Kinetic Isotope Effects and Aliphatic Diazo-compounds. Part V.[†] Secondary Isotope Effects in General Acid Catalysis

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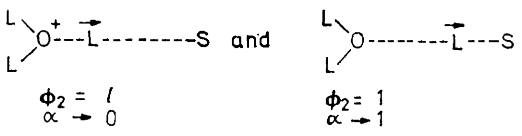
Data are reported for the secondary isotope effect on the reaction of 3-diazobutan-2-one with CL_3CO_2H and LCO_2H. The data obtained by the differential method are accurate enough to determine an isotopic α_{HA} from the relationship $(k_D/k_H) = (K_D/K_H)^{\alpha_{HA}}$. The isotope substitution differentiates the Brønsted plot and the values of α_{HA} agree with the α_B found from the conventional Brønsted plot for the carboxylic acids.

FOR A–S_E2 reactions Gold suggested[1] that there would be a relationship (1) between the size of the secondary solvent isotope effect and the degree of proton transfer in, or symmetry of, the transition state, where ϕ_2 is the

$$\phi_2 = l^{1-\alpha_{L^+}} \quad (1)$$

fractionation factor of the secondary site, l is the fractionation factor of L_3O^+ and ϕ_2 varies between the two extremes as indicated in the Scheme. Originally Gold suggested that α in this relationship would be the same as the α from the Brønsted catalysis law. This identity of the α values was criticised by Albery[2] who thought that the α values might be different since the change in acid strength and in rate of reaction is caused in the case of the isotopic substitution by different energy states with the same potential-energy surface and electronic distribution as opposed to the much grosser change in the Brønsted case where the potential-energy surface and electronic distribution are altered. For the acid-catalysed decomposition of ethyl diazopropionate and 3-diazobutan-2-one α_{L^+} is certainly not equal to α_B measured from the carboxylic acids.[3] This could be because isotopic α values are not generally equal to Brønsted α values or a completely different explanation could be that, following the theory of Marcus,[4] α shifts with the strength of the catalyst. To decide between these two explanations we have investigated secondary isotope effects on the decomposition of 3-diazobutan-2-one using CD_3CO_2H and DCO_2H as catalysts. We thus are determining an isotopic α for



SCHEME

[†] Part IV, W. J. Albery, A. N. Campbell-Crawford, and R. W. Stevenson, preceding paper.

[1] V. Gold, *Trans. Faraday Soc.*, 1960, **56**, 255.

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

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

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

the same catalysts as were used to measure the Brønsted α.

EXPERIMENTAL

The chemicals and solutions have been described.[3,5] The $CD_3{\cdot}CO_2H$ and DCO_2H were commercial (stated purity 99·5%). Since the differences in the reaction rates were small the differential technique was employed.[3] The difference for $CD_3{\cdot}CO_2H$ is particularly small and the technique was modified for this acid by carrying out pairs of differential determinations with the $CD_3{\cdot}CO_2H$ first in the reference compartment and secondly in the sample compartment. Blank runs with the same solution in both compartments showed that this procedure removed systematic errors (for instance a small difference in temperature) and led to an average (taken in pairs) of 1·0008 ± 0·0002.

The initiation procedure was also modified to obtain greater accuracy. About 4 ml of each buffer solution (made up by weight) were thermostatted in small volumetric flasks outside the spectrophotometer. Two separate solutions of 3-diazobutan-2-one, one twice as concentrated as the other had been prepared. The reaction was initiated by adding *ca.* 0·090 ml of each of the diazo-ketone solutions from a Hamilton syringe to each of the buffer solutions; the more concentrated diazo-ketone solution was added to the buffer solution that was to be used in the reference compartment. A sample (2 ml) from each buffer was then transferred to the cells in the spectrophotometer. The concentration of 3-diazobutan-2-one was such that ½ h elapsed before the optical density readings were less than 2 and so could be observed; this was to allow thermal equilibrium to be established.

The buffer solutions were made up by weight from equal quantities of a standard acid solution (m_{HA} M) (diluted by weight from pure acid) and a stock alkali solution (m_{OH^-} M). The concentration of base was *ca.* 10^3K_A so that [HA] = *ca.* 10^3[H$^+$]. Then the ratio (2) obtains, where HA′ refers

$$\frac{[\mathrm{HA}]}{[\mathrm{HA'}]} = \frac{m_{\mathrm{HA}} - m_{\mathrm{OH^-}}}{m_{\mathrm{HA'}} - m_{\mathrm{OH^-}}} = 1 + \frac{m_{\mathrm{HA}} - m_{\mathrm{HA'}}}{m_{\mathrm{HA'}} - m_{\mathrm{OH^-}}} \qquad (2)$$

to the deuteriated acid. The advantage of this procedure is that since $m_{HA} \simeq m_{HA'}$, we do not have to know m_{OH^-} very accurately.

