3^+S$. This step will be more unfavourable for positively charged catalysts than for the neutral carboxylic acids. Hence we may expect that w_R will be different for H_3O^+ and AcOH.

Before we can calculate λ we have to make an assumption about w_P. For the carboxylic acids we assume that for reaction (8) $K_{DP} = ca.$ 1 mol l^{-1} and hence

$$A^-HS^+ \rightleftharpoons A^- + HS^+ \qquad (8)$$

$w_P \simeq RT \ln K_{DP} \simeq 0$. This leads to equation (9)

$$\Delta G_{TD}^{\circ} - w_P \simeq -RT\,[\ln (K_{HA}q/p) - \ln (K_{HS})] \qquad (9)$$

where K_{HS} is the dissociation constant for reaction (10).

$$SH^+ \rightleftharpoons S + H^+ \qquad (10)$$

For H_3O^+, for the step (11) $w_P = 0$ and, since the pro-

$$H_2OHS^+ + H_2O \rightleftharpoons H_2O + H_2OHS^+ \qquad (11)$$

tonation is the reverse of the SH^+ dissociation, we obtain equation (12). From equations (3), (4), (9), and (12) we obtain equations (13)—(16). We then obtain

$$\Delta G_{\ddagger.HA} = w_{R.HA} + \lambda\alpha_{HA}^2 \qquad (13)$$

$$\Delta G_{\ddagger.H_3O^+} = w_{R.H_3O^+} + \lambda\alpha_{H_3O^+}^2 \qquad (14)$$

$$2\alpha_{HA} = 1 - \lambda^{-1}[RT \ln (qK_{HA}/P) - RT \ln (K_{HS}) + w_{R,HA}] \qquad (15)$$

$$2\alpha_{H_3O^+} = 1 + \lambda^{-1}[RT \ln (K_{HS}) - w_{R,H_3O^+}] \qquad (16)$$

equation (17) where $\bar{k}_{HA}$ and $\bar{K}_{HA}$ are values near the

$$\lambda = \frac{RT \ln (\bar{k}_{HA}/qk_{H_3O^+}\bar{K}_{HA})}{(\alpha_{HA} - \alpha_{H_3O^+})(2 - \alpha_{HA} - \alpha_{H_3O^+})} \qquad (17)$$

middle of the range of carboxylic acids studied; $w_{R.HA}$ and $w_{R.H_3O^+}$ can be obtained by substitution in equations (13) and (14).

Values of $\lambda/4$, the free-energy barrier for the symmetrical proton transfer, and w_R are given in Table 2. Despite the uncertainty the values are in reasonable agreement. Our value of $\lambda/4$ is somewhat smaller than that of Kreevoy and Konasewich;[7] this agrees with a larger change in α for 3-diazobutan-2-one and ethyl

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[9] M. Eigen, *Angew. Chem.*, 1963, **75**, 489.

diazopropionate than for diazoacetate anion. We have also shown in Table 2 the effect on w_R of taking Kreevoy's value of $\lambda/4$; diazoacetate anion reacts more rapidly than our compounds and so Kreevoy and Konasewich have been able to study a wider range of catalysts.[4]

TABLE 2

Estimates of Marcus parameters

	Eqn.	3-Diazobutan-2-one	Ethyl diazopropionate
A	5	$0{\cdot}26 \pm 0{\cdot}04$	$1{\cdot}60_5 \pm 0{\cdot}025$
B	5	$0{\cdot}40_5 \pm 0{\cdot}09$	$0{\cdot}34 \pm 0{\cdot}09$
C	5	$-0{\cdot}037 \pm 0{\cdot}016$	$-0{\cdot}047 \pm 0{\cdot}013$
$\lambda/4$/kJ mol^{-1}	6	10	8
$w_{R.HA}$/kJ mol^{-1}	7	65	60
$\lambda/4$/kJ mol^{-1}	17	7	8
$w_{R.HA}$/kJ mol^{-1}	13	70	59
$w_{R.H_3O^+}$/kJ mol^{-1}	14	73	62
$\lambda/4 = 17$ kJ mol^{-1}	12[a]		
$w_{R.HA}$/kJ mol^{-1}	13	55	46
$w_{R.H_3O^+}$/kJ mol^{-1}	14	69	59

[a] For diazoacetate anion, $w_{R.HA} = 34$ kJ mol^{-1} and $\lambda/4 = 17$ kJ mol^{-1}.

Whatever the method of calculation, the figures in Table 2 confirm quantitatively the qualitative conclusion given above that for the same catalyst, the change in $\Delta G_{\ddagger}°$ caused by changing the diazo-compound is nearly all in the w_R term.

