1247. *Hydrogen Isotope Effects in Olefin Hydration. The Relationship of Isotope Effects to the Mechanism of Proton Transfer from the Hydronium Ion*

By V. Gold and M. A. Kessick

The effect of deuterium and tritium substitution in the solvent on the hydration of isobutene has been examined in aqueous solutions of dilute perchloric acid at 25°. A distinction is made between "rate isotope effects" and "product isotope effects." In the system investigated both types are measurable under the same conditions. The reaction velocity in protium oxide is 1·45 ± 0·10 times greater than that in deuterium oxide at the same concentration of catalyst. In mixtures of these two solvents the reaction velocities are greater than those calculated by linear interpolation. The abundance of deuterium in the newly formed C–H bond of the product is 3·9 times smaller than the abundance of deuterium in the solvent, when the reaction is carried out in H_2O–D_2O mixtures. The corresponding ratio for tritium as a tracer in protium oxide is 7·1; for tritium as a tracer in deuterium oxide it is 1·9. Linearly interpolated values apply to the tritium product isotope effect in H_2O–D_2O mixtures.

A theoretical treatment of these phenomena in terms of the fractionation of hydrogen isotopes between hydronium ions and water and the relative concentrations and reactivities of isotopically different hydronium ions is developed on the basis of previously derived equations. A consistent and satisfactory interpretation of all observations is possible without the postulation of medium effects. The results indicate that the Brönsted exponent α has a value of *ca.* 0·9 in this reaction, and imply that the rate-limiting step is proton transfer from the hydronium ion to isobutene; the transfer is nearly complete in the transition state.

The interpretation implies that the proton transfer involves one of the group of three equivalent protons of the hydronium ion and not a proton from the solvation shell (*e.g.*, one of the group of six outer protons of $H_9O_4^+$).

Several apparently conflicting statements and conclusions concerning kinetic hydrogen-isotope effects in the acid-catalysed hydration of olefins are to be found in the literature. Purlee and Taft,[1] comparing the rates of hydration of 2-methylbut-2-ene and 1-methylcyclopentene in ordinary water with those in deuterium oxide, concluded that the effect was small. Manassen and Klein [2] derived both deuterium and tritium isotope effects for 2-butene from the relative abundance of the isotopes in the carbon-bound hydrogen atoms of the product relative to the isotope abundance in an isotopically mixed aqueous medium, and concluded that the enrichment of protium in the product indicated an appreciable kinetic isotope effect ($k_H/k_D \sim 2·7$, $k_H/k_T \sim 5·7$) in that reaction. Other product isotope effects, derived in a similar manner for solvents other than water and different olefins, likewise indicated an isotope effect favouring the lighter isotope.[3,4] Although several explanations of the contrasting findings have been suggested,[2,4] it was also noted [4] that the two types of result were obtained by different experimental procedures. In view of the importance attached to the isotope effects in discussions of the mechanism of olefin hydration this question required investigation, from both an experimental and a theoretical point of view. This study is now reported.

For the sake of clarity the terms "rate isotope effect" and "product isotope effect"

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[1] E. L. Purlee and R. W. Taft, jun., *J. Amer. Chem. Soc.*, 1956, **78**, 5807.

[2] J. Manassen and F. S. Klein, *J.*, 1960, 4203.

[3] A. E. Shilov, R. D. Sabirova, and V. I. Gorshkov, *Doklady Akad. Nauk S.S.S.R.*, 1958, **119**, 533.

[4] V. Gold and J. S. Coe, *J.*, 1960, 4571.

are introduced.[5] The former denotes an isotope effect deduced from observed chemical reaction rates on isotopically different systems; the latter is obtained from the isotopic fractionation detectable in a reaction, *i.e.*, in the present instance from the difference in deuterium or tritium abundance among the hydrogen nuclei of the reactant solvent system and in the paraffinic hydrogen atom gained by the olefin on hydration. The two terms are used in an operational sense, and have meaning irrespective of the supposed theoretical cause (" primary," " secondary," etc.) of the observed isotope effects.

Isobutene (2-methylpropene) was chosen as the substrate, mainly because of its convenient rate of hydration and because the reaction is chemically simple and clean. The hydration of this particular olefin has been kinetically investigated[6] in some detail by different methods and there exist very precise rate measurements against which new techniques can be checked. Using aqueous solutions at 25° and dilute perchloric acid as catalyst we have now measured in this system all rate and product isotope effects that can be obtained by deuterium and tritium substitution in the solvent, with the exception of those that would entail the use of tritium above tracer level.

From earlier work it is known that the reaction is catalysed by mineral acid and subject to unusually large specific electrolyte effects,[6] even at very low acid concentration where the distinction between acid concentration and acidity functions is generally not important. Ciapetta and Kilpatrick could not detect general acid catalysis in the reaction whence it follows that the Brönsted exponent α must have a value considerably greater than 0·5 and probably close to unity. General acid catalysis by formic acid has quite recently been established for hydration of the structurally related substrate *p*-methoxy-α-methylstyrene.[7] The form of the catalysis by strong acids has been studied and discussed for several olefins; the evidence has recently been reviewed in connection with the interconversion of propene and propan-2-ol.[8]

In the light of this information it is possible to restrict the consideration of mechanisms to acid-catalysed paths.

EXPERIMENTAL

Isobutene was prepared by heating t-butyl alcohol (100 ml.) with oxalic acid dihydrate (37 g.), then passed through a train of Drechsel bottles, two containing water and the last one 40% sodium hydroxide solution, and finally through a soda-lime tube. It was condensed at −78° into ampoules which were used in the preparation of solutions by bubbling the gas through water. Gas chromatography (silver nitrate–glycerol on Celite) on similiarly prepared ether solutions of isobutene was used to establish the removal of impurities, especially t-butyl alcohol. In all purity checks or purifications by gas chromatography the efficiency of the column under the operating conditions employed was established by experiments with deliberate addition of known or likely impurities.

t-Butyl alcohol for the above preparation was used without purification, the only impurities evident in the gas chromatogram being insignificant amounts of water and n-butanol. For use as carrier in the tracer-level hydration experiments with tritium this specimen was purified by gas chromatography (F and M model 770 Automatic Preparative Gas Chromatograph, using Carbowax 1500 on silanised Celite).

Sulphuryl chloride was distilled under nitrogen. Tritiated water was obtained from the Radiochemical Centre at a nominal activity of 0·2 curie per ml. The producer's (Norsk Hydro) analysis figures were accepted for deuterium oxide (99·80 or 99·95%).

