

Secondary Deuterium Isotope Effects in Proton Transfers from 2-Nitropropane

By Martin H. Davies,† Department of Chemistry, University of Stirling, Stirling

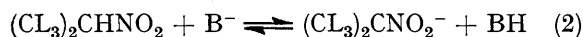
Kinetic and equilibrium secondary isotope effects have been measured for the deprotonation of 2-nitropropane by hydroxide and acetate ions. Although the Brønsted coefficients deduced lie between 0 and 1, they cannot be regarded as 'degrees of proton transfer' within the formalism of the Marcus theory. The isotope effects are interpreted in terms of two contributions, one of which does not change monotonically along the reaction co-ordinate. A recently reported dependence of the primary isotope effect upon isotopic solvent composition is discussed in the context of the rule of the geometric mean. A revised value of the equilibrium constant for iodination of the 2-nitropropanion is reported.

IN proton transfer reactions between carbon acids and oxygen bases, values of the Brønsted coefficient ($\beta = \delta\Delta G_{\ddagger}^{\circ}/\delta\Delta G^{\circ}$) may depend upon which species is modified to bring about the change in standard free energy.^{1,2} We adopt a nomenclature such that β_1 and β_2 refer to substitution in the carbon and oxygen acid-base pairs respectively. Thus Bordwell *et al.*² have reported $\beta_1 = 1.61$ for the deprotonation of a series of 1-aryl-2-nitropropanes, whereas Bell and Goodall³ found $\beta_2 = 0.55$ for the reaction of 2-nitropropane with acetate and chloroacetate bases. These values have attracted comment regarding the validity of the interpretation of Brønsted coefficients in terms of transition state symmetry.⁴⁻⁶ Whereas β_1 does not satisfy the requirement $0 \leq \beta \leq 1$, the value of β_2 is >0.5 which is as anticipated³ from the Hammond postulate⁷ for a proton transfer with positive standard free energy ($\Delta G^{\circ} > 0$).

Secondary isotope effects may be used to define isotopic Brønsted coefficients according to equation (1)

$$\lg(k_D/k_H) = \beta^D \lg(K_D/K_H) \quad (1)$$

where k_D/k_H and K_D/K_H are the respective secondary isotope effects on the kinetics and equilibria of proton transfer. Albery *et al.*^{4,8} have recently shown that for the protonation of 3-diazobutan-2-one by carboxylic acids, β_2 and β_2^D are equal and may be regarded as a measure of transition state symmetry within the framework of Marcus theory.^{9,10} To test the generality of the identity of normal and isotopic Brønsted coefficients and to examine the use of β_1^D (the isotopic analogue of Bordwell's value²) as a 'degree of proton transfer' parameter, measurements of kinetic and equilibrium isotope effects are reported for reaction (2) where



L = H or D with hydroxide ($\Delta G^{\circ} < 0$) and acetate ($\Delta G^{\circ} > 0$) bases. Isotopic Brønsted coefficients have been determined for a number of other reactions^{11,12}

† Present address: University Chemical Laboratory, Canterbury, Kent.

‡ Note added in proof: Secondary isotope effects on the ionization of 2-nitropropane have also been recently determined by Kresge and his co-workers (A. J. Kresge, personal communication). They have obtained similar results to those reported here.

¹ R. P. Bell and S. Granger, personal communication.

² F. G. Bordwell, W. J. Boyle, and K. C. Yee, *J. Amer. Chem. Soc.*, 1970, **92**, 5926.

³ R. P. Bell and D. M. Goodall, *Proc. Roy. Soc.*, 1966, **A**, 294, 273.

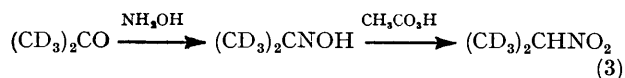
⁴ W. J. Albery, A. N. Campbell-Crawford, and J. S. Curran, *J.C.S. Perkin II*, 1972, 2206.

although not, as far as the author is aware, involving substitution in the carbon acid.‡

The following notation is adopted for our 2-nitropropanes: $2\text{NP}_0 = (\text{CH}_3)_2\text{CHNO}_2$ and $2\text{NP}_1 = (\text{CD}_3)_2\text{CHNO}_2$. In practice, isotope effect measurements were made on a mixture of 2NP_1 and analogues with less deuterium. The mixture is denoted as 2NP_m where m is the atom fraction of deuterium in the 1- and 3-positions. The abbreviation 2NP refers to both 2NP_0 and 2NP_m .

EXPERIMENTAL

Preparation of 2-Nitropropanes.—Commercial 2NP_0 (Koch-Light) was purified by preparative g.l.c. using a Carbowax 20M column. Subsequent analytical g.l.c. indicated at least 99.95% purity. 2NP_m was prepared by route (3) using the following method. To 7M-aqueous



hydroxylamine hydrochloride (30 cm³) at 0 °C was added 7M-sodium hydroxide solution (15 cm³). Portions (1 cm³) of [²H₆]acetone (Ryvan) and 7M-sodium hydroxide were added consecutively until 10 g (11 cm³) of the former had been consumed. This procedure keeps the pH near 4.5 where the reaction rate is at a maximum.¹³ The temperature was held below 10 °C. Ether (20 cm³) was then added to dissolve the precipitated acetoxime. After separation, the aqueous layer was extracted with ether (3 × 20 cm³). To the combined ether samples was added light petroleum (b.p. 40–60°) (20 cm³). After distillation of the ether, the acetoxime crystallized on cooling. A solution of peracetic acid prepared from 87% hydrogen peroxide (7.8 g), acetic anhydride (26.6 g), acetonitrile (100 cm³), and concentrated sulphuric acid (3 drops) was added over 48 h to a rapidly stirred and gently refluxing solution of the acetoxime in acetonitrile (200 cm³) containing urea (2 g) and disodium hydrogen orthophosphate (78 g).¹⁴ The reaction mixture was then filtered and

⁵ R. A. Marcus, *J. Amer. Chem. Soc.*, 1969, **91**, 7224.

⁶ A. J. Kresge, *J. Amer. Chem. Soc.*, 1970, **92**, 3210.

⁷ G. S. Hammond, *J. Amer. Chem. Soc.*, 1955, **77**, 334.

⁸ W. J. Albery, J. R. Bridgeland, and J. S. Curran, *J.C.S. Perkin II*, 1972, 2203.

⁹ R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 891.

¹⁰ A. O. Cohen and R. A. Marcus, *J. Phys. Chem.*, 1968, **72**, 4249.

¹¹ M. M. Kreevoy and D. E. Konasewich, *J. Phys. Chem.*, 1970, **74**, 4464.

¹² V. Gold, *Adv. Phys. Org. Chem.*, 1969, **7**, 259.

