Kinetic Isotope Effects and Aliphatic Diazo-compounds. Part IV.[1] Primary Isotope Effects in General Acid Catalysis

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Data are presented for the solvent isotope effect on the decomposition of 3-diazobutan-2-one and of ethyl diazopropionate catalysed respectively by pyridinium ion and by acetic acid, together with data on the isotopic content of the products of the reactions. The agreement between the kinetic and product data shows that there is direct proton transfer from the acid to the diazo-compound, although there is probably also a small contribution from terms describing the solvation of the transition state. Four different models involving proton transfer through a solvent bridge are considered and rejected. Results for the decomposition of 3-diazobutan-2-one in basic solutions of H_2O and D_2O show that there is a direct reaction with water in which the OH^- formed in the proton-transfer step acts immediately as a nucleophile in the second step.

THE disagreement between α_{L^+} and α_B reported in Part III[1] for the acid-catalysed decomposition of $N_2{\cdot}CMe{\cdot}COR$ where R is Me for 3-diazobutan-2-one and is OEt for ethyl diazopropionate led us to examine in more detail the nature of the transition state for catalysis by weak acids. We have measured the solvent isotope effect and have carried out isotopic product analysis for the systems (I) and (II). Experimentally system (I) is

$$\text{(I)}\quad AcOH + N_2{\cdot}CMe{\cdot}CO_2Et$$
$$\text{(II)}\quad C_5H_5N^+H + N_2{\cdot}CMe{\cdot}COMe$$

easier to study since acetic acid does not absorb in the same part of the spectrum as the diazo-compounds, and the faster rate of reaction of system (I) is more convenient. However acetic acid suffers from the disadvantage that an anion is formed as a result of the proton transfer. The fractionation in the solvation sheath of an anion is larger than that of either a cation or a neutral substance; thus the description of systems with anions is less certain.[2,3] System (II) does not have any anions but the u.v. spectrum of the pyridinium–pyridine buffer means that the absorption of ethyl diazopropionate is completely masked and 3-diazobutan-2-one can only be followed on the side of the peak. The slower reaction of the diazo-ketone with pyridinium ion (HPy^+) led to the discovery of a spontaneous water rate and some experiments are reported of the decomposition in basic solution.

EXPERIMENTAL

The chemicals and solutions have been described.[1,4] Pyridine perchlorate was prepared by the direct addition of 60% $HClO_4$ to a solution of AnalaR pyridine in ethanol. The salt (m.p. 290 °C) crystallised.

The kinetic experiments were carried out in the normal single mode.[4] The rates of reaction for system (II) were so slow that one would have to wait a week to obtain an infinity value. The data were therefore plotted by Guggenheim's method.[5] The reactions were studied for long enough (*ca.* 2 days) so that at least two half-lives separated the two batches of readings. The water rate was even slower so the reaction in basic solution was studied in a zeroth-order fashion and the first-order rate constant calculated from equation (1), where $\overline{\mathrm{OD}}$ was the optical density at the half-way point.

$$k = (\mathrm{dOD}/\mathrm{d}t)/\overline{\mathrm{OD}} \qquad (1)$$

Because the pyridinium buffers absorb in the u.v. region it was important to have blanks containing the buffer solution and not just solvent in the reference compartment.

The isotopic analysis of the products was carried out as described.[1] The slow reaction with HPy^+ meant that the 3-diazobutan-2-one had to be decomposed during 2—3 weeks.

RESULTS

Kinetics for System (I).—This system was studied in mixtures of H_2O and D_2O with $[HA] + [H^+] = 19{\cdot}9$ mM and $[Na^+] = [A^-] - [H^+] = 49{\cdot}7$ mM. The observed first-order rate constants[6,7] are given in Table 1; each result is the mean of three separate runs except that five runs were carried out at $x = 0$.

Kinetics for System (II).—This system was studied in H_2O and D_2O at a buffer ratio of unity with 10 mM $\leqslant [PyH^+] \leqslant$ 100 mM. The results are plotted in Figure 1 and we obtain $k_{HPy^+} = 100 \pm 3$ l mol^{-1} Ms^{-1} with an intercept of $5{\cdot}7 \pm 0{\cdot}3$ Ms^{-1} for H_2O, and $k_{DPy^+} = 23 \pm 2$ l mol^{-1} Ms^{-1} with an intercept of $1{\cdot}4 \pm 0{\cdot}1$ Ms^{-1} for D_2O.