Other reagents were of AnalaR grade.

Stoicheiometry of Reaction.—The quantitative nature of the hydration

$$\mathrm{Me_2C{=}CH_2 + H_2O \longrightarrow Me_3C{\cdot}OH}$$

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[5] V. Gold and M. A. Kessick, *Proc. Chem. Soc.*, 1964, 295.

[6] H. J. Lucas and W. F. Eberz, *J. Amer. Chem. Soc.*, 1934, **56**, 460; G. R. Lucas and L. P. Hammett, *ibid.*, 1942, **64**, 1938; F. G. Ciapetta and M. Kilpatrick, *ibid.*, 1948, **70**, 639.

[7] W. M. Schubert, B. Lamm, and J. R. Keefe, *J. Amer. Chem. Soc.*, 1964, **86**, 4727.

[8] V. Gold and R. S. Satchell, *J.*, 1963, 1930.

was checked by comparing chemical analysis figures for the initial olefin concentration with determinations of the concentration of the alcohol at complete reaction.

Isobutene determination. A known weight of an aqueous olefin solution was injected from a syringe below the surface into a 2-ml. portion of bromine reagent. Distilled water was then added to make the total volume up to 5 ml. After 10 min. the optical density of the solution was measured at 4000 Å (absorption maximum of bromine). The difference between this reading and one obtained with a similarly prepared solution without olefin was determined in a series of isobutene solutions prepared by quantitative dilution of a stock solution; it was found to be proportional to the olefin concentration. The bromine reagent was prepared from a solution containing 0·28 g. of potassium bromate and 16·0 g. of potassium bromide per litre. For an analysis a 20-ml. portion of this stock was acidified with *ca.* 0·20 ml. of 70% perchloric acid and left for 2 hr.

t-Butyl alcohol determination. The reagent consisted of a freshly prepared solution (0·2%) of *NN*-dimethylaminobenzaldehyde in 70% sulphuric acid, which was added to 0·5-ml. aliquot portions of the alcohol solution (2×10^{-4} to 10^{-3}M) up to a total volume of 10 ml. A blank solution was prepared by use of water in place of the alcohol solution. The solutions were then heated at 100° for 30 min., cooled, and examined in a spectrophotometer at 3980 Å. Because of the instability of the reagent a complete calibration curve was constructed, solutions of t-butyl alcohol of known composition being also used at the same time. With this limitation, the method, which is a modification of Kolesnikov's method for terpene alcohols,[9] proved reliable. (Reid and Truelove's method [10] based on ceric ammonium nitrate was found to be unsuitable at the low concentrations employed.)

Correlation between alcohol and olefin analyses. An unacidified aqueous solution of isobutene was drawn into a weighed syringe and the concentration of olefin in it determined by bromine addition as described above. The amount of olefin solution remaining was established by reweighing. A known weight of aqueous perchloric acid was then drawn into the syringe to mix with the olefin solution and to furnish a medium with an acid concentration of *ca.* 0·5M. After being kept at 25° for 24 hr., a time interval sufficient to ensure complete reaction, the solution was analysed for t-butyl alcohol in the manner described. The following results were obtained:

$10^3 \times$ initial olefin concentration	$10^3 \times$ final alcohol concentration
6·85	6·74
6·93	6·81

The results appear to show that, while there might be a slight loss of olefin (<2%) from the solution by this procedure, no impurities interfering with the analyses are formed and there are no significant side-reactions.

Rate Measurements.—The progress of hydration was followed by spectrophotometric observation of olefin at the absorption maximum (1937 Å in water). The extinction coefficient of t-butyl alcohol at that wavelength was found to be *ca.* 10^4 times smaller than that of the olefin. Deoxygenated solutions (olefin concentration 6—8 $\times$ 10^{-4}M) were introduced into a cell of 1 mm. path-length which was then sealed off with a minimum vapour space (in a capillary side-arm). The cell and a corresponding reference cell without olefin in the solution were placed in a specially constructed thermostat-controlled cell compartment of the vacuum ultraviolet spectrophotometer.* The 1 mm.-cell permitted the use of solutions with relatively high olefin concentration so as to minimise interference from absorption due to residual dissolved oxygen.

First-order rate constants were obtained from plots of log D_t/D_∞ against time (D_t being the optical density at time t). Calibration experiments with a series of olefin solutions of known dilution had established the proportionality between optical density and olefin concentration. The absolute concentration of olefin in these calibration solutions was independently determined by bromine addition (see below). Combination of the optical density with the chemical analysis figure for olefin led to the extinction coefficient for isobutene, $\varepsilon_{\text{max.}}$ (1937 Å) = 10,700. [$\varepsilon_{\text{max.}}$ (1880 Å) = 11,300 for isobutene in n-heptane.[11]]

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* The spectrophotometer itself was constructed in the Physics Department of King's College and was used by permission and with the co-operation of Professor W. C. Price, Dr. G. R. Wilkinson, and Mr. D. M. Roessler, whom we thank.

[9] P. A. Kolesnikov, *Biokhimiya*, 1957, **22** (4), 622.

[10] V. W. Reid and R. K. Truelove, *Analyst*, 1952, **77**, 325.

[11] L. C. Jones and L. W. Taylor, *Analyt. Chem.*, 1955, **27**, 228.

The reaction velocity was determined by this method at four concentrations of perchloric acid in ordinary water. The rate constants (Table 1) obtained fall exactly on the smooth curve defined by the precise dilatometric rate constants reported by Ciapetta and Kilpatrick.[6] This method was then used to determine the rate variation at fixed concentration of perchloric acid (0·442N) for different proportions of deuterium in the medium (Table 2).

TABLE 1

Rate constants as a function of acid concentration in H_2O

$[HClO_4]$ (M)	0·185	0·296	0·396	0·440
10^4k (sec.$^{-1}$)	0·845	1·57	2·23	2·65

Preparation of $[2H_1]$*t-Butyl Alcohol*.—The alcohol with one C–H bond fully deuteriated was prepared by the reaction of isobutene with a fully deuteriated acid medium prepared by allowing purified sulphuryl chloride (3·2 g.) to react with 50 g. of 99·95% deuterium oxide. The hydration was performed in a closed system at 25°. The system was flushed with nitrogen and filled with olefin. The reaction was allowed to proceed for 4 days, its progress being indicated by the pressure change. The alcohol specimen was salted out by addition of solid sodium hydroxide, and separated. The sample was then washed with ten successive lots of an equal volume of 40% sodium hydroxide solution, in order to remove hydroxylic deuterium,[12] and dried ($MgSO_4$). This drying agent was shown to leave *ca.* 1·5% of water in the alcohol. The infrared absorption of this specimen, at the C–D stretching frequency (4·6 μ), and of samples prepared from it by dilution with ordinary t-butyl alcohol was used for calibration of the infrared analysis of mixtures of $[^2H_1]$t-butyl alcohol and ordinary t-butyl alcohol used in experiments on the product deuterium isotope effect. Absorption at the C–H stretching frequency was still intense in this specimen.