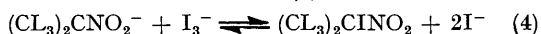
¹³ W. P. Jencks, *J. Amer. Chem. Soc.*, 1959, **81**, 475.

¹⁴ W. D. Emmons and A. S. Pagano, *J. Amer. Chem. Soc.*, 1955, **77**, 4557.

water (100 cm³) added. After extraction with dichloromethane (3 × 50 cm³) the combined extracts were washed with saturated aqueous sodium hydrogen carbonate and dried (MgSO₄). Solvents were distilled off until 10 cm³ of solution remained.

Details of purification and analysis were the same as for 2NP₀. The final yield of 2NP_m was 23% and ¹H n.m.r. gave the isotopic assay as $m = 0.92 \pm 0.005$. A sample of 2NP₀ prepared by this method was found to have the same rate constants as the purified commercial material.

Kinetic and Equilibrium Measurements.—All rate and equilibrium constants were determined in water at 25 °C using spectrophotometric methods. For the reaction of 2NP with hydroxide, the formation of the nitro-anions was followed at 222 nm. With acetate, the deprotonation does not run to completion. In this case, the nitro-anions were scavenged with iodine and the disappearance of I₃⁻ was followed at 353 nm. To calculate the rate constants from the rates of iodination, it was necessary to measure K_2 , the equilibrium constant for reaction (4).



The isotope effect on the ionization equilibria of 2NP [equation (2)] is the same for all bases. This is because isotopic substitution in only the carbon acid is involved. Equilibrium constants were determined for the deprotonation of 2NP by tris-hydroxymethylaminomethane (Tris).

Absorbance measurements were made using a Gilford 2400S spectrophotometer. The temperature in the cell compartment was determined with a platinum resistance probe. It was found to be stable to ± 0.02 °C. In the kinetic experiments absorbances were output directly onto paper tape. Measurements on 2NP₀ and 2NP_m were carried out at the same time to reduce systematic errors. Reagents were either of AnalaR or Volumetric grade. Water was deionized and distilled.

(a) *Reaction with hydroxide.* 2×10^{-4} M-2NP was caused to react with 10^{-2} M-sodium hydroxide. Since precise rate constants are required, it was necessary to exclude carbonate from the reaction mixture. To this end, the sodium hydroxide solutions were prepared in a nitrogen-filled glove box using water distilled under the same gas. Subsequently, samples (2.5 cm³) were transferred to spectrophotometric cells which were sealed with serum caps before being exposed to the air. Reactions were initiated by injecting 2×10^{-2} M-aqueous 2NP (25 mm³) and were followed for seven half-lives.

(b) *Reaction with acetate.* Buffers with $0.2\text{M} \leq [\text{CH}_3\text{CO}_2^-] \leq 0.5\text{M}$ and $[\text{CH}_3\text{CO}_2^-] : [\text{CH}_3\text{CO}_2\text{H}] = 19$ were made up from sodium acetate and hydrochloric acid solutions. Observed and predicted pH values agreed to ± 0.01 units. Stock solutions of 2NP in water (4×10^{-2} M) were prepared with accurately known concentrations. Samples of these (1.2 cm³) were weighed out into spectrophotometric cells (1 cm path length) together with the same amount of buffer. Scavenging was initiated by the injection of 10^{-2} M-iodine (12 mm³) in either 1 or 2M-potassium iodide. This gives an initial iodine concentration of 5×10^{-5} M and [KI] is 5×10^{-3} or 10^{-2} M. To correct for spontaneous loss of iodine in the buffer, a 'blank' cell was monitored during the reaction. Buffers and stock solutions were stored at 5 °C between runs. Periodically the latter were analysed for possible decomposition by diluting

portions with 10^{-2} M-sodium hydroxide and determining the anion absorbance.

(c) *Nitro-anion iodination equilibrium.* Solutions of nitro-anion at known concentration were prepared as follows: 2×10^{-4} M-2NP₀ was dissolved in 10^{-2} M-sodium hydroxide and after 1 h, when the reaction was complete, the solution was neutralized to pH 8 with 1M-hydrochloric acid using a glass electrode. To hold the pH near this value, Tris buffer was added to give $[\text{TrisH}^+] = [\text{Tris}] = 10^{-3}$ M. The nitro-anion concentration was then determined spectrophotometrically at 222 nm. Under these conditions the anion was found to be stable. The solutions were subsequently made up to 0.3, 0.5, or 0.7M in potassium iodide and known volumes of 10^{-2} M-iodine in 1M-KI added. Finally, [I₃⁻] was determined at 353 nm. The equilibrium was found to be set up very rapidly. From the known concentrations and measured absorbances, K_2 may be calculated. No attempt was made to measure the isotope effect on K_2 .

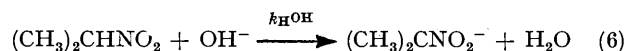
(d) *Equilibrium with Tris.* Buffers were made up with $1.5 \leq [\text{TrisH}^+] : [\text{Tris}] \leq 10$ by partially neutralizing 0.25 or 0.5M-Tris with hydrochloric acid of the same concentration. Samples (0.4 cm³) of freshly prepared 5×10^{-3} M stock solutions of 2NP were weighed into calibrated flasks (10 cm³) and buffer, 10^{-2} M-hydrochloric acid, or 10^{-2} M-sodium hydroxide were added. Equilibrium in the buffer was reached within 24 or 48 h at 25 °C and within 1 h for the H⁺ and OH⁻ solutions. In the latter cases, the 2NP is entirely in the neutral and ionized forms respectively. We then have equation (5) for the buffers¹⁵ where A is the absorbance of 2NP at 222 nm in the indicated solutions.

$$\frac{[(\text{CL}_3)_2\text{CNO}_2^-]}{[(\text{CL}_3)_2\text{CHNO}_2]} = \frac{A(\text{buffer}) - A(\text{H}^+)}{A(\text{OH}^-) - A(\text{buffer})} \quad (5)$$

RESULTS

Standard errors are used throughout. Characteristics of the u.v. spectra for the nitro-anions were found to be: $(\text{CH}_3)_2\text{CNO}_2^-$, λ_{max} 222.5 \pm 0.5 nm ($10^{-5}\epsilon$ 1.003 \pm 0.004 m² mol⁻¹); $(\text{CD}_3)_2\text{CNO}_2^-$, λ_{max} 221.5 \pm 0.5 nm ($10^{-5}\epsilon$ 0.998 \pm 0.003 m² mol⁻¹).