Thus an interesting difference appears in the effect on $\Delta G_{\ddagger}°$ of changing $\Delta G_{TD}°$ between changing the catalyst for the same diazo-compound and changing the diazo-compound for the same catalyst. In the first case α changes continuously with the catalyst;[7] in the second case α remains approximately constant and w_R changes. This difference in behaviour must be connected with the fact that the catalysts are oxygen and nitrogen bases whereas in the diazo-compounds the proton is transferred to carbon with attendant changes in the π-system of the diazo-compound. The Marcus theory assumes that w_R is connected with solvation changes, and Kreevoy and Konasewich discuss[7] the value of $w_R = ca.$ 30 kJ for diazoacetate anion in terms of localisation of the reactants and desolvation of one H bond. The values of w_R for 3-diazobutan-2-one and ethyl diazopropionate seem to be too large to be attributed to the first diffusive step in the reaction scheme. Indeed, following Kreevoy and Konasewich,[7] we have a further argument that w_R must be a substantial term since $\alpha = ca. \frac{1}{2}$ when the catalysing acid has pK *ca.* 1·5. From equation (15), if w_R were to be negligible, when $\alpha = \frac{1}{2}$, equation (18) would be required. It is however

$$K_{HS} \simeq 2K_{HA} \simeq 3 \times 10^{-2} \text{ mol l}^{-1} \tag{18}$$

very unlikely that K_{HS} is as small as this; ethyl diazoacetate is not protonated to any significant extent in 2·5M-HClO$_4$.[10]

But, again following Kreevoy and Konasewich,[7] when the k_2 step is rate-determining $k_{-D}[A^-] > 10k_2$, where $k_{-D} = ca.\ 10^{10}$ l mol^{-1} s^{-1}, and describes the diffusion-controlled rate of $A^- + SH^+$. The inequality arises from the fact that the diffusion step between the proton transfer and k_2 does not become rate-determining. The lowest concentration of A^- where the k_2 step is partially rate determining is $[A^-] = ca.\ 10^{-2}$M, whence $k_2 < 10^7$ s^{-1}. In the case of diazoacetate anion the A^- is OH^-.

Therefore from the data in Table 1 we obtain equations (19) and (20), which give values of $K_{HS} < 10^5$ mol l^{-1}

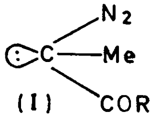
$$k'_{H_2O} < 10^5 \text{ s}^{-1} \tag{19}$$

$$K_{HS} = k'_{H_2O}/k_{H^+} \tag{20}$$

for 3-diazobutan-2-one, or $<5 \times 10^3$ mol l^{-1} for ethyl diazopropionate, or <1 mol l^{-1} for diazoacetate anion. Substitution of the values from Table 2 in equation (16) gives $K_{HS} = ca.\ 10^{10}$ mol l^{-1} for 3-diazobutan-2-one and *ca.* 10^8 mol l^{-1} for ethyl diazopropionate. These values do not agree with the inequalities deduced above. Even for diazoacetate anion, using equation (15) and Kreevoy and Konasewich's values[7] we get equation (21).

$$K_{HS} = 10^2 \text{ mol l}^{-1} \tag{21}$$

In order to explain this apparent discrepancy and the large values of w_R for 3-diazobutan-2-one and ethyl diazopropionate we have considered a model in which the acid–base properties of the diazo-compound varies continuously with its solvation and geometry. We write S_1 for the diazo-compound in its normal solvation and HS_2^+ for the normally solvated protonated intermediate; then $K_{HS_1} \gg 1$ and $K_{HS_2} \ll 1$. When $\alpha_B = ca. \frac{1}{2}$, $K_{HS\ddagger} = ca.\ K_{HA}$ where $HS_{\ddagger}$ and $S_{\ddagger}$ are the intermediate species between which the proton transfer takes place. The more basic intermediate $S_{\ddagger}$ may differ from S_1 in solvation and the rotation of the C–C bond which destroys the diazo π-system. In the limit S_2 would have tetrahedral bond angles and would be shown in structure (I). The change in free energy with solvation and degree of proton transfer is plotted schematically in Figure 1(a). It is worth mentioning that a scheme such as this must hold for the effect of salts on reaction rates, for instance a solvolysis reaction, as shown in Figure 1(b). In dilute solutions the time in which an ionic atmosphere can form is several orders of magnitude less than the time for atom transfer. Thus the formation of the ionic atmosphere must be a pre-equilibrium followed by a rate-determining atom transfer; in other words from all the reactant molecules in different ionic environments those that react have an



(I)

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[10] W. J. Albery and R. P. Bell, *Trans. Faraday Soc.*, 1961, **57**, 1942.

abnormal atmosphere for the reactants but one that is particularly suited for the transition state. In this case because of the different time scales a sort of Franck–Condon principle applies. For the solvation–proton transfer case it is difficult to know whether the solvation changes are closely coupled with the proton transfer or not. If they are not then motion on the reaction surface in Figure 1(a) has to be a series of horizontal and vertical steps; if the vibrations are coupled then some diagonal motion is also possible. Since the solvent motions have a large rotational component we will assume that the vibration of the proton is not too closely coupled. Figure 1(a) is idealised in Figure 1(c) where we have assumed a linear free-energy relationship between the effect of the changes in solvation on S and on HS^+.