TABLE 2

Rate constants in H_2O–D_2O mixtures

($[HClO_4]$ = 0·442M)

n *	0·000	0·103	0·206	0·310	0·412	0·518	0·624	0·730	0·830	0·914	1·000
10^4k (sec.$^{-1}$)	2·65	2·78	2·75	2·80	2·75	2·75	2·69	2·52	2·33	2·12	1·85 †

* n = atom fraction of deuterium in medium. † Extrapolated, see Figure, ±0·08.

To examine the possiblity of the introduction of deuterium into more than one C–H bond per molecule through exchange of the alcohol with deuteriated acid, a solution of t-butyl alcohol (4·1 g.), dissolved in acidified (0·48M-perchloric acid) deuterium oxide (50 ml.) was left at 25° for 4 days. The alcohol sample was then isolated as before; infrared analysis of this specimen showed no measurable deuterium content.

The absence of hydrogen exchange between t-butyl alcohol and aqueous alkali under the conditions used in the extraction had previously been established.[12]

Both these possibilities of error are further eliminated by experiments with tritium detailed below.

Deuterium Product Isotope Effect.—This determination entailed slight modification of the foregoing preparation of $[^2H_1]$t-butyl alcohol in that the reaction flask was charged with a deuterium oxide–protium oxide mixture, acidified with perchloric acid, in place of the fully deuteriated medium. The procedure was carried out for nine different isotopic compositions in the range n = 0·159—0·930 (n = atom fraction of deuterium in the solvent mixture).

For each batch of isotope analyses on the product alcohol a complete calibration of log (I_0/I) as a function of m was carried out at the same time as the measurements of the unknowns, where

$$m = [Me_2C(OH)CH_2D]/\{[Me_3C{\cdot}OH] + [Me_2C(OH)CH_2D]\}.$$

The measurements and deuterium product isotope effects, r, defined by equation (1), are tabulated (Table 3).

$$r = n(1 - m)/m(1 - n) \qquad (1)$$

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[12] J. S. Coe and V. Gold, *J.*, 1960, 4185.

TABLE 3

Deuterium product isotope effects

$[HClO_4] = 0{\cdot}44$—$0{\cdot}47$M

n	0·159	0·204	0·319	0·406	0·498	0·600	0·690	0·810	0·930
m	0·050	0·062	0·112	0·145	0·212	0·272	0·378	0·525	0·760
r	3·6 ± 0·6	3·9 ± 0·6	3·7 ± 0·3	4·0 ± 0·3	3·7 ± 0·2	4·0 ± 0·2	3·7 ± 0·2	3·9 ± 0·2	4·2 ± 0·3

n, m, r are defined in the text. The stated limits of errors are estimated maximum errors due to the limits of precision of the isotope analysis.

Tritium Assay.—Activities of samples were measured in an Ekco Scintillation Counter type N612B, kept at −20°. The scintillator fluid consisted of a 0·3% solution of 2,5-diphenyloxazole (PPO) in AnalaR toluene, diluted with an equal volume of absolute ethanol (Burroughs).

The isotope-effect determinations entailed the precise comparison of activities of water and t-butyl alcohol. To eliminate quenching effects, counting solutions were made up for each experiment with the following compositons: (*a*) 0·5 ml. inactive water, *ca.* *x* g. inactive t-butyl alcohol, ~10 ml. scintillator fluid (background); (*b*) 0·5 ml. inactive water, *x* g. active t-butyl alcohol, ~10 ml. scintillator fluid; (*c*) 0·5 ml. active water, *x* g. active t-butyl alcohol, ~10 ml. scintillator fluid. The volume of scintillator fluid used is exactly defined by the following details. A known weight of the extracted active t-butyl alcohol was dissolved in scintillator solution to a fixed total volume of solution. Portions (10 ml.) of this solution were then used in making up the counting mixtures (*b*) and (*c*). The procedure was duplicated with approximately the same weight of inactive t-butyl alcohol for the background counting mixtures (*a*). The weight *x* was in the range 0·001—0·005 g.

Since the required information in these assays was the comparison of the activity of the product alcohol relative to that of the reaction medium, the active "water" in mixture (*c*) consisted of diluted portions of the reaction medium, *i.e.*, aqueous solutions containing *ca.* 0·5M-perchloric acid and *ca.* 6×10^{-3} M-t-butyl alcohol which were diluted at least 5000 times with ordinary water.

In addition to the counting mixtures (*a*), (*b*), and (*c*), a fourth mixture (*d*) was prepared in each case with 0·5 ml. of active water and *ca.* *x* g. of inactive t-butyl alcohol as an internal check of the procedure, the evaluated activities of t-butyl alcohol ($c - d$) and "water" ($d - a$) generally agreeing with the alternative pairs ($b - a$) and ($c - b$) to within 5%. It is thought that such small discrepancies as did appear were attributable to mixture (*d*), mainly on the ground that, whereas active and inactive water could be expected to exert identical quenching effects, it could not be assumed that active and inactive alcohol samples would likewise behave identically, since the history of the samples, particularly in respect of exposure to β-radiation, was not absolutely identical. The differences ($b - a$) and ($c - b$) were therefore used to evaluate the activities contained in *x* g. of t-butyl alcohol and 0·5 g. water, respectively. The activities are expressed in terms of counts registered in 100 sec./mole. A count of C_A obtained from a sample containing *x* g. of active alcohol corresponds to an activity $A_A = C_A \times (M_A/x)$ counts per mole of alcohol (M_A being the molecular weight of the alcohol). Similarly a count of C_M for a 0·5-ml. sample of the diluted medium (1 ml. $\longrightarrow$ *V* ml.) corresponds to a count of $C_M \times (VM_w/0{\cdot}5\,\rho)$ per mole of water where M_w is the (mean) molecular weight and ρ the density of the water in the medium. Since M_w/ρ is virtually constant ($=18{\cdot}0$) over the entire range of H_2O–D_2O compositions, $A_M = C_M \times 36V$. For the results in Table 4 the diluted volume *V* was 5000 ml.