(a) *Reaction with Hydroxide.*—The proton transfer (6)



follows second-order kinetics running to completion with the consumption of 2% hydroxide under the experimental conditions. In view of the precision needed, it is inadequate to take [OH⁻] as constant thereby treating the reaction as pseudo-first order. However, rather than use a complete second-order analysis, it proved more convenient to correct for small departures from first-order behaviour. Where a and b are the initial concentrations of 2NP and hydroxide respectively, application of the condition $a/b \ll 1$ to the usual integrated second-order rate equation¹⁶ leads to expression (7). In this equation $g_{\text{H}} = (b - a)t +$

$$[2\text{NP}_0] = a \exp - (k_{\text{H}^{\text{OH}}} g_{\text{H}}) \quad (7)$$

$a\{1 - \exp[-(b - a)k_{\text{H}^{\text{OH}}}t]\}/bk_{\text{H}^{\text{OH}}}$, t is time, and $k_{\text{H}^{\text{OH}}}$ is the second-order velocity constant. The second term in g_{H} allows for the changing [OH⁻].

For 2NP_m there is the additional complication that we have several isotopic subspecies in significant proportions which react in parallel ($m = 0.92$). The Appendix treats

¹⁵ R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' Butterworths, London, 1959, p. 344.

¹⁶ A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' Wiley, New York, 1961, p. 17.

this situation in the case of each subspecies reacting in a first-order manner. Thus equation (49) with $c = [2\text{NP}_m]$, $n = 6$, $k_D = k_D^{\text{OH}b}$ and $k_D^{1-1/n}k_H^{1/n} = (k_D^{\text{OH}})^{5/6}(k_H^{\text{HO}})^{1/6}b$ describes the kinetics within the approximation that $[\text{OH}^-]$ is invariant. k_D^{OH} is the second-order rate constant for the deprotonation of 2NP_1 . It may be shown that allowing $[\text{OH}^-]$ to change by a small amount leads to equation (8). In this equation $g_m = (b - a)t + a\{1 - \exp[-(b - a)k_m^{\text{OH}}t]\}/bk_m^{\text{OH}}$ where $k_m^{\text{OH}} = (1 - m)k_H^{\text{OH}} + mk_D^{\text{OH}}$. It can be seen that g_m and g_H are analogous

$$[2\text{NP}_m] = a\{[1 - 6(1 - m)] \exp - (k_D^{\text{OH}}g_m) + 6(1 - m) \exp - (k_D^{\text{OH}})^{5/6}(k_H^{\text{OH}})^{1/6}g_m\} \quad (8)$$

functions. To determine optimum values of k_H^{OH} and k_D^{OH} , absorbances A were fitted to expression (9) by means of a

$$A = A_\infty + (A_0 - A_\infty)[2\text{NP}]/a \quad (9)$$

generalized least squares program.¹⁷ In the former case $[2\text{NP}]/a$ was taken from equation (7) whereas in the latter equation (8) was used together with the known values of k_H^{OH} and m . A_0 and A_∞ are initial and final absorbances, respectively. Residuals were rarely greater than 0.002 units. Table 1 summarizes the results of nine determinations of the secondary isotope effect. The present value

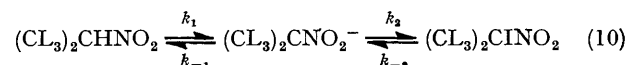
TABLE 1

Kinetic isotope effect (OH^-)

$t = 25.03^\circ\text{C}$; Ionic strength $\mu = 10^{-2}\text{M}$		
$k_H^{\text{OH}}/1 \text{ mol}^{-1} \text{ s}^{-1}$	$k_D^{\text{OH}}/1 \text{ mol}^{-1} \text{ s}^{-1}$	$k_D^{\text{OH}}/k_H^{\text{OH}}$
0.360 ₆	0.323 ₁	0.896
± 0.001	± 0.001	± 0.002

of k_H^{OH} is in reasonable accord with previous determinations [Gold and Grist,¹⁸ 0.352 (± 0.003) $1 \text{ mol}^{-1} \text{ s}^{-1}$ at $\mu = 0.1\text{M}$; Bell and Goodall,³ 0.316 (± 0.014) $1 \text{ mol}^{-1} \text{ s}^{-1}$ at $\mu = 0.2\text{M}$]. The observed differences may be a salt effect.

(b) *Reaction with Acetate*.—For the iodination of 2NP in acetate buffers, we may outline the mechanism as in reaction (10).¹⁹ First-order velocity coefficients are shown.



These are dependent upon concentrations of other species in the system. In particular equation (11) holds and

$$k_1 = k^A[\text{CH}_3\text{CO}_2^-] + k^{\text{OH}}[\text{OH}^-] + k^0 \quad (11)$$

$k_2 = k_2^*[\text{I}_2^*]$ where $[\text{I}_2^*] = [\text{I}_2] + [\text{I}_3^-]$. The rate constants k^A , k^{OH} , and k^0 describe the deprotonation of 2NP by acetate, hydroxide, and water respectively and k_2^* is the second-order rate constant for iodination of the nitro-anion. The buffer composition and hence k_1 was essentially constant for each run. It may be shown that only when iodination is irreversible ($k_2/k_{-2} \gg 1$) and scavenging limitingly efficient ($k_2/k_{-1} \gg 1$) will the rate of reaction be independent of $[\text{I}_2^*]$. Under these conditions the observed rate constant is k_1 . However in practice, the iodination of 2NP is only approximately zero order in iodine³ and similar behaviour has been observed for nitromethane.²⁰ In view of this, it is necessary to treat the kinetics in some detail.

¹⁷ L. G. Sillen, *Acta Chem. Scand.*, 1964, **18**, 1085.

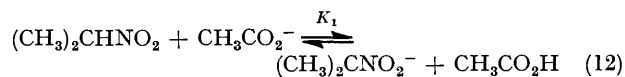
¹⁸ V. Gold and S. Grist, *J.C.S. Perkin II*, 1972, 89.

¹⁹ K. J. Pedersen, *K. danske vidensk. Selsk. Skr. Mat.-fys. Medd.*, 1932, **12**, 1.

²⁰ J. A. Feather and V. Gold, *J. Chem. Soc.*, 1965, 1752.

²¹ D. Turnbull and S. H. Maron, *J. Amer. Chem. Soc.*, 1943, **65**, 212.