Kinetics for the System NaOL + 3-*Diazobutan*-2-*one*.—The system was studied at various [NaOL] in H_2O and D_2O. The results are plotted in Figure 2. The average value of the rate constants are $0{\cdot}75 \pm 0{\cdot}02$ Ms^{-1} in H_2O and $0{\cdot}90 \pm 0{\cdot}02$ Ms^{-1} in D_2O. Blank runs were carried out to see that these rates were not caused first by photochemical decomposition from the spectrophotometer lamp and secondly by evaporation of the ester. The photochemical hypothesis was tested by taking readings for the first 2 h, switching the lamp off for 14 h, and then taking further readings for 1 h. The results are plotted as in Figure 2;

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[1] Part III, W. J. Albery and A. N. Campbell-Crawford, preceding paper.

[2] D. M. Goodall and F. A. Long, *J. Amer. Chem. Soc.*, 1968, **90**, 238.

[3] V. Gold, *Adv. Phys. Org. Chem.*, 1969, **7**, 259.

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

[5] E. A. Guggenheim, *Phil. Mag.*, 1926, **75**, 538.

[6] H. S. Harned and B. B. Owen, 'The Physical Chemistry of Electrolytic Solutions,' Reinhold, New York, 1958, p. 676.

[7] V. Gold and B. M. Lowe, *J. Chem. Soc.* (*A*), 1968, 1923.

they are not significantly different from the other results. The evaporation hypothesis was tested by varying the conditions and by using acetone as a test compound. Acetone is more volatile than 3-diazobutan-2-one and the results show that evaporation is negligible (unless the top is left off the cell).

TABLE 1

First-order rate constants for system (I)

x	k_{obs} / ks^{-1}	$k_{\text{obs}}(1 + f)$ / ks^{-1}	$10^5 K_{\text{LA}}$ [a] / mol l^{-1}	$k_{\text{L}^+}[\text{L}^+]$ / ks^{-1}	k_{LA} / ks^{-1}	y [b] / ks^{-1}	y [c] / ks^{-1}	y [d] / ks^{-1}
0·000	$2{\cdot}85_5 \pm 0{\cdot}00_5$	3·31	2·58	0·21	155	3·10	3·08	3·05
0·152	$2{\cdot}48 \pm 0{\cdot}01_4$	2·82	2·19	0·17	133	2·65	2·69	2·68
0·317	$2{\cdot}14 \pm 0{\cdot}01_4$	2·42	1·82	0·13	115	2·28	2·28	2·29
0·515	$1{\cdot}74 \pm 0{\cdot}00_6$	1·92	1·45	0·09	92	1·82	1·81	1·83
0·713	$1{\cdot}33 \pm 0{\cdot}00_4$	1·44	1·14	0·06	69	1·37	1·37	1·37
0·898	$0{\cdot}95_8 \pm 0{\cdot}00_1$	1·02	0·91	0·04	49·1	$0{\cdot}96_8$	$0{\cdot}96_6$	$0{\cdot}95_9$
						σ	$0{\cdot}01_9$	$0{\cdot}02_5$

[a] Data from refs. 6 and 7; $[\text{L}^+] = K_{\text{LA}}/5$. [b] Calculated from experimental data; $y = k_{\text{LA}}[\text{LA}](1 - x + \phi_{\text{HA}}x)$. [c] Calculated from $3{\cdot}08\,(1 - 0{\cdot}725x)\,(1 - 0{\cdot}12x + 0{\cdot}072x^2)$. [d] Calculated from $3{\cdot}05\,(1 - 0{\cdot}748x)\,(1 - 0{\cdot}05x + 0{\cdot}001x^2)$.