The acid concentrations of the reaction solutions were also estimated by weighed titration with base by use of a Radiometer TTTIC titrator both to titrate to the end-point and to control the addition of alkali (each increment *ca.* 5 µl). This technique was improved by the development of a titration vessel which could be weighed with the electrodes in position. The small tube through which the base was added was made of Teflon so that it did not become wet and the solution was stirred magnetically. At the completion of the titration the tube was removed and the electrodes disconnected from the titrator by means of two extra jacks and sockets introduced into the leads close to the electrode; the whole vessel plus electrodes was then weighed.

RESULTS AND DISCUSSION

The purpose of these experiments is to measure $k_{HA}/k_{HA'}$ accurately enough to determine the value of α_{HA} given by equation (3), where HA′ is HA with

$$k_{\mathrm{HA'}}/k_{\mathrm{HA}} = (K_{\mathrm{HA'}}/k_{\mathrm{A}})^{\alpha_{\mathrm{HA}}} \qquad (3)$$

deuterium substitution. Equation (2) is a linear free-energy relationship of the same form as the Brønsted catalysis law. For $\alpha \longrightarrow 0$ the proton transfer has hardly started in the transition state and $k_{HA'} \longrightarrow k_{HA}$; for $\alpha \longrightarrow 1$ the proton transfer is almost complete and one gets the full effect seen in the dissociation of HA or HA′ into ions. For work with the solvent isotope effect we use fractionation factors and equation (3) can also be expressed very simply in the same form. The fractionation factor ϕ still measures a free-energy difference for isotopic substitution even though CL exchange does not take place rapidly in aqueous solution. Then for formic acid we obtain equations (4) and (5). From equation (1) we obtain equation (6). In the

$$K_{\mathrm{HA'}}/K_{\mathrm{HA}} = \phi_{\mathrm{A^-}}/\phi_{\mathrm{HA}} \qquad (4)$$

$$k_{\mathrm{HA'}}/k_{\mathrm{HA}} = \phi^{\ddagger}/\phi_{\mathrm{HA}} \qquad (5)$$

$$\phi^{\ddagger} = \phi_{\mathrm{HA}}{}^{1-\alpha_{\mathrm{HA}}}\phi_{\mathrm{A^-}}{}^{\alpha_{\mathrm{HA}}} \qquad (6)$$

particular case of transfer from L_3O^+ $\phi_{HA} = l$, $\phi_{A^-} = 1$, and $\phi^{\ddagger} = \phi_2$, the secondary solvent isotope factor. From equation (6) we obtain (7), which is exactly the

$$\phi_2 = l^{1-\alpha_{\mathrm{L^+}}} \qquad (7)$$

relation suggested by Gold.[1]

Returning to equation (3), since the ratios are close to unity we write equations (8), (9), and then (10).

$$k_{\mathrm{HA}}/k_{\mathrm{HA'}} = 1 + \kappa \qquad (8)$$

$$K_{\mathrm{HA}}/K_{\mathrm{HA'}} = 1 + \Lambda \qquad (9)$$

$$\alpha_{\mathrm{HA}} = \kappa/\Lambda \qquad (10)$$

Now the observed rate constant is given by equation (11).

$$k_{\mathrm{obs}} = \frac{k_{\mathrm{HA}}[\mathrm{HA}] + k_{\mathrm{H^+}}[\mathrm{H^+}]}{1 + (k'_{\mathrm{A^-}}[\mathrm{A^-}] + k'_{\mathrm{H_2O}})/k_2} \qquad (11)$$

Neglecting the small k'_{H_2O} term we obtain equation (12),

$$1 + \kappa = (1 + \delta)(1 + \gamma)\left[1 + \frac{\zeta - \zeta'}{1 + \zeta'}\right]\left[1 - \frac{\rho - \rho'}{1 + \rho}\right] \qquad (12)$$

where $k_{obs}/(k_{obs})' = 1 + \delta$, [HA′]/[HA] $= 1 + \gamma$, ζ is given by equation (13), ρ is given by (14), and the primes, as in ρ', refer to the deuteriated acid.