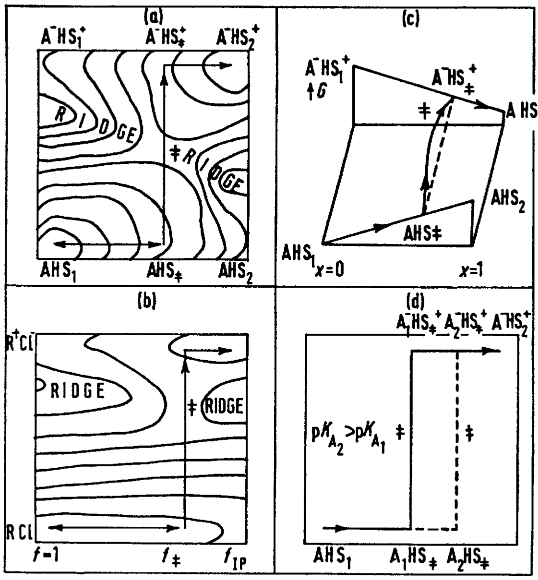


FIGURE 1 Schematic free-energy surfaces for the continuous model; (a), proton transfer–solvation; (b), atom transfer, ionic atmosphere; (c), idealised form of (a); (d), effect of changing catalyst

We write equations (22) and (23) where $\chi = 0$ for S_1

$$w_R = w_{R,O} + m_R\chi \qquad (22)$$

$$w_P = 0 - m_P(1 - \chi) \qquad (23)$$

and $\chi = 1$ for HS_2^+. The term $m_R\chi$ would explain why $w_R > w_{R,O}$ where $w_{R,O}$ is the value for the first diffusive step. Then equation (24) follows, where α_{PT} is given

$$\Delta G_\ddagger^\circ = w_{R,O} + m_R\chi + \lambda\alpha_{PT}^2 \qquad (24)$$

by equation (25) and describes the symmetry of the proton-transfer part of the reaction. For the saddle

$$\alpha_{PT} = \tfrac{1}{2}\left(1 + \frac{\Delta G_{TD}^\circ - w_{R,O} - m_R\chi + m_P - m_P\chi}{\lambda}\right) \qquad (25)$$

point at the transition state we obtain equation (26)

$$\partial\Delta G_\ddagger^\circ/\partial(m_R\chi) \simeq 0 = 1 - \alpha_{PT}(1 + m_P/m_R) \qquad (26)$$

which leads to (27) and then (28).

$$\alpha_{PT} = 1/(1 + m_P/m_R) \qquad (27)$$

$$\begin{aligned}\alpha &= \partial\Delta G_\ddagger^\circ/\partial\Delta G_{TD}^\circ \\ &= m_R\partial\chi/(m_R + m_P)\partial\chi = \alpha_{PT}\end{aligned} \qquad (28)$$

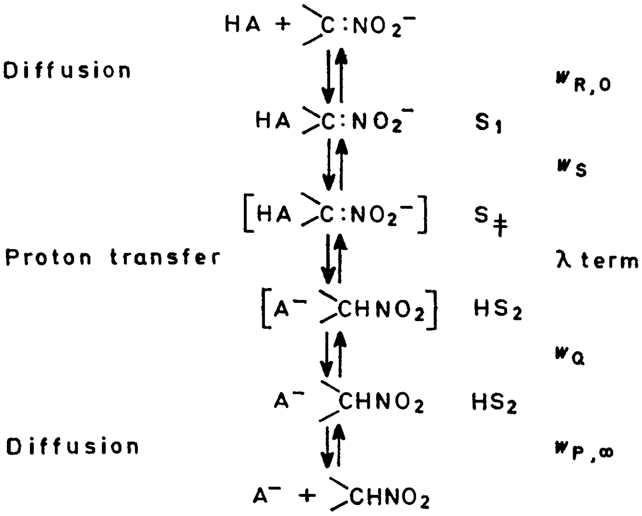
Thus this model has the surprising result that α is constant and does not vary with catalyst strength. Figure 1(d) shows the effect of changing the catalyst for $\alpha = \frac{1}{2}$ ($m_R = m_P$); the stronger catalyst requires a smaller value of χ. Even though α is fixed by m_R and m_P it still describes the symmetry of the transition state. This model may be applicable to reactions which show little deviation from a linear Brønsted plot but unfortunately it does not fit the data for the diazo-systems. We therefore have to reject a model in which ΔG_R° is a continuous function of the change in solvation.

We replace the smooth monotonic variation of G along the solvation co-ordinate with a more 'up-and-down' model in which the differently solvated states are better defined and are separated from one another by free energy barriers. Instead of equation (29) we write (30)

$$w_R = w_{R,O} + m_R\chi \qquad (29)$$

$$w_R = w_{R,O} + w_S \qquad (30)$$

and instead of $m_P(1 - \chi)$ we write w_Q, where w_S and w_Q are constants (and not variable terms) for each diazo-compound for changing S_1 to $S_\ddagger$ and $HS_\ddagger^+$ to HS_2^+ respectively. From the analysis of the continuous model the change S_1 to $S_\ddagger$ may well be such that α is very approximately equal to $\frac{1}{2}$. The protonation and deprotonation (Scheme 2) of a nitro-compound is very



SCHEME 2

similar to the first step of our system. Hence for both diazo- and nitro-compounds we have equation (31).