TABLE 4

Tritium product isotope effects in H_2O–D_2O mixtures

$[HClO_4] = 0{\cdot}45$M

n	10^5x	Counts/100 sec.			C_M	C_A	$10^{-7}A_M$	$10^{-6}A_A$	R_n	
	(g.)	*a*	*b*	*c*	$c - b$	$b - a$			Expt.	Calc.*
0	187	1585	36,686	144,076	107,390	35,101	1933	1391	7·0	7·1
0·204	476	2936	69,867	142,536	72,669	66,931	1308	1042	6·3	6·0
0·406	241	1337	45,437	120,553	75,116	44,100	1352	1356	5·0	5·0
0·600	301	1464	60,130	125,398	65,268	58,666	1175	1445	4·1	4·0
0·810	120	1659	43,731	129,209	85,478	42,072	1539	2599	3·0	2·9
0·970	113	1528	89,071	217,513	128,442	87,543	2312	5742	2·0	2·1

* Calc. from equation (14) with $R_0 = 7{\cdot}1$, $R_1 = 1{\cdot}9$.

Tritium Product Isotope Effect.—The experiments were carried out in the same apparatus as those on the deuterium product isotope effect. The reaction flask was charged with media of constant acid concentration (0·45M-perchloric acid), prepared by accurate dilution of stock perchloric acid and tritiated water with varying amounts of protium and deuterium oxide. Part of the reaction mixture was used for the determination of the activity of the medium, as described above. From the main portion a specimen of the product alcohol was isolated, freed from label in the hydroxyl group, as described for the preparation of [$^2H_1$]t-butyl alcohol, and then assayed for tritium.

The tritium product isotope effect (R_n) in a medium containing an atom fraction n of deuterium, and tritium at tracer level, is defined as

$$R_n = \frac{\text{activity per g.-atom exchangeable hydrogen in solvent}}{\text{activity per g.-atom in new C–H bond of alcohol}}$$

or

$$R_n = A_M/2A_A \qquad (2)$$

To examine the possibility of error through hydrogen exchange of t-butyl alcohol during the salting-out and washing of the alcohol or during its time in the acid reaction medium the following experiments were performed. Quantities of t-butyl alcohol (2 ml.) of known activity were dissolved in 50-ml. portions of distilled water and then re isolated and washed in the same manner as in the isotope-effect experiments. The activity of the alcohol was then compared with that of the original sample. The mean difference in activity between these two types of sample was of the order of ±5%. It can be concluded that there is no appreciable loss of activity. The figure of ±5% indicates the reproducibility of experiments of this nature. In order to check that the washing procedure was sufficient to remove all hydroxylic tritium, the activity of three samples was determined after both nine and ten washings with an equal volume of 40% sodium hydroxide; the activities were the same within the statistical counting error. The possible introduction of tritium into t-butyl alcohol by exchange in the acid medium was investigated by dissolving inactive t-butyl alcohol in a tritiated acid medium of high activity and re-isolating after 4 days at 25°. The alcohol was then extracted and washed as before. The activity of the alcohol was compared with that of the reaction medium, with the following results

A_M	A_A
$1·53 \times 10^{10}$	$1·86 \times 10^7$
$1·62 \times 10^{10}$	$1·84 \times 10^7$

Comparison of these results with those in Table 4 shows that exchange can contribute less than 1% of the activity of any of the alcohol samples in the isotope-effect measurements. These results strengthen the analogous but less sensitive measurement with deuterium. A cursory examination of tritium exchange of t-butyl alcohol in 4·7M-perchloric acid indicated a half-life of the order of one month at this higher acid concentration.

The foregoing measurements of deuterium and tritium product isotope effects were performed on two-phase systems whereas the rate isotope effects relate to homogeneous solutions. These differences in procedure are not thought to be serious since, in the two-phase system, reaction almost certainly occurs only after solution of the olefin in the aqueous phase. The following control experiments were, however, carried out on the tritium isotope effect in the absence of a vapour phase to test this assumption.

Freshly prepared aqueous solutions of isobutene were acidified with perchloric acid and a trace amount of tritiated water was added. After mixing was complete, the reaction mixture was drawn up into a 25-ml. Pyrex syringe. After removal of any bubbles from the syringe, a capillary glass sleeve with a closed end was pushed over the needle. The syringe was then placed, plunger uppermost, inside a close-fitting glass well contained in a thermostat bath at 25°. After about eight half-lives a known volume (20 ml.) of the reaction mixture was added to sodium hydroxide solution (40%, *ca.* 10 ml.) and the resulting solution shaken with inactive t-butyl alcohol (y g.). The alcohol layer was separated and washed and dried as before (p. 6721). The content of carbon-bound tritium was then assayed by the same set of measurements as used in the preceding experiments, except that a larger weight x of alcohol (*ca.* 0·75 g.) was used. Of the remaining reaction solution, 1 ml. was diluted 25,000 times (*i.e.*, $V = 25{,}000$)

and used for determining the activity of the medium, as before. Another 1-ml. portion was analysed for t-butyl alcohol by the procedure described, and a further portion was titrated with alkali. In these experiments the weight x in mixture (c) was sometimes not exactly the same as in mixture (b) and the two counts were brought to the same basis by assuming that the differences ($b - a$) and ($c - a$) were proportional to the weight of active alcohol. In view of the quenching effect, this assumption is probably not altogether correct. The results are probably not as precise as those in Table 4, particularly since a much larger weight of alcohol was used in the counting samples. The results of three repeat experiments in H_2O are detailed in Table 5. The relationship between C_A and A_A is in this case $A_A = 1000y\ C_A/20x[\mathrm{Bu^tOH}]$.

TABLE 5

Tritium product isotope effects in H_2O (homogeneous solution)

x (g.)	y (g.)	$10^5[\mathrm{Bu^tOH}]$ (M)	Counts/100 sec. a	b	c	C_M $c - b$	C_A $b - a$	$10^{-8}A_M$	$10^{-7}A_A$	R_0
0·747	15·44	561	2444	22,351	78,215	55,864	19,907	503	367	6·85
0·701	15·42	564	2584	21,984	79,127	57,143	19,400	514	378	6·79
0·752	15·24	662	2366	26,066	83,647	57,581	23,700	518	363	7·13

DISCUSSION

Our main results may thus be summarised:

(a) Hydration of isobutene in an isotopically labelled medium does not lead to t-butyl alcohol labelled in all nine C–H bonds, but to a product in which only one position is labelled.