Product Analysis.—The product analyses were carried out at $x = \frac{1}{2}$ and so do not have to be corrected for the breakdown of the rule of the geometric mean.[8] The crude values for $\phi_{\text{P}}{}^*$ where $\phi_{\text{P}}{}^*$ is defined by equation (2) are

$$\phi_{\text{P}}{}^* = \frac{[\text{D in product}]}{[\text{H in product}]} \cdot \frac{(1 - x)}{x} \tag{2}$$

$0{\cdot}27_5 \pm 0{\cdot}01$ for system (I) and $0{\cdot}24_8 \pm 0{\cdot}01$ for system (II). These values have to be corrected first for the fact that some of the product was formed by H^+ catalysis and secondly for the interference from the second transition state[9] through equations (3) or (4) where terms are defined

$$\phi_{\text{P}}{}^* = \phi_{\text{P}} \frac{[1 + \rho\phi_{1,\text{H}^+}/\phi_{\text{P}}][1 + \zeta]}{[1 + \rho][1 + \phi_{\text{P}}\zeta]} \tag{3}$$

$$\phi_{\text{P}} = \frac{(1 + \rho)\phi_{\text{P}}{}^*/(1 + \zeta) - \rho\phi_{1,\text{H}^+}}{1 - \zeta(1 + \rho)\phi_{\text{P}}{}^*/(1 + \zeta)} \tag{4}$$

as in equations (5) and (6), ϕ is the factor for transfer from

$$\rho = \frac{k_{\text{H}^+}}{k_{\text{HA}}}(1 - x + \phi_{2,\text{H}^+}x)^2 = \frac{k_{\text{H}^+}}{k_{\text{HA}}}\left(\frac{1 + \phi_{2,\text{H}^+}}{2}\right)^2 \text{ for } x = \tfrac{1}{2} \tag{5}$$

$$\zeta = \left(\frac{k_{\text{A}^-}[\text{A}^-]}{k_2}\right)_{x=0} = \frac{k_{\text{H}_2\text{O}}{}'}{k_{2,\text{H}}} \frac{k_{\text{HA}}}{k_{\text{H}^+}} \frac{[\text{A}^-]}{K_{\text{A}}} \tag{6}$$

HA, and ϕ_{1,H^+} and ϕ_{2,H^+} are factors for transfer from H_3O^+.

Values for the calculation of the correction have been reported.[1,4,9] We then get $\phi_{\text{P}} = 0{\cdot}25_2 \pm 0{\cdot}01$ for system (I) and $\phi_{\text{P}} = 0{\cdot}25_6 \pm 0{\cdot}01$ for system (II). The ζ and ρ corrections predominate for systems (I) and (II) respectively.

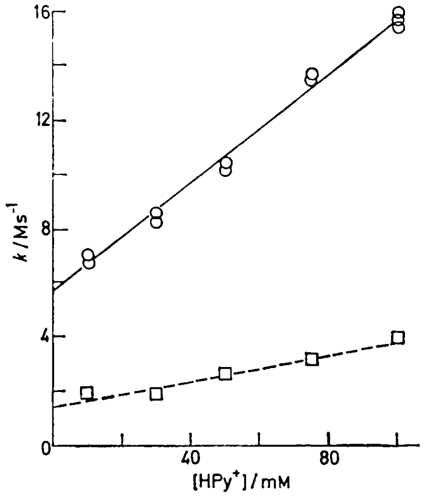


FIGURE 1 Observed first-order rate constants for 3-diazobutan-2-one + HPy^+ at buffer ratio of unity against $[\text{HPy}^+]$ in H_2O (○ and solid line) and in D_2O (□ and broken line)

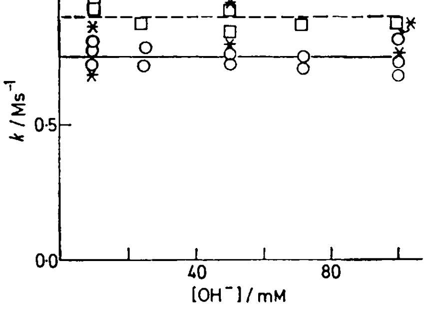


FIGURE 2 Observed first-order rate constants for 3-diazobutan-2-one in basic solutions; ○ and solid line, H_2O; □ and broken line, D_2O; * experiments to test photochemical decomposition in which the spectrophotometer lamp was switched off

DISCUSSION

The first point to note is that the rate constant for catalysis by HPy^+ does not lie on the Brønsted plot for the carboxylic acids. The Brønsted value (extrapolated over 0·6 unit of pK) is *ca.* 2 l mol^{-1} ks^{-1} whereas the observed value is 0·100 l mol^{-1} ks^{-1}; hence the reaction is 20 times slower than expected. Possible reasons for this are discussed in Part VI.