$$\Delta G_{\ddagger}{}^{\circ} = w_{\mathrm{R,O}} + w_{\mathrm{S}} + \frac{\lambda}{4}\left(1 + \frac{\Delta G_{\mathrm{TD}}{}^{\circ} - w_{\mathrm{R,O}} - w_{\mathrm{S}} - w_{\mathrm{Q}} - w_{\mathrm{P,\infty}}}{\lambda}\right)^2 \quad (31)$$

Now on changing the HA species one obtains an ordinary Brønsted plot and equation (19) is differentiated as in equation (4) with the w terms constant to obtain α_{B}. However on changing S, w_{S} and w_{Q} will not be constant and equation (32) reduces to equation (33) or,

$$\alpha_{\mathrm{S}} = \frac{\partial w_{\mathrm{S}}}{\partial \Delta G_{\mathrm{TD}}{}^{\circ}} + \alpha_{\mathrm{B}}\left[1 - \frac{\partial(w_{\mathrm{S}} + w_{\mathrm{Q}})}{\partial \Delta G_{\mathrm{TD}}{}^{\circ}}\right] \quad (32)$$

$$= \alpha_{\mathrm{B}} + (1 - a_{\mathrm{B}})\partial w_{\mathrm{S}}/\partial \Delta G_{\mathrm{TD}}{}^{\circ} - \alpha_{\mathrm{B}}\partial w_{\mathrm{Q}}/\partial \Delta G_{\mathrm{TD}}{}^{\circ} \quad (33)$$

for the base catalysed deprotonation, we obtain equation (34). Bordwell, Boyle, and Yee[11,12] have shown that

$$\beta_{\mathrm{S}} = \beta_{\mathrm{B}}(1 - \partial w_{\mathrm{S}}/\partial \Delta G_{\mathrm{TD}}{}^{\circ}) + (1 - \beta_{\mathrm{B}})\partial w_{\mathrm{Q}}/\partial \Delta G_{\mathrm{TD}}{}^{\circ} \quad (34)$$

for $\mathrm{ArCH_2{\cdot}CHMe{\cdot}NO_2}$ and $\mathrm{ArCHMe{\cdot}NO_2}$ β_{S} is found to be 1·61 and 1·37 respectively while[13] β_{B} is *ca.* 0·5. This yields equation (35). Substitution in equation (33) then

$$\partial(w_{\mathrm{Q}} - w_{\mathrm{S}})/\partial \Delta G_{\mathrm{TD}}{}^{\circ} \simeq 2 \quad (35)$$

gives a negative value for α_{S}. Since $\Delta G_{\mathrm{R}}{}^{\circ} = \Delta G_{\mathrm{TD}}{}^{\circ} - w_{\mathrm{R,O}} - w_{\mathrm{S}} - w_{\mathrm{Q}} - w_{\mathrm{P}}$, we obtain equation (36). Table

$$\partial \Delta G_{\mathrm{R}}{}^{\circ}/\partial \Delta G_{\mathrm{TD}}{}^{\circ} = 1 - \partial(w_{\mathrm{S}} + w_{\mathrm{Q}})/\partial \Delta G_{\mathrm{TD}}{}^{\circ} \quad (36)$$

3 gives three possible cases; two extreme ones and one intermediate case.

TABLE 3

Different assumptions about w_{S} and w_{Q} for nitro-systems from equations (35) and (36)

Case	$\partial w_{\mathrm{S}}/\partial \Delta G_{\mathrm{TD}}{}^{\circ}$	$\partial \Delta G_{\mathrm{R}}{}^{\circ}/\partial \Delta G_{\mathrm{TD}}{}^{\circ}$	$\partial w_{\mathrm{Q}}/\partial \Delta G_{\mathrm{TD}}{}^{\circ}$
(I)	-2	3	0
(II)	$-\frac{1}{2}$	0	$\frac{3}{2}$
(III)	0	-1	2

Figure 2 shows schematic free-energy profiles of the three cases and two different substrates (solid and dotted). We have taken the free energy of the protonated compound to be zero for each substrate so that the differences on deprotonation can be seen for a $\partial \Delta G_{\mathrm{TD}}{}^{\circ}$ of 1 arbitrary unit.

Possible reasons for similar differences to those in Figure 2 have been discussed by Bordwell *et al.*[12] For instance taking deprotonation in case (I) the substitution of an electron-withdrawing group (*e.g.*, m-$\mathrm{NO_2}$, solid line) for H (broken line) would not have much effect on the w_{Q} step since the system is still unconjugated. On the other hand the substitution has the biggest effect (3) on $S_{\ddagger}{}^{-}$ where the negative charge is most concentrated on the C atom; the effect on the transition state in between is a fraction (β_{B} = *ca.* 0·5) of that on $\mathrm{S_{\ddagger}{}^{-}}$ ($1\frac{1}{2}$). In the change $\mathrm{S_{\ddagger}{}^{-}}$ to $\mathrm{S_1{}^{-}}$ the development of the bond system with its correct solvation takes negative charge away from the C atom and into the $\mathrm{NO_2}$ group; the inductive effect of the m-$\mathrm{NO_2}$ group then has less effect on $\mathrm{S_1{}^{-}}$ (1) as the charge moves further from the aromatic ring. We cannot say yet whether the system actually passes through $\mathrm{HS_{\ddagger}}$ and $\mathrm{S_{\ddagger}{}^{-}}$ or whether because of coupling it cuts the corners as shown by the broken lines in Figure 2. A similar description can be carried out for cases (II) and (III); however, since for the reasons given above, $\mathrm{S_{\ddagger}{}^{-}}$ will be most sensitive to substitution, the nitro-systems are more like case (I) than the other two cases.