(b) The abundance of deuterium or tritium label in this one C–H bond of the product is considerably smaller than the abundance of label in the reaction medium. The factor (r) involved is 3·9 ± 0·2 in the case of deuterium with protium oxide (Table 3) and is substantially independent of the deuterium content of the medium. For tritium label with protium oxide, the corresponding ratio (R_0) is 7·1 ± 0·3. With tritium as a label in deuterium oxide–protium oxide mixtures having a deuterium atom fraction n, the ratio R_n decreases linearly as n goes from 0 to 1, reaching a value of 1·9 ± 0·1 in deuterium oxide (Table 4).

(c) The rate of hydration of isobutene varies with the deuterium abundance n of the reaction medium in a non-linear fashion (see Figure). The (slightly extrapolated) rate ratio in the isotopically pure solvents is $k_{H_2O}/k_{D_2O} = 1{\cdot}45 \pm 0{\cdot}1$ (Table 2).

The result (a) rules out from further consideration the mechanism

$$\mathrm{Me_2C{=}CH_2 + H^+ + H_2O \rightleftharpoons Me_3C^+ + H_2O \longrightarrow Me_3C{\cdot}OH + H^+}$$

with generation of a (classical) t-butyl cation (in low concentration) in a rapid pre-equilibrium, since this would lead to formation of an alcohol deuteriated in all methyl positions when the reaction is carried out in a deuterium-containing medium. This finding supports a similar conclusion for the hydration of 2-methylbut-2-ene.[13] It also accords with the fact that the dehydration of t-butyl alcohol is a slower reaction than oxygen isotope exchange of t-butyl alcohol,[14] a result which indicates that the rate-limiting step in dehydration must be rupture of a C–H rather than the C–O bond. It follows, by the principle of microscopic reversibility, that the reversal of this step (*i.e.*, C–H bond formation) must be the rate-limiting step in the reverse reaction (*i.e.*, the hydration of isobutene).

The characteristic bulge of the $k_n - n$ curve (Figure) mentioned under (b) is characteristic of equilibria of the form

$$\mathrm{H_3O^+ + S \rightleftharpoons SH^+ + H_2O}$$

in which the species SH^+ (which may be a transition state) contains a singular proton which is in isotopic equilibrium with the solvent.[15] The shape of the curve obtained is

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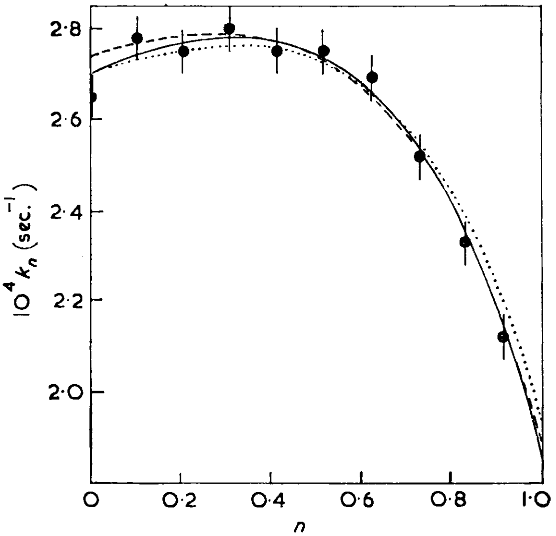
[13] J. B. Levy, R. W. Taft, jun., and L. P. Hammett, *J. Amer. Chem. Soc.*, 1953, **75**, 1253.

[14] I. Dostrovsky and F. S. Klein, *J.*, 1955, 791.

[15] For a review see E. L. Purlee, *J. Amer. Chem. Soc.*, 1959, **81**, 263.

less open to doubt than the analogous ones for the hydration of 2-methylbut-2-ene and 1-methylcyclopentene but accords with the conclusion drawn by Purlee and Taft.[1] We infer that the transition state of the reaction must contain the transferred proton in a singular position. It therefore follows from these results that proton transfer from the hydroxonium ion to the $=CH_2$ group has made considerable progress but is incomplete in the transition state. The incompleteness of this proton transfer *need* not require the incomplete detachment of the H_2O moiety from the hydroxonium ion but could be due to the circumstance that the proton has not reached its terminal position in the transition state (cf. several structures of the transition state proposed recently [2,16]). However, this latter alternative would not allow the possibility of general acid catalysis.



Rate isotope effect. Full curve: Calc. for $k_H = 2{\cdot}70 \times 10^{-4}$, $k_H/k_D = 1{\cdot}46$, $r = 4{\cdot}45$, *viz.*, the parameters deduced from k_n values *alone* to give the best least-squares fit to equation (5). (Corresponding value of α : 1·00)

Broken curve: Calc. for $k_H = 2{\cdot}74 \times 10^{-4}$, $k_H/k_D = 1{\cdot}46$, $r = 4{\cdot}21$, *viz.*, the parameters deduced from nine k_n values (first point omitted) *alone* to give the best least-squares fit to equation (5). (Corresponding value of α : 0·93)

Dotted cruve: Calc. for $k_H = 2{\cdot}70 \times 10^{-4}$; $k_H/k_D = 1{\cdot}40$, $r = 4{\cdot}00$. (Corresponding value of α : 0·91)

It is both more general and, in view of the occurrence of general acid catalysis in an analogous reaction, the hydration of *p*-methoxy-α-methylstyrene,[7] more plausible to adopt the formulation $(S \cdots H \cdots OH_2)^+$ of the transition state for the detailed discussion of the isotope effects.

The results (*b*) indicate that there is more discrimination against the heavy isotopes in the formation of product than superficial consideration of the rate ratio $k_{H_2O}/k_{D_2O} = 1{\cdot}45$ would suggest. On the basis of the above formulation of the transition state for the rate-limiting proton transfer it is possible to discuss both rate and product isotope effects in terms of a previously given theoretical treatment of the rates of slow proton transfer reactions in protium oxide–deuterium oxide mixtures.[17]

According to this theory the rates of proton and deuteron transfer from all isotopic hydroxonium ions taken together, to a substrate in a mixture of protium oxide and deuterium oxide, can be written in the form (cf. equation 14 of ref. 17).

$$v_H = (k^{H}_{H_3O}c/Q)\,(1 - n)\,(1 - n + nl_D^{\,1-\alpha})^2 \qquad (3)$$

$$v_D = (k^{D}_{D_3O}c/Q)nl_D^{\,1+2\alpha}(1 - n + nl_D^{\,1-\alpha})^2 \qquad (4)$$

where $k^{H}_{H_3O}$ and $k^{D}_{D_3O}$ are the rate constants of proton transfer, from H_3O^+ and deuteron transfer from D_3O^+, respectively, c is the sum of the concentrations of all isotopic hydroxonium ions, Q is satisfactorily approximated by the expression $(1 - n + nl_D)^3$,

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[16] R. H. Boyd, R. W. Taft, jun., A. P. Wolf, and D. R. Christman, *J. Amer. Chem. Soc.*, 1960, **82**, 4729.