[8] W. J. Albery and M. H. Davies, *Trans. Faraday Soc.*, 1969, **65**, 1059.

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

For general acid catalysis we start with equations[9] (7) and (8). For system (I) $[L^+]$ is so small that $[A^-]$

$$k_{obs} = \frac{k_{LA}[LA] + k_{L^+}[L^+]}{1 + (k'_{A^-.L}[A^-] + k'_{L_2O})/k_{2.L}} \qquad (7)$$

$$\frac{k_{LA}k'_{L_2O}}{k'_{A^-,L}k_{L^-}} = K_{A,L} \qquad (8)$$

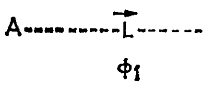
and [LA] are virtually constant. So we can write equation (9) where f is given by (10) and $k'_{H_2O}/k_{2.H} =$

$$k_{LA}[LA] = k_{obs}(1 + f) - k_{L^+}[L^+] \qquad (9)$$

$$\simeq \frac{k'_{H_2O}}{k_{2,H}}\left[\frac{k_{obs}}{k'_{H^+}[H^+]} + (1 - x + \phi_{1.H^+}x)(1 - x + \phi_{2.H^+}x)^2\right] \qquad (10)$$

$1{\cdot}0 \times 10^{-2}$ (ref. 9); $k'_{H^+} = 19{\cdot}1$ l mol^{-1} s^{-1} (ref. 4); $[H^+] = 1{\cdot}03 \times 10^{-5}$M; $\phi_1 = 0{\cdot}21$;[1] and $\phi_2 = 0{\cdot}78$.[1] Small errors in the quantities in f and the error in the substitution of k_{obs} for $k_{LA}[LA]$ are unimportant since f is small. The stages of the calculation are shown in Table 1.

The variation of k_{LA} with x, the atom fraction of D in the solvent for the simple transition state (III) is given



(III)

by[10] equation (11), where ϕ_{HA} describes the fractionation in the reactant acetic acid and the terms in ϕ_S

$$\frac{k_{LA.x}}{k_{LA,0}} = \frac{(1 - x + \phi_1 x)(1 - x + \phi_S x)^n}{(1 - x + \phi_{HA}x)} \qquad (11)$$

describe possible solvation fractionation in the transition state.[11] These terms should be included especially since during the reaction negative charge is created on A^-. However ϕ_S is likely to be close to unity and so we can expand the solvation term to give equation (12)

$$(1 - x + \phi_S x)^n \simeq 1 + n\theta_S x + \ldots \qquad (12)$$

where $\theta_S = \phi_S - 1$. Gold and Lowe have measured the value of ϕ_{HA} in D_2O solutions to be $\phi_{HA} = 0{\cdot}96$.[3,7] In order to minimise the errors due to the breakdown of the rule of the geometric mean this should be corrected[8] to a value pertaining to $x = \frac{1}{2}$ of $\phi_{HA} = 0{\cdot}99$. Writing $\theta_1 = \phi_1 - 1$ and y by equation (13), the values of y are

$$\begin{aligned} y &= (1 - x + \phi_{HA}x)k_{LA.x}[LA] \\ &= k_{LA.0}[LA](1 + \theta_1 x)(1 + n\theta_S x + \ldots) \end{aligned} \qquad (13)$$

fitted to equation (14), whence by equating the coefficients we obtain equations (15) and (16). By