The validity of the condition $k_2/k_{-1} \gg 1$ was tested in the following way. A solution of $2 \times 10^{-4}\text{M}$ -nitro-anion at pH 8 was prepared as described in the Experimental section (c). To a sample in a spectrophotometric cell was added enough iodine in potassium iodide solution to give $[\text{I}_2^*] = 2 \times 10^{-5}\text{M}$ in the absence of reaction but however rapid the mixing, it was impossible to measure the decay of I_3^- . Thus we can write $2 \times 10^{-4}k_2^* > 1 \text{ s}^{-1}$ or $k_2^* > 5 \times 10^3 \text{ l mol}^{-1} \text{ s}^{-1}$. To estimate k_{-1} it is necessary to consider the equilibrium (12) and we have equation (13). The dissociation constants



$$k_1/k_{-1} = K_1[\text{CH}_3\text{CO}_2^-]/[\text{CH}_3\text{CO}_2\text{H}] \quad (13)$$

of 2NP_0 ^{21,22} and acetic acid²³ give the equilibrium constant $K_1 = 1.1 \times 10^{-3}$. From experiment, $k_1 \leq 6 \times 10^{-7} \text{ s}^{-1}$ (Table 2) and we know the buffer ratio under the reaction conditions. Using these values in equation (13) gives $k_{-1} \leq 3 \times 10^{-5} \text{ s}^{-1}$. Combining the limits on k_2^* and k_{-1} yields relation (14) and the condition $k_2/k_{-1} \gg 1$ is satisfied to high accuracy down to at least $[\text{I}_2^*] = 5 \times 10^{-6}\text{M}$.

$$k_2/k_{-1} = k_2^*[\text{I}_2^*]/k_{-1} > 2 \times 10^8[\text{I}_2^*] \quad (14)$$

Having demonstrated the efficiency of scavenging, we ascribe the dependence of the observed rate on $[\text{I}_2^*]$ to the reversibility of the second step in equation (10). Further, the inequalities $k_{-1} > k_1$ and $k_2 \gg k_{-1}$ may be combined to give the relation $k_2 + k_{-2} \gg k_1 + k_{-1}$. This condition requires that the second equilibrium is set up much more rapidly than the first and hence the nitro-anions and the iodo-derivatives are present in equilibrium concentrations during the reaction. Thus from equation (4) we may write (15) and we also have equation (16). Using the

$$\frac{[(\text{CL}_3)_2\text{CNO}_2^-]}{[(\text{CL}_3)_2\text{CINO}_2]} = \frac{[\text{I}^-]^2}{K_2[\text{I}_3^-]} = \frac{k_{-2}}{k_2} \quad (15)$$

$$K_3 = [\text{I}_3^-]/[\text{I}_2][\text{I}^-] \quad (16)$$

stoichiometric relationships (17) and (18) together with

$$[2\text{NP}]_0 = [2\text{NP}] + [(\text{CL}_3)_2\text{CNO}_2^-] + [(\text{CL}_3)_2\text{CINO}_2] \quad (17)$$

$$[\text{I}_2^*]_0 = [\text{I}_2^*] + [(\text{CL}_3)_2\text{CINO}_2] \quad (18)$$

equations (15) and (16) we can relate the change in $[2\text{NP}]$ to the observed change in $[\text{I}_3^-]$ by expression (19). Under

$$[2\text{NP}]_0 - [2\text{NP}] = ([\text{I}_3^-]_0 - [\text{I}_3^-]) \left(1 + \frac{1}{K_3[\text{I}^-]} \right) \left(1 + \frac{[\text{I}^-]^2}{K_2[\text{I}_3^-]} \right) \quad (19)$$

the experimental conditions $[\text{I}^-]$ is effectively constant. Values of K_2 are discussed below and $K_3 = 713 \text{ l mol}^{-1}$.²⁴ Equation (19) relates $[2\text{NP}]$ and $[\text{I}_3^-]$ rather than a simple linear expression because all the 2NP which ionizes is not iodinated.

By combining equations (13), (15), and (17) with the rate law (20) it may be shown that for all but the last 10% of

$$-d[2\text{NP}]/dt = k_1[2\text{NP}] - k_{-1}[(\text{CL}_3)_2\text{CNO}_2^-] \quad (20)$$

²² G. W. Wheland and J. Farr, *J. Amer. Chem. Soc.*, 1943, **65**, 1433.

²³ G. Kortum, W. Vogel, and K. Andrussov, 'Dissociation Constants of Organic Acids in Aqueous Solution,' Butterworths, London, 1961.

²⁴ D. J. Barnes and R. P. Bell, *Proc. Roy. Soc.*, 1970, **A**, **318**, 421.

the iodination, [2NP] follows a first-order course which is characterized by k_1 to within 0.1%. Consequently, after subtracting a small contribution for spontaneous loss of iodine in the 'blank' cell (<2% of the rate), absorbances for 90% reaction were fitted¹⁷ to expression (21) where

$$A = A_0 - F[2NP]_0(1 - \exp - k_1 t) \quad (21)$$

equation (22) applies and ϵ is the extinction coefficient of

$$F^{-1} = (1 + 1/K_3[I^-])(1 + [I^-]^2\epsilon/K_2A)/\epsilon \quad (22)$$

I_3^- . Residuals were invariably less than 0.003 units. The correction term, $[I^-]^2\epsilon/K_2A$ reaches a maximum value of 0.01. The same kinetic treatment was used for both 2NP_m and 2NP₀. This is because, in contrast to the hydroxide reaction, only 0.25% of 2NP_m is deprotonated and hence the isotopic composition is constant throughout the iodination. The observed isotope effect is corrected by using equation (50) (see Appendix).

To obtain k^A , the other contributions to k_1 are required [equation (11)]. The known values, $k_{H^{OH}} = 0.36 \text{ l mol}^{-1} \text{ s}^{-1}$ and $[OH^-] = 1.1 \times 10^{-8} \text{ M}$ together with the estimate,³ $k_{H^0} = 4 \times 10^{-9} \text{ s}^{-1}$ give $k_{H^A} = (k_{1H} - 8 \times 10^{-9})/[CH_3CO_2^-]_H$. Since the correction to k_1 is never larger than 3% and the dependence of the secondary isotope effect on the base is small, a value of k_m^A/k_H^A for each experiment was evaluated directly from equation (23). Subscripts H, m, and D show

$$k_m^A/k_H^A = k_{1m}[CH_3CO_2^-]_H/k_{1H}[CH_3CO_2^-]_m \quad (23)$$

the isotopic composition to which the rate constants or concentrations refer. Table 2 summarizes the kinetic

TABLE 2

Kinetic isotope effect ($CH_3CO_2^-$)					
$t = 24.98^\circ\text{C}$; $N =$ number of runs					
$[CH_3CO_2^-]_H/M$	μ/M	N	$10^7 k_{1H}/s^{-1}$	$10^6 k_{H^A}/s^{-1}$	k_m^A/k_H^A
0.0937	0.1	3	2.57	2.66	0.917
			± 0.03	± 0.03	± 0.005
0.1407	0.15	4	3.69	2.57	0.917
			± 0.03	± 0.03	± 0.004
0.1862	0.2	2	5.00	2.64	0.911
			± 0.04	± 0.02	± 0.004
0.2317	0.25	4	6.32	2.69	0.913
			± 0.04	± 0.02	± 0.004

Constants for equation (21): $K_2 = 2.6 \times 10^3 \text{ mol l}^{-1}$; $K_3 = 713 \text{ l mol}^{-1}$; $\epsilon = 2.55 \times 10^5 \text{ m}^2 \text{ mol}^{-1}$ (from ref. 24)

data for acetate. The mean value of $10^6 k_{H^A}$, $2.64 (\pm 0.03) \text{ l mol}^{-1} \text{ s}^{-1}$, is lower than $3.02 (\pm 0.14) \text{ l mol}^{-1} \text{ s}^{-1}$ as found by Bell and Goodall.³ Independent measurements²⁵ carried out in this laboratory using 2NP₀ prepared by spinning band distillation give $10^6 k_{H^A} = 2.71 (\pm 0.1) \text{ l mol}^{-1} \text{ s}^{-1}$. The mean isotope effect $k_D^A/k_H^A = 0.907 \pm 0.007$. Uncertainties in the composition of the stock solutions are included in the standard error.