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

α is the exponent of the Brönsted catalysis law and l_{D} an equilibrium constant characterising the isotope fractionation between hydrogen ions and water

$$\{l_{\mathrm{D}} = [(\mathrm{H_2O})^3(\mathrm{D_3O^+})^2/(\mathrm{D_2O})^3(\mathrm{H_3O^+})^2]^{1/6}\}.$$

If the values of $k^{\mathrm{H}}_{\mathrm{H_3O}}$ and $k^{\mathrm{D}}_{\mathrm{D_3O}}$ can be assumed to be independentof the isotopic composition of the medium, the total rate of reaction can be expressed as the sum of the rates v_{H} and v_{D}, the values of $k^{\mathrm{H}}_{\mathrm{H_3O}}$ and $k^{\mathrm{D}}_{\mathrm{D_3O}}$ being the observed rate constants ($k_{\mathrm{H_2O}}$,$k_{\mathrm{D_2O}}$) in media with $n = 0$ and $n = 1$, respectively. The equation

$$k_n = [(1 - n + nl_{\mathrm{D}}{}^{1-\alpha})^2/(1 - n + nl_{\mathrm{D}})^3]\ [k^{\mathrm{H}}_{\mathrm{H_3O}}(1 - n) + k^{\mathrm{D}}_{\mathrm{D_3O}}nl_{\mathrm{D}}{}^{1+2\alpha}] \qquad (5)$$

should therefore express the rate constant in an isotopically mixed medium.

The ratio of isotopic products will be given by the ratio of the rates of proton and deuteron transfer, *i.e.*,

$$\frac{m}{1 - m} = \frac{v_{\mathrm{D}}}{v_{\mathrm{H}}} = \frac{nl^{1+2\alpha}}{1 - n}\ \frac{k^{\mathrm{H}}_{\mathrm{H_3O}}}{k^{\mathrm{D}}_{\mathrm{D_3O}}} \qquad (6)$$

and the isotope effect defined by equation (1) can be expressed as

$$r = \frac{k^{\mathrm{H}}_{\mathrm{H_3O}}}{k^{\mathrm{D}}{}_{\mathrm{D_3O}}l_{\mathrm{D}}{}^{1+2\alpha}} \qquad (7)$$

i.e., the rate isotope effect ($k_{\mathrm{H_2O}}/k_{\mathrm{D_2O}} = k^{\mathrm{H}}_{\mathrm{H_3O}}/k^{\mathrm{D}}_{\mathrm{D_3O}}$) should differ from the product isotope effect by the factor $l_{\mathrm{D}}{}^{1+2\alpha}$.

The same treatment can be extended to the tritium product isotope effect R. Proceeding as in the derivation given in ref. 17 but including the three-isotope ion $\mathrm{HDTO^+}$ among the species from which triton transfer must be considered,[18] we then deduce that

$$v_{\mathrm{T}} = (k^{\mathrm{T}}_{\mathrm{T_3O}}c/Q)\ (1 - n + nl_{\mathrm{D}}{}^{1-\alpha})^2\ F\ l_{\mathrm{T}}{}^{1+2\alpha} \qquad (8)$$

where F is the fractional abundance of tritium in the medium and

$$l_{\mathrm{T}} = [(\mathrm{H_2O})^3(\mathrm{T_3O^+})^2/(\mathrm{T_2O})^3(\mathrm{H_3O^+})^2]^{1/6}.$$

The expression for v_{T} is simple because $F \ll 1$, whence $[\mathrm{H_2TO^+}] \gg [\mathrm{HT_2O^+}]$ and $[\mathrm{HOT}] \gg [\mathrm{T_2O}]$, etc., so that all higher powers of F can be neglected compared with F. If P is the fractional abundance of [$^3\mathrm{H}_1$] t-butyl alcohol in the product, the ratio F/P will measure the product isotope effect and can be expressed in terms of measured activities A_{M} and A_{A}; *i.e.*,

$$R_n = F/P = A_{\mathrm{M}}/2A_{\mathrm{A}} \qquad (9)$$

Since $P = v_{\mathrm{T}}/(v_{\mathrm{H}} + v_{\mathrm{D}})$ [because $(v_{\mathrm{H}} + v_{\mathrm{D}}) \gg v_{\mathrm{T}}$], combination of equations (9) and (10) yields

$$R_n = F(v_{\mathrm{H}} + v_{\mathrm{D}})/v_{\mathrm{T}} = \frac{1 - n + nl_{\mathrm{D}}{}^{1+2\alpha}k^{\mathrm{D}}_{\mathrm{D_3O}}/k^{\mathrm{H}}_{\mathrm{H_3O}}}{l_{\mathrm{T}}{}^{1+2\alpha}k^{\mathrm{T}}_{\mathrm{T_3O}}/k^{\mathrm{H}}_{\mathrm{H_3O}}} \qquad (11)$$

The limiting values of this expression for $n = 0$ and $n = 1$ are

$$R_0 = k^{\mathrm{H}}_{\mathrm{H_3O}}/k^{\mathrm{T}}_{\mathrm{T_3O}}l_{\mathrm{T}}{}^{1+2\alpha} \qquad (12)$$

$$R_1 = k^{\mathrm{D}}_{\mathrm{D_3O}}l_{\mathrm{D}}{}^{1+2\alpha}/k^{\mathrm{T}}{}_{\mathrm{T_3O}}l_{\mathrm{T}}{}^{1+2\alpha} \qquad (13)$$

These expressions are the analogues of equation (7). It also follows that R_n should be a linear function of n, *i.e.*, a weighted mean of R_0 and R_1

$$R_n = (1 - n)\,R_0 + n\,R_1 \qquad (14)$$

as found experimentally (Table 4).