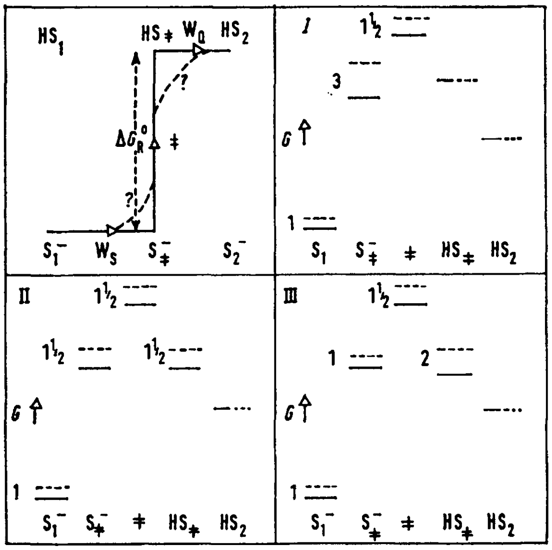


FIGURE 2 Schematic free-energy diagrams for nitro-systems $\mathrm{ArCHMeNO_2}$ and $\mathrm{ArCH_2{\cdot}CHMeNO_2}$. Roman numerals refer to cases in Table 3

Returning to the diazo-systems we cannot measure $\Delta G_{\mathrm{TD}}{}^{\circ}$ and so we cannot find α_{S} directly. However as discussed above the change of S makes little difference to the proton transfer but does make a difference to the overall rate.

Hence in equations (4) and (36) for different S α_{B} is approximately constant, so we obtain equations (37)

$$\partial \Delta G_{\mathrm{R}}{}^{\circ}/\partial \Delta G_{\mathrm{TD}}{}^{\circ} \simeq 0 \quad (37)$$

and (38). In neglecting the w_{Q} term we have assumed,

$$\partial(w_{\mathrm{S}} + w_{\mathrm{Q}})/\partial \Delta G_{\mathrm{TD}}{}^{\circ} \simeq \partial w_{\mathrm{S}}/\partial \Delta G_{\mathrm{TD}}{}^{\circ} \simeq 1 \quad (38)$$

for much the same reasons, that the diazo-system is like

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[11] F. G. Bordwell, W. J. Boyle, J. A. Hautala, and K. C. Yee, *J. Amer. Chem. Soc.*, 1969, **91**, 4002.

[12] F. G. Bordwell, W. J. Boyle, and K. C. Yee, *J. Amer. Chem. Soc.*, 1970, **92**, 5926.

[13] F. G. Bordwell and W. J. Boyle, *J. Amer. Chem. Soc.*, 1971, **93**, 512.

the nitro-system and is case (I). Equation (33) then gives $\alpha_S \simeq 1$. The large and different values of w_R for the three diazo-compounds (Table 2) are caused by w_S. The extra driving force for the proton transfer from w_S explains why, although the overall transfer is uphill ($K_{HS} \gg K_{HA}$), we find that α_B lies in the range 0·3—0·6. But from equation (20) for each compound K_{HS} and hence $\Delta G_{TD}°$ has an upper limit; w_S by itself would then drive the proton transfer too hard leading to very low values of α_B. Hence we have to introduce the w_Q term, which is the counterpart of w_S on the other side of the proton transfer, and, being negative, reduces the driving force. The w_Q term also explains equation (19); this is a slowish rate for a downhill proton transfer. Values of w_Q for 3-diazobutan-2-one are given in Table 4 for different values of w_R and the two limiting values of K_{HS}.

TABLE 4

Possible values of w_Q for 3-diazobutan-2-one (all energies in kJ mol^{-1})

w_R	55	65	70
$K_{HS} = 10^2$	−35	−45	−50
$K_{HS} = 10^5$	−18	−28	−33

Comparing equation (39) with the similar equation

$$\partial w_S/\partial \Delta G_{TD}° = +1 \qquad (39)$$

for the case (I) of the nitro-system [equation (40)], we

$$\partial w_S/\partial \Delta G_{TD}° = -2 \qquad (40)$$

find there is a difference in sign between the diazo-compounds and the nitro-compounds. However for the nitro-compounds the effect of the changes is mainly inductive, changing the rate typically by a factor of 30; for the three diazo-compounds the changes are more drastic involving the conjugation of COMe, CO_2Et, and CO_2^- with the diazo-group and a change in rate of a factor of 10^5. It is therefore not surprising that there is this difference.