$$y = a + bx + cx^2 \qquad (14)$$

$$\phi_1 = 1{\cdot}0 + b/a - c/d - \tfrac{1}{2}c^2a/b^3 \qquad (15)$$

$$\Pi\phi_S = 1 + c/b(1 + \tfrac{1}{2}c/b) \qquad (16)$$

considering the next term in the binomial expansion and expanding about $x = \frac{1}{2}$,[12] one can show that the error in this procedure is less than a few parts in a thousand. Values of ϕ_1 and $\Pi\phi_S$ with standard errors are $\phi_1 = 0{\cdot}27_5 \pm 0{\cdot}01$ and $\Pi\phi_S = 0{\cdot}88 \pm 0{\cdot}04$. This value of ϕ_1 has been obtained entirely from the kinetic data. It is in reasonable agreement with that obtained from product analysis: $\phi_P = 0{\cdot}25_2 \pm 0{\cdot}01$. The corresponding value of $\Pi\phi_S$ is 0·95. This value is somewhat closer to unity than the value from the kinetic data alone, and is perhaps more plausible. In Table 1 we have compared the calculated and observed values of y; good agreement is found with either pair of values. The kinetic and product data taken together suggest values of $\phi_1 = 0{\cdot}26 \pm 0{\cdot}01$ and $\Pi\phi_S = 0{\cdot}93 \pm 0{\cdot}04$. We conclude that the transition state for the reaction of ethyl diazopropionate with acetic acid is the simple one with the addition of a small but significant solvation term. This solvation term may be concerned with the developing acetate ion (in the dissociation of acetic acid $\Pi\phi_S =$ *ca.* 0·92[7]) or it may be concerned with solvation changes around the ethyl diazopropionate.

In system (II), from the comparatively low value of k_{HPy^+} the barrier to proton transfer is higher and this means that the correction for the second transition state is always <2% which is smaller than the experimental scatter.

We write equation (17) for the simple transition state.

$$\frac{k_{DPy^+}}{k_{HPy^+}} = \frac{\phi_1'\Pi\phi_S'}{\phi_{HPy^+}} = 0{\cdot}23_3 \pm 0{\cdot}02 \qquad (17)$$

Bellobono and Beltrame[13] have measured the pyridinium dissociation constant in H_2O and D_2O and, assuming that the solvation fractionation on the cations and neutral species is negligible, we write equation (18).

$$\phi_{HPy^+} = l^3K_{HPy^+}/K_{DPy^+} = 1{\cdot}05 \pm 0{\cdot}07 \qquad (18)$$

Substituting this value and $\phi_1' = 0{\cdot}25_6 \pm 0{\cdot}01$, we then obtain equation (19). This value is close enough to

$$\Pi\phi_S' = 0{\cdot}96 \pm 0{\cdot}11 \qquad (19)$$

unity to support the simple model for the transition state. The uncertainty in the value of ϕ_{HPy^+} and in the kinetic data means that we have not yet a precise value for the transition-state solvation. The kinetic data are less certain in system (II) than in system (I) because first the reactions are inconveniently slow and secondly

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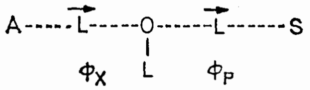
[10] A. J. Kresge, *Pure and Appl. Chem.*, 1964, **8**, 243.

[11] V. Gold, *Trans. Faraday Soc.*, 1968, **64**, 2143.

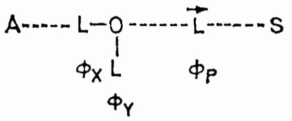
[12] W. J. Albery and M. H. Davies *J.C.S. Faraday I*, 1972, 167.

[13] I. R. Bellobono and P. Beltrame, *J. Chem. Soc.* (*B*), 1969, 1906.

the contribution from catalysis by L^+ is more important. A point of general interest concerning proton transfers in water is whether the transfer takes place through a solvent bridge or not.[14] Our data for these systems support previous hypotheses and arguments [14,15] that there is no solvent bridge for transfer to carbon. We examine four possible transition states (IV)—(VIII) with a solvent bridge, and show that they are much less probable than the simple unbridged transition state discussed hitherto.