[18] V. Gold, *Trans. Faraday Soc.*, 1964, **60**, 738.

The value of l_D is known [19,20] to within fairly close limits of error (0·69 ± ·01). Direct determinations of l_T have not so far been reported although one of the methods recently used [20] for measuring l_D could be applied [21] to the measurement of l_T. However, it is likely that the usual method of relating deuterium and tritium isotope effects [22] in terms of zero-point energy differences of harmonic oscillators is applicable in this case, *i.e.*, $l_T = l_D^{1\cdot442} = 0\cdot59$.

The assumption that the values of equilibrium and rate constants may be taken to be independent of the isotopic composition of the medium must represent an approximation,[23] but the fact that r is independent of n (and also that R_n is a linear function of n) suggests that it cannot be seriously in error. We therefore refrain from elaborating the equations by including such a medium effect, as could be done by the formal introduction of unknown activity coefficients.[23]

It follows from the preceding two paragraphs that the product isotope effects r, R_0, and R_1, given by equations (7), (12), and (13), should be inter-related according to

$$r = R_0^{1/1\cdot442} = R_1^{1/0\cdot442}$$

We note that

$$3\cdot9 = 7\cdot1^{1/1\cdot442} = 1\cdot82^{1/0\cdot442}$$

and since the experimental values are $r = 3\cdot9 \pm 0\cdot2$, $R_0 = 7\cdot1 \pm 0\cdot3$, $R_1 = 1\cdot9 \pm 0\cdot1$, the product isotope effects obtained by different methods and in different media are in excellent agreement. The value $r = 3\cdot9$ therefore appears to be known slightly more reliably than the experimental limits of error, based on the direct determination of r, suggest.

Combination of this result with the rate isotope effect allows the evaluation of $l_D^{1+2\alpha}$ from equation (7). In this way we obtain $\alpha = 0\cdot85 \pm 0\cdot10$. In this calculation r, l_D, and $k^{H}_{H_3O}/k^{D}_{D_3O}$ are subject to some experimental uncertainty, the rate ratio being the weakest link, since it is based on some extrapolation. The value of α obtained confirms the view that proton transfer from the hydroxonium ion to isobutene is far advanced but not complete in the transition state.

The general correctness of this analysis can be tested by substituting a reasonable value of α in equation (5) and calculating the reaction velocities in protium oxide–deuterium oxide mixtures, or by calculating α and r solely from the reaction velocities. The values thus derived (see legend of Figure) are in reasonable agreement with those obtained by direct determination of r. In the Figure calculated curves obtained in this way are shown along with the experimental points.

It has been pointed out [24] that a large isotope effect is to be expected for half-transfer of the proton (*i.e.*, when $\alpha = 0\cdot5$), whereas small normal or inverse isotope effects may be found for highly unsymmetrical transition states ($\alpha \sim 0$ or $\alpha \sim 1$). It is consistent with this view that a much larger rate isotope effect ($k^{H}_{H_3O}/k^{D}_{D_3O} = 2\cdot23$) has been noted in the hydration of *p*-methoxy-α-methylstyrene. With this substrate general acid catalysis is observed and, by combination of the results for formic acid and the hydrogen ion, a tentative value of $\alpha = 0\cdot34$ can be calculated. We conclude that the sizeable rate isotope effects for other styrenes likewise indicate a favourable situation for the detection of general acid catalysis. Proton transfers to aromatic carbon may not be entirely comparable with these transfers to olefinic carbon, but the result for 1,3,5-trimethoxybenzene [25] ($\alpha = 0\cdot52$,

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[19] V. Gold, *Proc. Chem. Soc.*, 1963, 141; A. J. Kresge and A. L. Allred, *J. Amer. Chem. Soc.*, 1964, **68**, 744.

[20] K. Heinzinger and R. E. Weston, jun., *J. Phys. Chem.*, 1964, **68**, 744.

[21] R. W. Lambert, Ph.D. Thesis, London, 1959.

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

[23] E. A. Halevi, F. A. Long, and M. A. Paul, *J. Amer. Chem. Soc.*, 1961, **83**, 305; P. A. Salomaa, L. L. Schaleger, and F. A. Long, *ibid.*, 1964, **86**, 1; C. G. Swain and E. R. Thornton, *ibid.*, 1961, **83**, 3884.

[24] F. H. Westheimer, *Chem. Rev.*, 1961, **61**, 265; J. Bigeleisen, *Pure Appl. Chem.*, 1964, **8**, 217.

[25] A. J. Kresge and Y. Chiang, *J. Amer. Chem. Soc.*, 1959, **81**, 5509; 1961, **83**, 2877; 1962, **84**, 3976; B. D. Batts and V. Gold, *J.*, 1964, 4284.

$k^{\mathrm{H}}_{\mathrm{H_3O}}/k^{\mathrm{D}}_{\mathrm{D_3O}} = 3{\cdot}0$) and azulene[26] ($\alpha = 0{\cdot}61$ for monocarboxylic acids, $k^{\mathrm{H}}_{\mathrm{H_3O}}/k^{\mathrm{D}}_{\mathrm{D_3O}} = 2{\cdot}4$) fall roughly into the general pattern. In a more detailed analysis it will be necessary to consider the role of steric effects more closely.[26]

If the value of α is known it is, of course, possible to calculate the secondary isotope effect on a particular proton transfer reaction from the hydronium ion, *e.g.*, the (statistically corrected) ratio of rate constants $k^{\mathrm{H}}_{\mathrm{H_3O}}$ and $k^{\mathrm{H}}_{\mathrm{HD_2O}}$. Interest in such values has recently ben expressed.[27] Explicit formulæ for calculating these secondary isotope effects were given by one of us in 1960 (equation 13 of ref. 17) whence, for example, $k^{\mathrm{H}}_{\mathrm{H_3O}}/3k^{\mathrm{H}}_{\mathrm{HD_2O}} = l_{\mathrm{D}}{}^{2\alpha}$. It also follows that overall rate isotope effects ($k^{\mathrm{H}}_{\mathrm{H_3O}}/k^{\mathrm{D}}_{\mathrm{D_3O}}$) are composed of primary and secondary contributions, whereas ratios $k^{\mathrm{H}}_{\mathrm{H_3O}}/3k^{\mathrm{D}}_{\mathrm{H_2DO}}$ should express solely the primary effect. From previously given expressions[17] we have

$$k^{\mathrm{H}}_{\mathrm{H_3O}}/3k^{\mathrm{D}}_{\mathrm{H_2DO}} = k^{\mathrm{H}}_{\mathrm{H_3O}}/k^{\mathrm{D}}_{\mathrm{D_3O}}l_{\mathrm{D}}{}^{2\alpha},$$

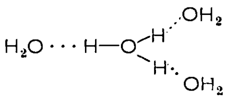
and the numerical values for $k^{\mathrm{H}}_{\mathrm{H_3O}}/k^{\mathrm{D}}_{\mathrm{D_3O}}$ can thus be corrected for the secondary isotope effect which they include. The results of such calculations are given in Table 6.

