361. *The Kinetics of Hydrogen Isotope Exchange Reactions. Part XI.** *Tritium Exchange between Secondary Alcohols and Acidic Media.*

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The six β-hydrogen atoms of isopropyl alcohol undergo isotope exchange with a strongly acidic solvent (3—8M-perchloric acid) containing tritium. The exchange velocity at 100° is proportional to $h_0^{0\cdot 9}$ and is consistent with the view that the reaction involves dehydration to propene followed by re-addition of water.

In cyclohexanol the corresponding reaction involves all eleven C–H bonds and is compatible with an analogous mechanism *via* cyclohexene.

The work to be described in this and the succeeding paper is concerned with the exchange of aliphatic hydrogen atoms of alcohols with acidic media. Hydroxylic hydrogen is also exchanged under these conditions but this process is invariably very rapid compared with the exchange of other hydrogen atoms.[1]

It has previously been suggested that the hydrogen exchange in t-butyl alcohol can be explained by a dehydration–hydration mechanism involving the intermediate formation of isobutene.[2] The present experiments are largely concerned with the applicability of such a mechanism to secondary alcohols.

Experimental

Isopropyl alcohol (80 ml.) was refluxed with magnesium turnings (5 g.) activated with iodine (0·5 g.), after which more of the alcohol (1 l.) was added. After fractional distillation the main portion was kept for dilution purposes and a small middle fraction was reserved for kinetic experiments. This fraction was stored under reduced pressure in the dark over 2,4-dinitrophenylhydrazine and samples were freshly vacuum-distilled from this stock as required. No impurities could be detected in this specimen by gas-chromatography, column packings of Celite impregnated with a saturated solution of silver nitrate in glycerol (column A) and of Silicone oil on Celite (column F) being used.

Cyclohexanol (May and Baker) was once fractionally frozen and then fractionally distilled. Material of m. p. >23° was collected and a middle fraction of this was employed in kinetic

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* Part X, *J.*, 1960, 2461.

[1] Gold and (D. P. N.) Satchell, *Quart. Rev.*, 1955, **9**, 51.

[2] Coe and Gold, *J.*, 1960, 4185.

experiments. Gas-chromatography (column A) indicated a common impurity in all fractions. This was almost certainly cyclohexanone. Its concentration was 0·04% in the middle fraction. Later fractions of the distillate contained two other impurities, possibly methylcyclohexanols.

Cyclohexene (Hopkin and Williams) was found by gas-chromatography (column A) to contain four impurities in insignificant amount.

Perchloric acid media were prepared by dilution of 60% or 70% acid (B.D.H., " AnalaR ") and standardised against potassium iodate. The solutions were enriched with tritium by introducing tritiated water (Radiochemical Centre) during the dilution.

Mixtures of trifluoroacetic acid (Eastman), perchloric acid (70%), and water were prepared by weight.

Radioactivity was measured with a liquid scintillation counter (Ekco N 612), cooled to −16°, used in conjunction with an E.H.T. unit (I.D.L. type 532A) and a conventional scaler.

Kinetics of Tritium Exchange in Isopropyl Alcohol.—Samples of aqueous perchloric acid (5·02 ml.), *ca.* 0·12M in isopropyl alcohol, were sealed in Pyrex ampoules with a minimum of air space above the solution. The tubes were immersed in a bath at 100°. After various times they were chilled. The ampoules were broken by shaking them in a 500-ml. reagent bottle containing water (20 ml.) and inactive isopropyl alcohol (50 ml.). The liquid contents of the flask were transferred to a separatory funnel and saturated with sodium chloride (" AnalaR "). After agitation the layers were allowed to separate and the lower (aqueous) layer was discarded. The alcoholic layer was shaken with ten successive 100-ml. portions of 40% aqueous sodium hydroxide so as to remove hydroxylic tritium. After drying ($MgSO_4$; K_2CO_3) the alcohol was distilled and 2-ml. portions of the distillate were used for the assay of radioactivity. In some counts a distillate of the alcohol–water azeotrope was used.