(IV)



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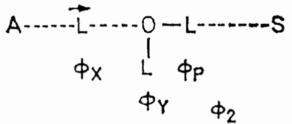

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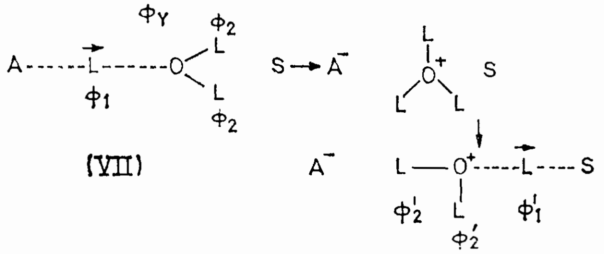


(VII)

Models (IV) and (V) may be rejected because ϕ_X for (IV) and $\phi_X\phi_Y$ for (V) would be smaller than the measured $\Pi\phi_S$; $\Pi\phi_S$ for both systems is too close to unity for ϕ_X or ϕ_Y in (IV) or (V) to have plausible values. Model (VI) may be rejected out of hand because the measured value of ϕ_P could not refer to a bound proton in the transition state. Model (VII) envisages the rate-determining step being followed by rotation of the L_3O^+ unit followed by the transfer to S of any of the three L species. The isotopic scheme is set out in Scheme 1. Analysis of this scheme gives equations (20)—(22) where $\phi_P{}^*$ is given by equation (23) and, since

$$\phi_P{}^* = \frac{\phi_1\phi_2{}^2x^2 + 2\phi_1{}'\phi_2x(1-x)\dfrac{2\phi_1+\phi_2}{2\phi_1{}'+\phi_2{}'} + \phi_1{}'(1-x)^2\dfrac{\phi_1+2\phi_2}{\phi_1{}'+2\phi_2{}'}}{\phi_2\phi_2{}'x^2\dfrac{2\phi_1+\phi_2}{2\phi_1{}'+\phi_2{}'} + 2\phi_2{}'x(1-x)\dfrac{\phi_1+2\phi_2}{\phi_1{}'+2\phi_2{}'} + (1-x)^2} \qquad (20)$$

$$\simeq \phi_1{}' + \phi_2{}^2x^2(\phi_1 - \phi_1{}'\phi_2/\phi_2{}')(1 - x + \phi_2x)^{-2} \qquad (21)$$

$$\simeq \phi_1{}' \text{ at } x = \tfrac{1}{2} \qquad (22)$$

$$\phi_P{}^* = \frac{[\text{D in product}]}{[\text{H in product}]}\,\frac{(1-x)}{x} \qquad (23)$$

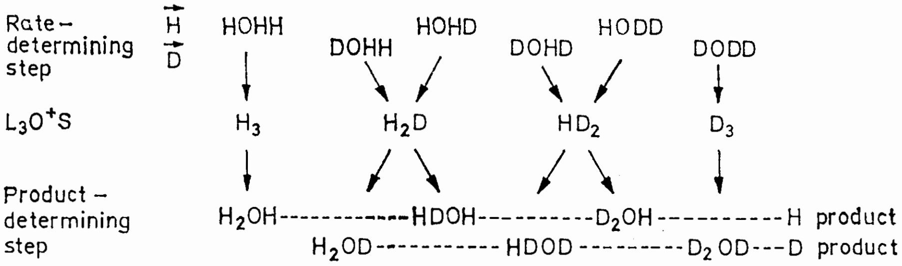
$$\frac{2\phi_1+\phi_2}{2\phi_1{}'+\phi_2{}'} \simeq \frac{\phi_1+2\phi_2}{\phi_1{}'+2\phi_2{}'} \simeq \frac{\phi_2}{\phi_2{}'} \qquad (24)$$

$\phi_1 < \phi_2$, we have used the approximation (24). In this model $\phi_P{}^*$ does not tell us about the rate-determining step, hence we have to rely on the values of $\Pi\phi_S$ reported from the analysis of the kinetic data alone. The value of 0·88 ± 0·04 does seem too close to unity to accommodate $\phi_2{}^2$; a proton transfer with $\phi_2 = 0{\cdot}94$ would be unlikely to have ϕ_1 as low as 0·26.[16] Further it must be doubtful whether the lifetime of the L_3O^+S unit would be long enough to allow the necessary rotations; it is likely that downhill proton transfers are faster than such a rotation.