TABLE 3
Values of K_2

$t = 25^\circ\text{C}$			
$[I^-]/M$	0.3	0.5	0.7
$10^{-3}K_2/M$	2.34 ± 0.08	2.67 ± 0.11	2.77 ± 0.06

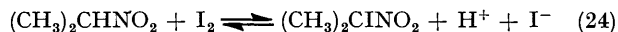
(c) *Nitro-anion Iodination Equilibrium*.—Table 3 gives values of K_2 . Each is the mean of three determinations.

²⁵ B. G. Cox and A. Gibson, personal communication.

²⁶ R. P. Bell and E. Gelles, *Proc. Roy. Soc.*, 1952, *A*, **210**, 310.

²⁷ R. G. Bates and H. B. Hetzer, *J. Phys. Chem.*, 1961, **65**, 667.

We may compare the final value, $K_2 = 2.6 \times 10^3 \text{ mol l}^{-1}$, with the potentiometric measurements of Bell and Gelles.²⁶ They determined the equilibrium constant for reaction (24)



which gives $K_2 = 3 \times 10^2 \text{ mol l}^{-1}$ when combined with K_3 and the acid dissociation constant for 2NP₀.^{21,22} We attempted to study equilibrium (24) by the spectrophotometric determination of I_3^- but this was rendered impractical by the oxidation of I^- to I_2 by 2NP. Use of the value $K_2 = 3 \times 10^2 \text{ mol l}^{-1}$ in equation (21) gave a significantly poorer fit to the kinetic data. It is also notable that Bell and Gelles obtained more precise results for the iodination of ketones than for the nitroalkanes. In the direct determination of K_2 , no slow proton transfer step is involved so the equilibrium is set up very rapidly and problems of oxidation do not arise.

(d) *Equilibrium with Tris*.—Equilibrium constants were calculated from equation (25) where the activity coefficient

$$K^T = \Gamma \frac{[(CL_3)_2CNO_2^-][TrisH^+]}{[(CL_3)_2CHNO_2][Tris]} \quad (25)$$

product Γ was evaluated using expression (26). Small

$$\lg \Gamma = -1.02\mu^3(1 + \mu^3)^{-1} \quad (26)$$

corrections were applied to the Tris buffer ratio to allow for the ionization of 2NP. Values of K^T showed no systematic pH dependence. Results are summarized in Table 4. Combining the mean value of K_H^T with the

TABLE 4

Equilibrium isotope effect				
$t = 25.0^\circ\text{C}$; $C^T = [Tris] + [TrisH^+]$				
C^T/M	N	K_m^T	K_H^T	K_m/K_H
0.12	7	1.73 ± 0.05	2.16 ± 0.05	$0.79_8 \pm 0.01$
0.24	5	1.77 ± 0.04	2.28 ± 0.04	$0.77_8 \pm 0.01$

dissociation constant²⁷ for $TrisH^+$ ($pK_a = 8.07$) gives $pK_a = 7.72 (\pm 0.02)$ for 2NP₀. This is in excellent agreement with the values $7.68 (\pm 0.03)$ and $7.7-7.8$ obtained potentiometrically.^{21,22} The mean value of K_m/K_H is corrected by the equilibrium analogue of equation (50) (see Appendix) to give the result $K_D/K_H = 0.77_4 (\pm 0.01)$.

DISCUSSION

Table 5 summarizes the secondary isotope effect data. β_1^D is obtained by using equation (1) and $\Delta pK_a = 7.72 - pK_a(BH)$ ²³ [equation (2)].

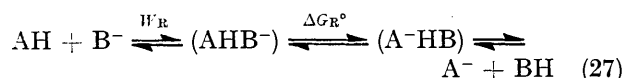
TABLE 5
Collected results

B ⁻	k_D^B/k_H^B (or K_D/K_H) *	β_1^D	ΔpK_a
OH ⁻	0.896 ± 0.002	0.43 ± 0.02	-8.03
CH ₃ CO ₂ ⁻	0.907 ± 0.007	0.38 ± 0.03	2.97
* Tris	0.774 ± 0.009		

(a) *Isotopic and Normal Brønsted Coefficients*.—Our value of $\beta_1^D = 0.43$ for OH⁻ differs from the result $\beta_1 = 1.61$ obtained by Bordwell *et al.*² for the deprotonation of 1-aryl-2-nitropropanes by OH⁻-OMe⁻. It is thus not true that in general isotopic and normal Brønsted coefficients are the same for carbon acids. This contrasts with an increasing body of evidence in

the case of oxygen acids.^{4,8,28} Further, β_1^D for acetate is significantly different from the value $\beta_2 = 0.55 (\pm 0.02)$ obtained by Bell and Goodall³ for the reaction of 2NP_0 with acetate and chloroacetate.

(b) *Application of Marcus Theory.*—A *prima facie* interpretation of the β_1^D versus ΔpK_a data in Table 5 might be that the 'degree of proton transfer' is 0.41 for $-8 \leq \Delta pK_a \leq 3$ and the increasing product-like character of the transition state predicted from the Hammond postulate⁷ as ΔpK_a becomes more positive is small compared with experimental error. This view is inconsistent with the Marcus treatment of proton transfer reactions^{5,9,10} as we now show. For the equilibria (27) Marcus gives equations (28) and (29).



$$\Delta G_{\ddagger}^\circ = W_R + \lambda(1 + \Delta G_R^\circ/\lambda)^2/4 \quad (28)$$

$$\Delta G^\circ = W_R + \Delta G_R^\circ + W_P \quad (29)$$

We follow the nomenclature of Albery *et al.*⁴ who describe the theory in more detail. The species in parentheses in equilibria (27) are collision complexes with standard free energies of formation, W_R and $-W_P$. $\lambda/4$ is the standard free energy of activation for their interconversion when the 'proton driving force,' ΔG_R° , is zero. To express a second-order rate constant k^B in terms of $\Delta G_{\ddagger}^\circ$ it is necessary to choose a standard state. Unit mole fraction seems most appropriate if for no other reason than because in expression (30) the pre-exponential factor is *ca.* $10^{11} \text{ l mol}^{-1} \text{ s}^{-1}$ as required by

$$k^B = (\hbar kT/h[\text{H}_2\text{O}]) \exp -\Delta G_{\ddagger}^\circ/RT \quad (30)$$

Marcus.⁹ We also need statistical factors. Where there are q equivalent basic sites on B^- and p equivalent acidic sites on BH [equation (2)] standard free energies are given by equations (31) and (32). The symbols

$$\Delta G_{\ddagger}^\circ = -RT\{\ln(k^B/q) - \ln(\hbar kT/h[\text{H}_2\text{O}])\} \quad (31)$$

$$\Delta G^\circ = -RT[\ln(p/q) - 2.3\Delta pK_a] \quad (32)$$

R , \hbar , h , and T have their usual significance and $[\text{H}_2\text{O}] = 55.6\text{M}$.