TABLE 6

Overall, primary, and secondary rate isotope effects in proton transfers to olefinic and aromatic carbon atoms

Substrate	α	Overall rate isotope effect ($k^{\mathrm{H}}_{\mathrm{H_3O}}/k^{\mathrm{D}}_{\mathrm{D_3O}}$)	Secondary rate isotope effect ($k^{\mathrm{H}}_{\mathrm{H_3O}}/3k^{\mathrm{H}}_{\mathrm{HD_2O}}$)	Primary rate isotope effect ($k^{\mathrm{H}}_{\mathrm{H_3O}}/3k^{\mathrm{D}}_{\mathrm{H_2DO}}$)
p-Methoxy-α-methylstyrene ...	~0·34	2·23	0·78	2·9
Trimethoxybenzene	0·52	3·0	0·68	4·4
Azulene	0·61	2·4	0·64	3·8
Isobutene	~0·9	1·45	0·53	2·7

Throughout the foregoing analysis the " hydrogen ion " from which a proton (deuteron or triton) is transferred is formulated as H_3O^+. This specific notation is based on the results of isotope fractionation between hydrogen ions and water obtained by different methods. It has been pointed out that n.m.r. measurements of this effect can be reconciled with earlier e.m.f. data only if it is assumed that the fractionation involves mainly three sites in every hydrogen ion.[19] The argument has been greatly strengthened by the demonstration that new determinations of isotope fractionation by vapour pressure measurements over mainly light acid solutions can be reconciled with the n.m.r. data again only if three sites are involved per hydrogen ion.[20] These fractionation results do not rule out a more complex formula for the hydrogen ion, such as (I) proposed by Eigen (who has recently reviewed[28] some of the relevant experimental evidence) since this would also include a group of three equivalent hydrogen nuclei which are expected to differ from water rather more than the six outer protons. It is therefore reasonable to expect that the isotope fractionation will involve the inner H_3O^+ group more than the three H_2O groups on the periphery, and that the latter positions will show only very little isotope fractionation relative to water.



(I)

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[26] J. Colapietro and F. A. Long, *Chem. and Ind.*, 1960, 1056; J. Schulze and F. A. Long, *J. Amer. Chem. Soc.*, 1964, **86**, 331; R. J. Thomas and F. A. Long, *ibid.*, p. 4770.

[27] A. J. Kresge and D. P. Onwood, *J. Amer. Chem. Soc.*, 1964, **86**, 5014; M. M. Kreevoy, P. J. Steinwand, and W. V. Kayser, *ibid.*, p. 5013.

[28] M. Eigen, *Angew. Chem.*, 1963, **75**, 489; *Angew. Chem. Internat. Ed.*, 1964, **3**, 1, and references to Eigen's work given therein.

If the bulk form of the hydrogen ion can be represented by the formula $[H_3O(H_2O)_3]^+$, the question arises whether the proton transferred to another species, as in the protonation of isobutene, comes from the inner or the outer group of protons. If the proton acquired by isobutene comes from the inner H_3O group, the foregoing quantitative treatment of the isotope effects could be based on this model in exactly the same way as it was previously based on the formula H_3O^+ for the hydrogen ion. The actual transfer might be preceded by substitution of isobutene for one of the outer water molecules of $H_9O_4^+$. Alternatively, creation of an H_3O^+ group immediately adjacent to the isobutene molecule by proton transfer from the inner H_3O group to one of the outer water molecules could achieve the same situation. In either case, contiguity between H_3O^+ and isobutene must not be supposed to lead to indiscriminate reaction. Since the hydration is found to be quite a slow reaction it is in fact necessary to assume that the proton transfer occurs much less rapidly than diffusion-controlled processes; it involves considerable activation. The life-time (and hence the concentration) of individual H_3O groups would therefore be related to their isotopic composition, and isotope effects would be characterised by the fractionation parameter l.

If, on the other hand, the proton acquired by isobutene is supposed to be initially one of the protons of an outer H_2O group of $H_9O_4^+$ it is necessary to postulate that the transfer of the outer proton is synchronous with proton transfer from the inner H_3O group to that outer water molecule [29] so that the transition state involves substantial changes in the bonding of two protons in transit and also changes in the H_2O residue of the inner H_3O group. Unless this assumption is made, the isotope effects could be ascribed only to the transfer of a proton from a water molecule to olefin, and would therefore be entirely independent of the fractionation parameter l. The double-transfer mechanism implies changes in the bonding of four protons, and the rate isotope effects will be governed by the isotope fractionation at these four positions. The product isotope effect, in this model, is determined solely by the changes concerning the outer proton in transit, but the rate isotope effects would contain more parameters than the simple model (with the hydrogen ion formulated as H_3O^+) requires. The fact that this simple model was shown to be adequate, within the limits of experimental error, to the theoretical interpretation of both product and rate isotope effects leads us to retain it as the description of the proton transfer process, although we cannot claim to have disproved more elaborate models.

Since our description requires a Brönsted exponent of less than unity and since general acid catalysis has been observed in a related system, the transition state for isobutene hydration is considered to include an olefin molecule and an entire molecule of Brönsted acid. The existing data do not, however, suffice to discriminate between structurally alternative formulations of transition states of the hydrogen-ion-catalysed reaction having the composition [olefin + proton + $(H_2O)_n$]. Pressure effects on hydration velocities have recently been used in an attempt to obtain information on this question.[30] The proton contained in the acid is lost and a new carbon–hydrogen bond is formed; such a reaction is regarded as a slow proton transfer, in spite of the fact that it may involve more atomic movements than the transit of a single proton. The same reservation may be made even about proton transfers which are superficially less complicated in producing no chemical reaction beyond that proton transfer.

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[29] M. M. Kreevoy and R. A. Kretchmer, *J. Amer. Chem. Soc.*, 1964, **86**, 2435.

[30] B. T. Baliga and E. Whalley, *Canad. J. Chem.*, 1964, **42**, 1019.