Now we turn to the ' water ' reaction. If there was no water reaction the intercepts of Figure 1 should agree with $k_{L^+}[L^+]$. Table 2 shows that the intercepts are significantly larger. We carried out the reaction in basic solutions to measure k_{L_2O}. The results are in Figure 2. If one writes equation (25) one gets reasonable

$$\text{Intercept} = k_{L^+}[L^+] + k_{L_2O} \qquad (25)$$

agreement as shown in Table 2. The value of k_{H_2O} is very roughly of the right order for a rate-determining proton transfer from water. If one extrapolates the



SCHEME 1

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[14] W. J. Albery, *Progr. Reaction Kinetics*, 1967, **4**, 353.

[15] J. M. Williams and M. M. Kreevoy, *Adv. Phys. Org. Chem.*, 1968, **6**, 63.

[16] R. A. More O'Ferrall, G. W. Koeppl, and A. J. Kresge, *J. Amer. Chem. Soc.*, 1971, **93**, 9.

Brønsted plot for carboxylic acids one gets an estimate of $k_{H_2O} = ca.\ 10^{-7}\ s^{-1}$, compared with the observed $k_{H_2O} = 7{\cdot}5 \times 10^{-7}\ s^{-1}$. However the results in D_2O show that this cannot be the right model since $k_{D_2O}/k_{H_2O} = 1{\cdot}2$. Also if k_{H_2O} did describe an A–S_E2 proton transfer then we can calculate that $k'_{OH^-}/k_2 = ca.\ 10^6\ l\ mol^{-1} \gg [OH^-]^{-1}$, and so the mechanism would have shifted in our basic system ($[OH^-] = ca.\ 0{\cdot}1$M) to A-1 or A-2. But this would mean that the rate of reaction was inversely proportional to $[OH^-]$; this behaviour is seen in diazoacetate ion.[17] But our reaction is independent of $[OH^-]$. Also if solvated OH^- is released before the rate-determining step we would expect an isotope effect as shown in equation (26);

TABLE 2

Values of intercept from Figure 1

	Intercept/Ms^{-1}	$k_{L^+}[L^+]$/Ms^{-1}	k_{L_2O}/Ms^{-1}	$k_{L^+} + k_{L_2O}$/Ms^{-1}
H_2O	$5{\cdot}7 \pm 0{\cdot}3$	$4{\cdot}3 \pm 0{\cdot}1$	$0{\cdot}75 \pm 0{\cdot}02$	$5{\cdot}1 \pm 0{\cdot}1$
D_2O	$1{\cdot}4 \pm 0{\cdot}1$	$0{\cdot}57 \pm 0{\cdot}03$	$0{\cdot}90 \pm 0{\cdot}02$	$1{\cdot}47 \pm 0{\cdot}0_4$

$$k_{D_2O}/k_{H_2O} \simeq K_{W.D_2O}/l^3K_{W,H_2O} = 0{\cdot}41 \qquad (26)$$

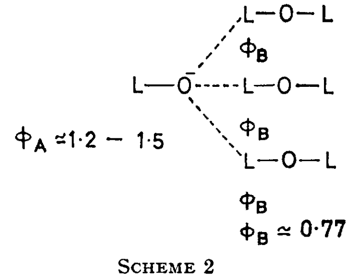
indeed for diazoacetate ion[17] a value of 0·52 is found. We find a value of 1·2.

These facts can be explained by postulating[17] that the OH^- also acts as a nucleophile so that equations (27) and (28) follow. Now if $k_{2.OH^-} \sim k'_{OH^-}$, then $k_{obs} \sim k_{H_2O}$, and so k_{obs} may well be close to the Brønsted extrapolation.

$$k_{obs.H_2O} = \frac{k_{H_2O}}{1 + \dfrac{k'_{OH^-}[OH^-] + k'_{H_2O}}{k_2 + k_{2.OH^-}[OH^-]}} \qquad (27)$$

$$= \frac{k_{H_2O}}{1 + k'_{OH^-}/k_{2,OH^-}} \text{ at large } [OH^-] \qquad (28)$$

It is also quite sensible that 3-diazobutan-2-one, like ethyl diazoacetate,[18,19] needs nucleophilic assistance for the second step while diazoacetate anion reacts by internal nucleophilic attack[17] by the CO_2^- group.