When W_R , W_P , and λ are invariant to changes in ΔG° , Marcus, by appealing to model proton transfers, interprets the Brønsted coefficient as a transition state symmetry parameter. Under the same conditions he gives equation (33) and the theory may then be regarded

$$\beta = \frac{1}{2}(1 + \Delta G_R^\circ/\lambda) \quad (33)$$

as an algebraic form of the Hammond postulate combined with Leffler's interpretation²⁹ of Brønsted coefficients. Since equation (28) is only valid for $-\lambda \leq \Delta G_R^\circ \leq \lambda$, the restriction, $0 \leq \beta \leq 1$ is imposed on equation (33). The value, $\beta_1 = 1.61$,² being outside this range, has been discussed variously in terms of changing λ ⁵ or changing W_R and W_P .⁴

²⁸ M. M. Kreevoy and D. E. Konasewich, *Adv. Chem. Phys.*, 1971, **21**, 243.

We proceed to examine whether β_1^D satisfies equation (33). If this is the case, we have from equation (28), equa-

$$\Delta G_{\ddagger}^\circ = W_R + \lambda(\beta_1^D)^2 \quad (34)$$

tion (34) and for the reverse reaction equation (35). For

$$\Delta G_{\ddagger}^\circ - \Delta G^\circ = -W_P + \lambda(1 - \beta_1^D)^2 \quad (35)$$

OH^- , W_P vanishes since HB [equation (27)] is simply a solvating water molecule and λ may be evaluated using equations (31), (32), and (35). We take $q = 1$ and $p = 2$. Values of k^B and ΔpK_a for 2NP_0 were selected although use of the corresponding quantities for 2NP_1 , or indeed different statistical factors does not change the result of the analysis. Knowing λ , we may use equation (35) with estimates of W_P to predict values of β_1^D for other bases with known rate and equilibrium constants. Carrying through this procedure we obtain $\beta_1^D = 0.53 (\pm 0.02)$ for acetate ($q = 2$, $p = 1$) when W_P is zero. Larger values of $-W_P$ only serve to increase β_1^D and it is unlikely that $-W_P < 0$. Hence observed [0.38 (Table 5)] and predicted (0.53) values of β_1^D for acetate do not agree and thus equation (33) does not hold for this parameter. Since the validity of (33) and the interpretation of β in terms of transition state symmetry have the same basis (constant W_R , W_P , and λ) the 'degree of proton transfer' is *not* simply related to β_1^D . This result is unchanged by using a standard state of unit molarity for $\Delta G_{\ddagger}^\circ$. Thus like β_1 , β_1^D does not give us transition state symmetry despite the fact that $0 \leq \beta_1^D \leq 1$.

Although there are insufficient data to carry out a complete Marcus analysis for changes in B^- [equation (2)], it is interesting to adopt a simplified approach by neglecting W_P and W_R [equations (28) and (29)]. Thus λ calculated from k^B and ΔpK_a for acetate can be used to predict β [equation (33)] and k^B [equation (28)] for any base of known pK_a . Results of this approach are given in Table 6. We anticipate that for hydroxide the transition state will be somewhat nearer to the re-

TABLE 6

Application of Marcus theory for $W_R = W_P = 0$

B^-	ΔpK_a	β^*	k^B * / $\text{l mol}^{-1} \text{ s}^{-1}$	k^B † / $\text{l mol}^{-1} \text{ s}^{-1}$	k_H/k_D ‡
OH^-	-8.03	0.43	4.9×10^{-1}	3.6×10^{-1}	7.4
CH_3CO_2^-	2.97	0.53	(2.6×10^{-6})	2.6×10^{-6}	7.6

* Predicted. † Observed. ‡ Primary isotope effects determined by Bell and Goodall.³

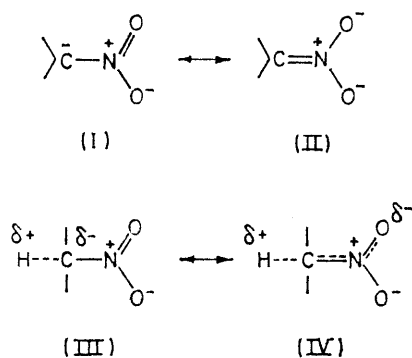
actants, whereas for acetate the 'degree of proton transfer' is somewhat >0.5 . This conclusion is not inconsistent with the primary isotope effects³ which suggest that both transition states are not far from symmetrical. Predicted and observed values of k^{OH} are in remarkable agreement considering both the simplicity of the treatment and the extrapolation over 11 pK_a units. Further, the predicted β for acetate is close to the experimental value,³ $\beta_2 = 0.55 (\pm 0.02)$. In the case of hydroxide, the equality of β_1^D (Table 5)

²⁹ J. E. Leffler and E. Grunwald, 'Rates and Equilibria in Organic Reactions,' Wiley, New York, 1963, p. 158.

with the value of β anticipated by the Marcus theory can only be fortuitous since as we have already shown β_1^D does not obey equation (33).

(c) *Interpretation of Secondary Isotope Effects.*—We now consider the secondary isotope effects in the light of a model needed to describe the influence of normal substituent changes in the nitroalkanes. To set up the model, three items of evidence are invoked. (1) pK_a values for the series CH_3NO_2 , $\text{CH}_3\text{CH}_2\text{NO}_2$, and $(\text{CH}_3)_2\text{CHNO}_2$. (2) Relative rate constants for the nitroalkanes in item (1) as a function of the pK_a of the deprotonating base. (3) Bordwell's Brønsted coefficient for the 1-aryl-2-nitroalkanes.^{2,30}

The pK_a values in item (1) are not in accord with the CH_3 group acting as an electron donor in the inductive



mode (Table 7). However, as has previously been pointed out,³ the order may be correlated with the familiar lowering of standard free energy³¹ which occurs in processes involving the formation of a π bond when CH_3 replaces hydrogen on an α -carbon atom. (This effect may arise from hyperconjugation.) We deduce that in the nitro-anions, structure (II) is dominant over structures of type (I). Table 7 collects together relative rate constants for the deprotonation of nitromethane, nitroethane, and 2NP. Values for each base are taken from a common source where possible. Here, in contrast to the equilibrium case, the α -methyl groups behave inductively although this effect tends to become less pronounced for weaker bases. Thus, it is necessary to invoke a transition state model in which resonance structures of type (III) are dominant. (For simplicity, we have omitted the base and show only one of the two possible resonance forms involving the nitro-group.) Structures (IV) are however becoming relatively more important for bases of low pK_a and since (II) is dominant in the product, this is in accordance with the Hammond postulate. Evidently proton transfer runs ahead of the delocalization of charge into the nitro-group. If this were not the case, structures (III) and (IV) would have

³⁰ F. G. Bordwell and W. J. Boyle, *J. Amer. Chem. Soc.*, 1972, **94**, 3907.