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

The expression on the right-hand side consists of the rate constant ratio (δ), the concentration ratio (γ), and

$$\zeta = k'_{\mathrm{A^-}}[\mathrm{A^-}]/k_2 = k'_{\mathrm{H_2O}}k_{\mathrm{HA}}[\mathrm{A^-}]/k_2k_{\mathrm{H^+}}K_{\mathrm{HA}} \quad (13)$$

$$\rho = k_{\mathrm{H^+}}[\mathrm{H^+}]/k_{\mathrm{HA}}[\mathrm{HA}] = k_{\mathrm{H^+}}K_{\mathrm{HA}}/k_{\mathrm{HA}}[\mathrm{A^-}] \quad (14)$$

two small correction terms, one (ζ) for the second transition state and one (ρ) for the catalysis by $\mathrm{H^+}$.

We first deal with the correction terms. First we write equation (15). From the method of making up the

$$\frac{\rho - \rho'}{1 + \rho} = \frac{\rho}{1 + \rho}\left[1 - \frac{K_{\mathrm{HA'}}}{K_{\mathrm{HA}}}\,\frac{k_{\mathrm{HA}}}{k_{\mathrm{HA'}}}\,\frac{[\mathrm{A^-}]}{[\mathrm{A'^-}]}\right] \quad (15)$$

buffer solutions, from equal weights of the same KOH solution, $[\mathrm{A^-}] = [\mathrm{A'^-}]$, and from equations (3) and (9) we obtain (16). Similarly we obtain equation (17) and

$$\frac{\rho - \rho'}{1 + \rho} \simeq \frac{\rho}{(1 + \rho)} \cdot \frac{\rho}{1 + \Lambda}(1 - \alpha_{\mathrm{HA}}) \simeq \rho\Lambda(1 - \alpha_{\mathrm{HA}}) \quad (16)$$

$$\frac{\zeta - \zeta'}{1 + \zeta'} = \frac{\zeta}{1 + \zeta'}\left[1 - \frac{k_{\mathrm{HA'}}}{k_{\mathrm{HA}}}\,\frac{K_{\mathrm{HA}}}{K_{\mathrm{HA'}}}\,\frac{[\mathrm{A'^-}]}{[\mathrm{A^-}]}\right] \simeq -\zeta\Lambda(1 - \alpha_{\mathrm{HA}}) \quad (17)$$

the approximation (18). Since $\rho\Lambda$ and $\zeta\Lambda$ are the products of two small quantities the correction terms can be combined in equation (12) to give (19) or (20).

$$\alpha_{\mathrm{HA}}\Lambda = \delta + \gamma + \gamma\delta - \Lambda(1 - \alpha_{\mathrm{HA}})(\rho + \zeta) \quad (19)$$

$$\alpha_{\mathrm{HA}} = \frac{\Lambda^{-1}(\delta + \gamma + \gamma\delta) - \rho - \zeta}{1 - \rho - \zeta} \quad (20)$$

The $[\mathrm{A^-}]$ is chosen so that the two correcting terms are of comparable size, leading to equation (21). In the

$$\rho = \frac{k_{\mathrm{H^+}}K_{\mathrm{HA}}}{k_{\mathrm{HA}}[\mathrm{A^-}]} = \frac{k'_{\mathrm{H_2O}}}{k_2\zeta} \sim \sqrt{\left(\frac{k'_{\mathrm{H_2O}}}{k_2}\right)} \sim \zeta \sim 10^{-1} \quad (21)$$

case of acetic acid $\Lambda =$ *ca.* 0·03 and so the whole effect is very small.[6] We have therefore in this case decomposed ethyl diazoacetate as well. These experiments serve as a useful check on the differential method, the estimation of the concentration ratio, γ, and the difference in dissociation constants Λ. Ethyl diazoacetate decomposes by the *A*-2 mechanism [equation (22)] and

$$\frac{k_{\mathrm{obs'}}}{k_{\mathrm{obs}}} = \frac{K_{\mathrm{HA'}}[\mathrm{HA'}][\mathrm{A^-}]}{K_{\mathrm{HA}}[\mathrm{HA}][\mathrm{A'^-}]} \quad (22)$$

for $[\mathrm{A^-}] = [\mathrm{A'^-}]$ we obtain equation (23). We have

$$\Lambda = \delta + \gamma + \gamma\delta \quad (23)$$

considered whether we should include a correction for the nucleophilic participation of the acetate ion but using the Swain–Scott nucleophilicity plot[7] with a value of $s = 0{\cdot}43$[8] and of $n = 2{\cdot}7$[7] it can be shown that the correction is negligible.

We could not use exactly the same buffer solution for decomposing 3-diazobutan-2-one and ethyl diazoacetate since for the diazoketone we wish to suppress the catalysis by $\mathrm{H^+}$ and this would make the reaction of the diazo-ester too slow. Thus there had to be one weighed dilution which was not common to both compounds. Table 1 gives the results for the test of equation (23). The values of γ from titration and from making up by weight are in reasonable agreement; the $\mathrm{CD_3{\cdot}CO_2H}$ was only stated to be 99·5% pure. Streitwieser and Klein[6] have measured Λ to be $(33 \pm 2) \times 10^{-3}$; the good agreement confirms our techniques and Streitwieser and Klein's value of Λ. From these results we have chosen to take $\gamma = -0{\cdot}004$ for the 3-diazobutan-2-one system.