SCHEME 2

The isotope effect of 1·2 also supports this hypothesis. Gold and Grist[20] have recently analysed the detailed fractionation factors for the solvated OH^- ion and obtained the results shown in Scheme 2. Our LO^- ion acting as a nucleophile would have a ϕ_A factor but no ϕ_B factor. Hence the isotope effect shown by equation (29). This work and Gold's analysis are therefore in good agreement. However one difficulty with this mechanism is that in the pyridinium–pyridine buffers where $[OH^-]$ is low, equation (7) would become (30).

$$k_{D_2O}/k_{H_2O} \simeq \phi_A \simeq 1{\cdot}2 \qquad (29)$$

$$k_{obs} \simeq k_{LA}[LA] + k_L\ [L^+] + k_{L_2O} \qquad (30)$$

To explain the isotope effect we have postulated that in equation (28) $k'_{OH^-} \gg k_{2.OH^-}$, and in the basic solutions we can write equation (31). But Table 2 shows that $k_{obs.L_2O}$ is a good correction for the pyridinium buffers. This difficulty can be resolved by assuming that the lifetime of the water-catalysed intermediate is so short that the OH^- does not have time to diffuse away before it is involved either as a base or as a nucleophile as shown in Scheme 3. One piece of direct experimental evidence

$$k_{obs.L_2O} \simeq k_{L_2O}\left(\frac{k_{2.OH^-}}{k'_{OH^-}}\right) \ll k_{L_2O} \qquad (31)$$

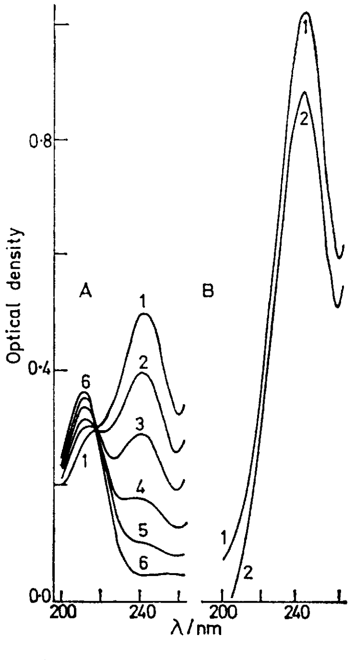


FIGURE 3 Successive u.v. spectra of the decomposition of 3-diazobutan-2-one (A) in 10^{-3}M-$HClO_4$ and (B) in 10^{-1}M-NaOH

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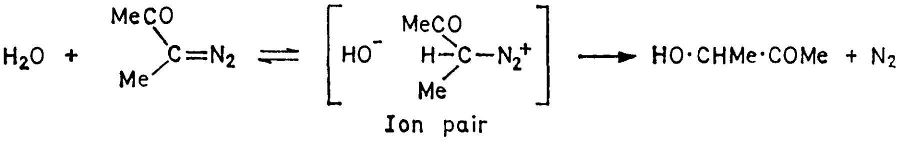
[17] M. M. Kreevoy and D. E. Konasewich, *J. Phys. Chem.*, 1970, **74**, 4464.

[18] W. J. Albery, J. E. C. Hutchins, R. M. Hyde, and R. H. Johnson, *J. Chem. Soc.* (*B*), 1968, 219.

[19] W. J. Albery and M. H. Davies, *Trans. Faraday Soc.*, 1969, **65**, 1066.

[20] V. Gold and S. Grist, *J.C.S. Perkin II*, 1972, 89.

that supports Scheme **3** is that whereas in acid solutions 25% of the product of the hydrolysis is methyl vinyl ketone, no olefin is found in the basic solutions. Figure 3 shows successive u.v. scans both for an acid solution, where we can see the isosbestic point and the olefin absorption building up, and for a basic solution where the **3**-diazobutan-2-one absorption decays uniformly. The suggested nucleophilic attack by OH^- in the ion pair would by more likely to yield acetoin than the olefin.



SCHEME 3

More work is in progress. At present we conclude that the results in base support the idea that the second transition state can become rate-determining and suggest that the second step for **3**-diazobutan-2-one involves nucleophilic participation. The different behaviour of **3**-diazobutan-2-one and diazoacetate anion in basic solutions reinforces the evidence that the second step for diazoacetic anion involves participation of CO_2^-, and will be further discussed in Part VI.

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