³¹ J. Hine, 'Physical Organic Chemistry,' McGraw-Hill, New York, 1962, p. 19.

³² D. D. Perrin, 'Dissociation Constants of Organic Bases in Aqueous Solution,' Butterworths, London, 1965.

³³ R. G. Pearson and F. V. Williams, *J. Amer. Chem. Soc.*, 1953, **75**, 3073.

the same relative weights as (I) and (II) at every point along the reaction co-ordinate.

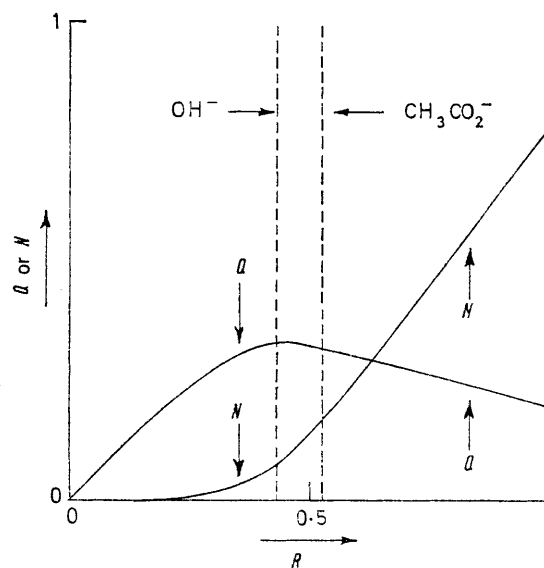
TABLE 7

Relative rate constants for the deprotonation of nitroalkanes					
B ⁻	pK_a	2NP	$\text{CH}_3\text{CH}_2\text{NO}_2$	CH_3NO_2	Ref.
OH^-	15.75	1	16	87	3
pyridine	5.20	1	9	37	3, 20, 32, 33
CH_3CO_2^-	4.75	1		13	23, 34
$\text{ClCH}_2\text{CO}_2^-$	2.87	1	5	18	23, 35
H_2O	-1.75	1*	9*	11*	3, 36, 37
Nitroalkane	pK_a	7.7	8.5	10.2	21, 22

* Estimate. All values refer to 25 °C in water.

A similar conclusion has been reached by Bordwell *et al.*² and we may use their findings for the deprotonation of 1-aryl-2-nitropropanes by OH^- - MeO^- to elaborate on our model. In these compounds, the reaction centre is insulated by a methylene link from the direct resonance effects of substituents in the phenyl group. Consequently, only inductive changes modify the rate and equilibrium constants. The value $\beta_1 = 1.61$ therefore implies that there is a greater charge on the α -carbon atom in the transition state than in the product. This is entirely feasible since the transition state is closer to (III) than (IV) whereas the product is nearer to (II).

It is helpful to express the model in diagrammatic form. The Figure shows the charge on the α -carbon



Model for the deprotonation of nitroalkanes: R = degree of proton transfer; Q = fractional negative charge on the α -carbon atom; N = order of π bonding to the nitro-group. Transition states for hydroxide and acetate ions are shown as described in the text

atom (Q) and the order of π bonding (N) as schematic functions of the extent of proton transfer (R). Thus the

³⁴ O. Reitz, *Z. Phys. Chem. A*, 1936, **176**, 363.

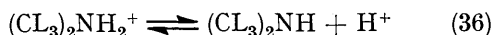
³⁵ T. Tenno and A. Talvik, 'Organic Reactivity,' Tartu State University, 1969, vol. 6, p. 889.

³⁶ R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, 1950, **72**, 3574.

³⁷ R. Junell, *Z. Phys. Chem. A*, 1929, **141**, 71.

values of Q and N at $R = 1$ are determined by the relative weights of structures (I) and (II) respectively. Values of R for hydroxide and acetate transition states are taken as β in Table 6. For both these bases, and indeed for all bases in Table 7, $Q > N$ because (III) dominates (IV). Further, Q in the region of the hydroxide transition state is drawn greater than Q at $R = 1$ as required by β_1 . Finally, we have imposed the constraint, $R = Q + N$.

It is often helpful to discuss secondary isotope effects in the same terminology as is employed for normal substituent effects and we adopt this approach here. Thus in proton transfer equilibria, deuterium remote from the reaction centre usually behaves as an electron donor.³⁸⁻⁴¹ Our result, $K_D/K_H = 0.77$, fulfils this expectation. This value is close to the isotope effect, $K_D/K_H = 0.76$, found for the dissociation (36) of the dimethylammonium ion,⁴¹ but here the change in



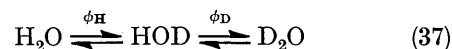
charge at the reaction centre is much greater than for 2NP. Thus the value $K_D/K_H = 0.77$ is too low to be ascribed to an inductive effect only and it appears that hyperconjugation (or some other effect arising from the presence of the π bond) is involved. We may therefore consider that the secondary isotope effect has two contributions, one depending on Q and the second upon N . The Figure shows how these quantities change along the reaction co-ordinate. The inductive component is larger in the kinetic isotope effect than in the equilibrium effect. Therefore we may ascribe the failure of β_1^D as a transition state symmetry parameter to the non-monotonic behaviour of Q with respect to proton transfer.

The complexity of both isotope and normal substituent effects in the nitroalkanes arises ultimately from the extensive electronic redistribution which accompanies proton abstraction. This contrasts with the simpler nature of changes occurring in the base. Thus for acetate, it seems likely that the charge on the carboxylic carbon atom changes monotonically along the reaction co-ordinate. It is therefore understandable that β_2 agrees with the prediction of transition state symmetry from the (simplified) Marcus theory.

(d) *Solvent Isotope Dependence of the Primary Isotope Effect.*—Gold and Grist¹⁸ have recently reported that the primary kinetic isotope effect for 2NP is dependent upon the isotopic composition of the solvent. We point out that the phenomenon may be interpreted as a manifestation of the breakdown of the 'rule of the geometric mean.'^{42,43} In the case of reaction with hydroxide we may also argue that the magnitude of the

effect is consistent with an approximately symmetrical transition state.