What is satisfactory is that our analysis of the diazo-system and Bordwell's analysis of the nitro-system can both be described by equation (31). Both systems require a w_S term, and in both systems we find a difference between changing $\Delta G_{TD}°$ with S or with HA, leading to the two different parameters α_S and α_B. Bordwell has rightly pointed out [11-13] that α_S cannot be a measure of the symmetry of the proton transfer. However if our model is correct, α_B still retains that significance. The agreement of the isotopic α_{LA} with α_B [6] makes us reluctant to abandon this interpretation, since the secondary isotopic substitution is a particularly sensitive and precise probe. The transfer of H^+ to C has been recognised as being more complicated [14,15] than the transfer on to O or N bases. The model presented here retains the form of the Marcus theory but introduces the extra parameters w_S and w_Q which depend only on S and describe the destruction of the π-system when C bases are protonated. The actual proton transfer term (the λ term) does not describe a large barrier and is therefore similar to the corresponding term for O and N bases. For 3-diazobutan-2-one and ethyl diazopropionate, $w_{R.O}$ would be *ca.* 15—30 kJ mol^{-1}, w_S 40—50 kJ mol^{-1}, and the proton-transfer term would have a barrier of *ca.* 10 kJ mol^{-1}. Another proton-transfer system relevant to 3-diazobutan-2-one is the deprotonation of ketones studied by Bell and his group.[14] We can fit Bell's data for 11 ketones to equation (41) where $z = pK_s - 15$, pK_s is the pK of the

$$\log R = A + Bz + Cz^2 \qquad (41)$$

ketone, and R is the rate for deprotonation to the conjugate base of a hypothetical acid of $pK_A = 4$. The standard deviation of the fit was 0·09. Then we obtain equation (42). Table 5 compares β_B for carboxylate

$$\beta_S = -B - 2Cz \qquad (42)$$

catalysis with β_S. Apart from the most unreactive compounds the agreement between β_B and β_S is very striking. Hence from equation (34) we conclude that for this system, whether we change S or A^-, $(\partial w_S/\partial \Delta G_{TD}°) \simeq 0$ and $(\partial w_Q/\partial \Delta G_{TD}°) \simeq 0$. Table 6 gives data on the Marcus parameters calculated from equations (6) and (7). For comparison with the other systems we have reported the data with the forward reaction as the protonation of the carbon base. It is interesting that

TABLE 5

Comparison of β_B and β_S for $B^- + {>}CH{\cdot}C(\dot{:}O)^-$. Data from ref. 14

S	β_B	β_S	pK_S
Me_2CO	0·88	1·13	20·0
$MeCO{\cdot}CH_2{\cdot}CH_2{\cdot}COMe$	0·89	1·07	18·7
$MeCO{\cdot}CH_2Cl$	0·82	0·90	16·5
$MeCO{\cdot}CH_2Br$	0·82	0·88	16·1
$MeCO{\cdot}CHCl_2$	0·82	0·80	14·9
R^1CO_2Et [a]	0·67	0·71	13·1
$MeCO{\cdot}CH_2CO_2Et$	0·59	0·59	10·7
$R^2{\cdot}CO_2Et$ [b]	0·58	0·55	10·0
$MeCO{\cdot}CH_2{\cdot}COPh$	0·52	0·54	9·7
$MeCO{\cdot}CH_2{\cdot}COMe$	0·48	0·51	9·3
$MeCO{\cdot}CHBr{\cdot}COMe$	0·42	0·47	8·3

[a] R^1 = Tetrahydropyran-2-yl. [b] R^2 = tetrahydro-2-furyl.

TABLE 6

Calculation of Marcus parameters for ketone system

			kJ mol^{-1}
A	$-4{\cdot}01 \pm 0{\cdot}02$	$\frac{\lambda}{4}$	14
B	$-0{\cdot}80 \pm 0{\cdot}01$	w_P	−59
C	$-0{\cdot}025 \pm 0{\cdot}002$	w_R	30

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[14] R. P. Bell, 'The Proton in Chemistry,' Cornell Univ. Press, Ithaca, 1959, p. 172.

[15] W. J. Albery, *Progr. Reaction Kinetics*, 1967, **4**, 355.

$\lambda/4$ is of the same order as the values found for the diazo-systems and is relatively small. The main barrier to deprotonation comes in the w_{P} term (43) and taking

$$w_{\mathrm{P}} = w_{\mathrm{Q}} + w_{\mathrm{P},\infty} \qquad (43)$$

a typical value of $w_{\mathrm{P},\infty} = ca.\ -20$ kJ mol^{-1} we obtain $w_{\mathrm{Q}} = ca.\ -40$ kJ mol^{-1}. Like $\lambda/4$ this value is again not too dissimilar from the values for 3-diazobutan-2-one in Table 5. Similarly $w_{\mathrm{R}} = w_{\mathrm{S}} + w_{\mathrm{R,O}}$; $w_{\mathrm{R,O}} = ca.\ 20$ kJ mol^{-1}; and $w_{\mathrm{S}} = ca.\ 10$ kJ mol^{-1}. Hence we find equation (44) because the system is case (I), and also equation (45) because the w_{S} term is so small. Another

$$\partial w_{\mathrm{Q}}/\partial \Delta G_{\mathrm{TD}}^{\circ} \simeq 0 \qquad (44)$$

$$\partial w_{\mathrm{S}}/\partial \Delta G_{\mathrm{TD}}^{\circ} \simeq 0 \qquad (45)$$

similar system with a small constant w_{S} of *ca.* 6 kJ mol^{-1} is the cyano-carbon bases studied by Long and his group.[16] This system is also well behaved in that $\alpha_{\mathrm{S}} = \alpha_{\mathrm{B}}$.