The kinetic results for 3-diazobutan-2-one and acetic acid in two different buffer solutions are given in Table 2.

TABLE 1

Data for decomposition of ethyl diazoacetate with acetic acid

Weighed titrations of buffer solutions

$$\frac{\text{Weight of acid solution}}{\text{Weight of added base solution}}$$

$\mathrm{CH_3{\cdot}CO_2H}$	$\mathrm{CD_3{\cdot}CO_2H}$
1·294	1·298
1·293	1·301
1·294	1·301
1·295	1·300
1·294 ± 0·001	1·300 ± 0·001

From titration $\gamma_{\mathrm{T}} = \dfrac{1{\cdot}294}{1{\cdot}300} - 1 = -(5 \pm 1) \times 10^{-3}$. From making up by weight $\gamma_{\mathrm{W}} = (0 \pm 5) \times 10^{-3}$

Differential kinetic results

$10^3\delta$	35	34	36	35

Mean $= (35 \pm 1) \times 10^{-3}$

Values of Λ

	Ref. 6	Equation (23) γ_{T}	Equation (23) γ_{W}
$10^3\Lambda$	33 ± 2	30 ± 2	35 ± 5

From our previous data[5,9] we can calculate that for $[\mathrm{A^-}] = 3$ mM, $\rho = 0{\cdot}12$ and $\zeta = 0{\cdot}07_5$.

Substitution in equation (20) gives equation (24). From

$$\alpha_{\mathrm{AcOH}} = \frac{(33)^{-1}(27{\cdot}5 - 4 - 0{\cdot}1) - 0{\cdot}195}{1 - 0{\cdot}195} = 0{\cdot}64 \quad (24)$$

the errors on δ, γ, and Λ the uncertainty in this value is *ca.* 10%. For the case of formic acid the following

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[6] A. Streitwieser and H. S. Klein, *J. Amer. Chem. Soc.*, 1963, **85**, 2759.

[7] C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, 1953, **75**, 141.

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

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

values were obtained: $\delta = -(56 \pm 4) \times 10^{-3}$; $\gamma = (123 \pm 1) \times 10^{-3}$; $\Lambda = 84 \times 10^{-3}$ from ref. 10; $\rho = 0{\cdot}14$ and $\zeta = 0{\cdot}067$ from refs. 5 and 9, and from equation (20) $\alpha_{HCO_2H} = 0{\cdot}64 \pm 0{\cdot}07$. The values of α obtained by the isotopic substitution of both acids are in good agreement with the Brønsted $\alpha_B = 0{\cdot}61 \pm 0{\cdot}03$, obtained from use of the same acids.[5] Hence we may conclude that *for the same acid* isotopic substitution and the Brønsted plot yield the same value of α. However the isotopic α for L_3O^+ is very different from the α values for the carboxylic acids, since[3] $\alpha_{L^+} = 0{\cdot}30 \pm 0{\cdot}03$. As shown by equation (3), the isotopic α values are formally equivalent and hence the change in catalyst has changed the equivalent parameter in each reaction. This means that it may be dangerous to use the Brønsted α in equation (1) to estimate ϕ_2 for catalysis by L_3O^+. The change in α is in the direction predicted by the Marcus theory[4] and will be further discussed in Part VI.

TABLE 2

Kinetic results for 3-diazobutan-2-one with acetic acid

[HA]/mM	[A⁻]/mM	$10^3\delta$	$-10^3\delta$ *	$10^3\bar{\delta}$
72	28	30	24	27
		29	23	26
		27	21	24
68	32	29	23	26
		33	29	31
		33	29	31
			Mean	$27{\cdot}_5 \pm 1$

* Runs with cells reversed; each pair of runs gives a value of $\bar{\delta}$.

In this work by the use of the differential method and isotopic substitution we have in a sense successfully differentiated the normal Brønsted plot, and obtained a value of α for each acid. This is similar to the use of the differential method[11] to determine $\Delta H^{\ddagger}$ and $\Delta C_p^{\ddagger}$ by differentiating the Arrhenius plot.

[2/450 *Received, 28th February*, 1972]

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[10] R. P. Bell and W. B. T. Miller, *Trans. Faraday Soc.*, 1963, **59**, 1147.

[11] W. J. Albery and B. H. Robinson, *Trans. Faraday Soc.*, 1969, **65**, 980.