The usual treatment of solvent isotope effects^{44,45} assumes that the fractionation factor ϕ for a given site does not depend upon whether other sites in the system are occupied by H or D. In other words, isotope effects on ϕ are neglected. Abandoning this assumption, we may define two different fractionation factors for exchange in the solvent [equation (37)]. Thus allowing



for statistical factors, processes (38) and (39) have



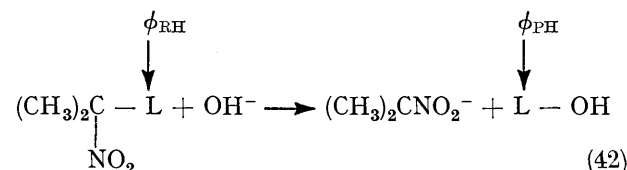
equilibrium constants $2\phi_H$ and $\phi_D/2$ respectively. We then have equations (40) and (41) where K is the equi-

$$\phi_H\phi_D = 1 \quad (40)$$

$$\phi_H = \frac{1}{2}K^{1/2} \quad (41)$$

ilibrium constant for $\text{H}_2\text{O} + \text{D}_2\text{O} \rightleftharpoons 2\text{HOD}$ and has the value 3.76⁴⁶ at 25 °C. Consequently, $\phi_H = 0.97$ and $\phi_D = 1.03$. (The usual approximation puts $\phi_H = \phi_D = 1$.)

For the reaction of $(\text{CH}_3)_2\text{CLNO}_2$ with OH^- , we consider the simplest model (42) and show the primary fractionation factors in the case of H_2O as solvent.



There will be another pair (ϕ_{RD} and ϕ_{PD}) for D_2O . In the reactant, the site L is at most only weakly hydrogen bonded to the solvent whereas in the product it becomes bound in a water molecule. This will remain true for more complicated models¹⁸ involving additional solvent molecules. We may therefore argue that for the equilibrium primary isotope effect, K_D/K_H , the greater part of the solvent dependence is attributable to ϕ_P rather than ϕ_R . Hence, equation (43) applies and

$$\left(\frac{K_D}{K_H}\right)_{\text{D}_2\text{O}} \left(\frac{K_D}{K_H}\right)_{\text{H}_2\text{O}}^{-1} = \frac{\phi_{PD}}{\phi_{PH}} \cdot \frac{\phi_{RH}}{\phi_{RD}} \approx \frac{\phi_D}{\phi_H} = 1.06 \quad (43)$$

from the data of Gold and Grist,¹⁸ we have equation (44).

$$\left(\frac{k_D}{k_H}\right)_{\text{D}_2\text{O}} \left(\frac{k_D}{k_H}\right)_{\text{H}_2\text{O}}^{-1} = 1.04 \pm 0.01 \quad (44)$$

Thus the solvent isotope dependence of the primary kinetic isotope effect lies about halfway between unity

³⁸ A. Streitwieser and H. S. Klein, *J. Amer. Chem. Soc.*, 1963, **85**, 2759.

³⁹ R. P. Bell and W. B. T. Miller, *Trans. Faraday Soc.*, 1963, **59**, 1147.

⁴⁰ A. J. Kresge and R. J. Preto, *J. Amer. Chem. Soc.*, 1967, **89**, 5510.

⁴¹ W. Van der Linde and R. E. Robertson, *J. Amer. Chem. Soc.*, 1964, **86**, 4504.

⁴² W. J. Albery and M. H. Davies, *Trans. Faraday Soc.*, 1969, **65**, 1059.

⁴³ J. Bigeleisen, *J. Chem. Phys.*, 1955, **23**, 2264.

⁴⁴ V. Gold, *Trans. Faraday Soc.*, 1960, **56**, 255.

⁴⁵ A. J. Kresge, *Pure Appl. Chem.*, 1964, **8**, 243.

⁴⁶ L. Friedman and V. J. Shiner, *J. Chem. Phys.*, 1966, **44**, 4639.

and the corresponding equilibrium value. This is satisfactory for a process with a near symmetrical transition state. Finally, we note that the solvent isotope effects for $(\text{CH}_3)_2\text{CHNO}_2$ and $(\text{CH}_3)_2\text{CDNO}_2$ will be slightly different.

APPENDIX

Kinetics for the Reactions of Statistical Isotopic Mixtures.—The species, XL_n has n equivalent non-exchanging sites which can be occupied by H or D. The constituent isotopic subspecies, $\text{XD}_r\text{H}_{n-r}$ undergo a first-order reaction in which all sites remain equivalent.

Symbols.—Symbols used are $c = [\text{XL}_n]$, k_r = first-order rate constant for $\text{XD}_r\text{H}_{n-r}$, $k_{\text{H}} = k_0$, and $k_{\text{D}} = k_n$. The following assignments apply at time $t = 0$: m = atom fraction of D in XL_n , k_m = observed first-order velocity coefficient, $a = c$, and $a_r = [\text{XD}_r\text{H}_{n-r}]$.

The system is characterized by equation (45) and the

$$c = \sum_{r=0}^n a_r \exp - k_r t \quad (45)$$

assumption of a statistical distribution of isotopes at $t = 0$ leads to expression (46).¹² If every deuteration

$$\frac{a_r}{a} = \frac{n!m^r(1-m)^{n-r}}{r!(n-r)!} \quad (46)$$

gives rise to the same isotope effect (constant k_{r+1}/k_r), equation (47) follows. Combination of equations (45)—(47)

$$k_r = k_{\text{D}}^{r/n} k_{\text{H}}^{(1-r/n)} \quad (47)$$

yields (48) and when m is close to unity this simplifies to

$$c = a \sum_{r=0}^n \left[\frac{n!m^r(1-m)^{n-r}}{r!(n-r)!} \exp - (k_{\text{D}}^{r/n} k_{\text{H}}^{(1-r/n)})t \right] \quad (48)$$

(49). First-order velocity coefficients may be found by

$$c = a \left\{ [1 - n(1-m)] \exp - (k_{\text{D}}t) + \frac{n(1-m)}{n(1-m)} \exp - (k_{\text{D}}^{1-1/n} k_{\text{H}}^{1/n})t \right\} \quad (49)$$

evaluating $-\ln c/dt$ from equation (48) and in particular k_m is given by equation (50). The similarity of equation

$$k_m = k_{\text{H}} \left[1 - m + m \left(\frac{k_{\text{D}}}{k_{\text{H}}} \right)^{1/n} \right]^n \quad (50)$$

(50) to the expressions of fractionation factor theory^{44,45} arises from the use of analogous assumptions.

I thank Professor R. P. Bell and Dr. W. J. Albery for discussions and Dr. R. L. Tranter for the arrangement of data acquisition and computing facilities.

[3/1530 Received, 20th July, 1973]