Considering 3-diazobutan-2-one as a ketone, with a β_{B} of 0·39, we would expect from equation (42) that, if it were an ordinary ketone, its pK_{S} would be 7. In fact its pK_{S} must lie in the range -2 to -5. This difference is seen in the different values of w_{S} for the diazo and ketone systems. Estimates of the various parameters are summarised in Table 7. The larger value of w_{S} for the diazo-ketone describes the destruction of the resonant π-system. Regardless of the algebra and the exact numbers the fact that 3-diazobutan-2-one has the same Brønsted slope for deprotonation as an ordinary ketone of pK_{S} 7 allows us to conclude that on deprotonation the extra stabilisation of the deprotonated diazo-ketone must largely take place after the proton transfer. This extra stabilisation makes the protonated diazo-ketone a strong acid but has much less effect on the kinetics of the deprotonation.

TABLE 7

Comparison of parameters for 3-diazobutan-2-one and the ketones (all values in kJ mol^{-1})

	$w_{\mathrm{R,O}}$	w_{S}	$\lambda/4$	w_{Q}	$w_{\mathrm{P},\infty}$
3-Diazobutan-2-one	20	45	10	−35	0
Ketones	20	10	14	−40	−20

Hence we may divide the carbon acids into two types, ' weak ' and ' strong '. The ' strong ' acids (*e.g.*, nitro- and diazo-compounds) are strong because they have extensive π-systems in the anion. This leads to large values of w_{S}; because of the delocalisation of the electrons the size of w_{S} is sensitive to substitution elsewhere in S and so $\partial w_{\mathrm{S}}/\partial \Delta G_{\mathrm{TD}}^{\circ} \neq 0$. Hence $\alpha_{\mathrm{S}} \neq \alpha_{\mathrm{B}}$. On the other hand the ' weak ' acids (*e.g.*, ketones and cyano-compounds) have small values of w_{S}, hence $\partial w_{\mathrm{S}}/\partial \Delta G_{\mathrm{TD}}^{\circ} = ca.\ 0$. For both types of acid $\partial w_{\mathrm{Q}}/\partial \Delta G_{\mathrm{TD}}^{\circ} = ca.\ 0$, since the protonated unconjugated species is less sensitive to substitution. Then for ' weak ' acids, since there are no changes in w_{S} and w_{Q}, $\alpha_{\mathrm{S}} \doteqdot \alpha_{\mathrm{B}}$. All problems can be ' solved ' by introducing enough parameters but we have tried to show that the parameters w_{S} and w_{Q} are required by the experimental data; they describe features of proton transfer to carbon bases that have long been discussed qualitatively. It is a measure of the increase in our knowledge that these more sophisticated models are now necessary; unlike Bordwell and Boyle[13] we are not abandoning hope but are looking forward to a more detailed understanding of proton-transfer reactions.

We now turn to the second steps in the original reaction scheme. The data for the three diazo-compounds show a remarkable similarity in $k_2/k'_{\mathrm{L_2O}}$. This may be because once the system is protonated the other two groups attached to $\mathrm{N_2^+HC}\!<$ have little effect on whether it loses a proton or whether it loses $\mathrm{N_2}$. This explanation supports the argument used above, since the transition state for the loss of the proton would not reflect the size of w_{S}; from the quantitative analysis of our model the substitution of equation (38) in equation (34) gives $\beta_{\mathrm{S}} \simeq 0$, and thus, as for the cyano-compounds,[16] $k'_{\mathrm{H_2O}}$ should be the same for the diazo-compounds. However, one must point out that for ethyl diazoacetate, which has one group ($\mathrm{CO_2Et}$) the same as ethyl diazopropionate and one group (H) the same as diazoacetate anion, we find that $(k_{\mathrm{H_2O}}'/k_2)$ for ethyl diazoacetate $>10^2 \gg 10^{-2}$, the value for 3-diazobutan-2-one and ethyl diazopropionate. Hence we believe that, while the agreement between ethyl diazopropionate and 3-diazobutan-2-one does reflect the small effect of having respectively OEt and Me at an unconjugated position β to the reaction site, and the observed constancy of $k_{\mathrm{H_2O}}'/k_2$ supports our model, the difference between ethyl diazoacetate and ethyl diazopropionate shows a marked effect on having H or Me α to the reaction site. This same difference would be found in diazoacetate anion compared with 3-diazobutan-2-one or ethyl diazopropionate. The fact that diazoacetate anion is not like ethyl diazoacetate must be because k_2 is enhanced by internal nucleophilic attack[4] and it is a coincidence that the ratio for diazoacetate anion is then so similar to that for 3-diazobutan-2-one and ethyl diazopropionate; the coincidence is that k_2 for the internal nucleophilic attack on $\geqslant$CH is much the same as k_2 for attack by $\mathrm{H_2O}$ on $\geqslant$C–Me.

Finally there is the difference in the reaction of 3-diazobutan-2-one and diazoacetate ion with $\mathrm{H_2O}$. In the case of the diazo-ketone if one uses equations (15) and $K_{\mathrm{HS}} = 10^8$ mol l^{-1} to calculate $\alpha_{\mathrm{H_2O}}$, whether one uses $\lambda/4 = 8$ or 16 kJ mol^{-1}, one obtains that $\alpha_{\mathrm{H_2O}}$ is greater than unity. Equation (1) of the Marcus theory only holds for $-\lambda < \Delta G_{\mathrm{R}}^{\circ} < \lambda$ or $0 < \alpha < 1$. $\mathrm{H_2O}$ is such a weak acid and $\mathrm{OH^-}$ such a strong base that the λ term is zero for the reverse reaction. Thus in Scheme 3 the model predicts a low activation free energy for $k_{\mathrm{OH^-}}'$; hence it is not surprising that the $k_{\mathrm{OH^-}}''$ step is

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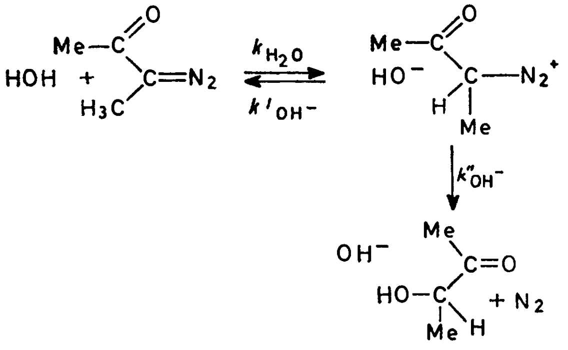
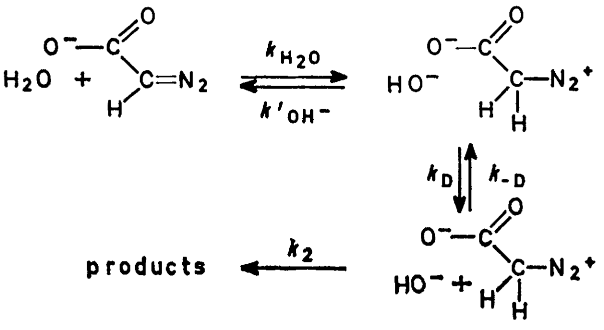
[16] F. Hibbert, F. A. Long, and E. A. Walters, *J. Amer. Chem. Soc.*, 1971, **93**, 2829.

rate-determining. For diazoacetate anion we have the rather different Scheme 4. The Marcus theory predicts[8]



SCHEME 3

that α_{H_2O} should be 0·99; that is, again the $k_{OH^-}{}'$ step should be very fast. In fact the first step can be rate-determining and the isotopic α[7] is 0·89; the H_2O point



SCHEME 4

in the reaction of diazoacetate anion is somewhat anomalous;[7] this point is also anomalous in the cyano-system.[16]

Considering the steps after the protonation, we obtain equations (46) and (47) and to prevent the diffusion step

$$k_{OH^-}{}'' > 10k_D \text{ for 3-diazobutan-2-one} \quad (46)$$

$$k_2k_D/k_{-D}[OH^-]_{max.} > 10(k_{OH^-}{}'') \text{ for diazoacetate anion} \quad (47)$$

becoming rate-determining, we have equation (48) where

$$k_{-D}[OH^-]_{min.} > 10k_2 \text{ for diazoacetate anion} \quad (48)$$

$[OH^-]_{max.} = 1\text{M}$ and $[OH^-]_{min.} = 10^{-2}\text{M}$ and describe the range of OH^- where the k_2 step is rate-determining. Hence, comparing 3-diazobutan-2-one and diazoacetate anion we obtain the relationship (49) since the two k_D terms are not going to be very different.

$$\begin{aligned}(k_{H_2O^-}{}'')_{N_2:CH\cdot CO_2^-} &< 10^{-2}(k_D)_{N_2:CH\cdot CO_2^-}[OH^-]_{min.}/[OH^-]_{max.} \\ &< 10^{-5}(k_{OH^-}{}'')_{N_2\cdot CMe\cdot COMe}(k_D)_{N_2:CH\cdot CO_2^-}/(k_D)_{N_2\cdot CMe\cdot COMe} \\ &\sim 10^{-5}(k_{OH^-}{}'')_{N_2\cdot CMe\cdot COMe}\end{aligned} \quad (49)$$

It might be thought that the factor of 10^5 was surprisingly large but since we have seen that $(k_{H_2O}{}'/k_2)$ for ethyl diazoacetate is *ca.* 10^4 the value for 3-diazobutan-2-one and ethyl diazopropionate, then if $k_{H_2O}{}'$ is the same for ethyl diazoacetate and ethyl diazopropionate ($\beta_S = 0$), k_2 for ethyl diazoacetate must be $< 10^{-4}k_2$ for ethyl diazopropionate for nucleophilic attack of H_2O. In addition the CO_2^- group and its solvation probably hinder the attack of the OH^- nucleophile on the opposite side of the C atom to the N_2. Hence this difference between 3-diazobutan-2-one and diazoacetate anion appears to be reasonable.

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