For counting purposes 2·01 ml. of isopropyl alcohol (or azeotrope) were added to 20 ml. of a mixture of equal volumes of absolute ethanol and of a solution (3 g./l.) of 2,5-diphenyloxazole (PPO) in " AnalaR " toluene, containing in addition 0·5 ml. of water. For the purpose of comparing the activity of the alcohol with that of the tritiated medium, counts were performed on three mixtures of identical chemical composition containing (1) inactive water and inactive isopropyl alcohol (background count), (2) inactive water and the active alcohol, and (3) appropriately diluted active water and the inactive alcohol. Counts are quoted for 100-sec. periods, each value representing the mean of at least five observations. From the relative activities of the medium and the alcohol, exchange numbers (N) were calculated. These are defined as the *apparent* number of hydrogen atoms per molecule of substrate involved in the exchange. They represent the product of the number of exchanging hydrogen atoms and the distribution coefficient α_T of tritium (α_T = the ratio of the fractional abundance of tritium in the exchangeable hydrogen of the solute to that in the solvent at equilibrium). For dilute solutions in a hydroxylic medium they are calculated as the ratio of the activity of the alcohol (per mole) to that of the medium (per g.-atom of exchangeable hydrogen).

Results for a specimen run and a summary of rate constants are given in Tables 1 and 2, respectively. The exchange numbers are calculated on the basis that the concentration of isopropyl alcohol in the solution remains unchanged throughout the experiment.

TABLE 1.

Specimen results for tritium uptake by isopropyl alcohol in 7·24M-aqueous perchloric acid at 100°.

[Pr$^\beta$OH] = 0·122M. Activity of medium = 9·59 mc/g.-atom of exchangeable hydrogen.*

Time (hr.)	Counts (x) per 100 sec.†	Activity ‡ (c)	N	10^6k_1 § (sec.$^{-1}$)
0	(0)	—	0	—
1	41,880	0·0136	1·42	87
2	74,930	0·0243	2·53	92
4	113,190	0·0367	3·83	90
5	126,140	0·0408	4·26	92
22(∞)	155,690	0·0504	5·26	—

* Calc. from nominal activity of tritiated water supplied. † For 2·01 ml. of diluted dry isopropy alcohol per assay. ‡ Activity per mole of alcohol in reaction medium; the calculation of these values uses the result that 0·5905 μc (nominal) corresponded to 74,130 counts/100 sec. under our conditions [in presence of isopropyl alcohol, see (3), preceding paragraph]. § Calc. as $k_1 = \{\ln (x_\infty - x_0)/(x_\infty - x)\}/t$.

TABLE 2.

Summary of results for tritium exchange of isopropyl alcohol in aqueous perchloric acid at 100°.

[HClO$_4$] (M)	$-H_0$ †	N	10^6k_1 (sec.$^{-1}$)	log k_1	log $k_1 + 0{\cdot}90H_0$
3·08	1·26	—	0·43	$\bar{7}{\cdot}63$	$\bar{8}{\cdot}50$
4·53	1·98	—	2·4	$\bar{6}{\cdot}39$	$\bar{8}{\cdot}61$
5·98	2·84	6·1	16·3	$\bar{5}{\cdot}21$	$\bar{8}{\cdot}65$
7·24	3·79	5·3*, 5·9	91*, 92	$\bar{5}{\cdot}96$	$\bar{8}{\cdot}55$
8·00	4·33	5·9	265	$\bar{4}{\cdot}42$	$\bar{8}{\cdot}53$

* Assay performed on dry isoproyl alcohol; all remaining analyses with isopropyl alcohol–water azeotrope. † Paul and Long, *Chem. Rev.*, 1957, **57**, 1. A table of H_0 values quoted from an unknown source by Deno, Berkheimer, Evans, and Peterson (*J. Amer. Chem. Soc.*, 1959, **81**, 2344) disagrees with this compilation.

In order to indicate the level of radioactivity at various stages of the experiments, the measured counts have generally been converted into absolute units of activity based on the figures given by the Radiochemical Centre for the activity of the tritiated water supplied. For comparative purposes the activities quoted in this manner are as accurate as the original counts, but in an absolute sense these figures are not reliable and are subject to the same uncertainty as the Radiochemical Centre's assay of tritiated water. Only relative values are utilised in the calculation of exchange numbers.

Formation of Isopropyl Alcohol from Propene.—Solutions of propene in 3·08M-perchloric acid were prepared by passing a mixture of propene and propane (kindly given by Petrochemicals Ltd.) through the acid. Portions (5·02 ml.) of this solution, in sealed-off ampoules with minimum gas space, were heated at 100° for various times, chilled, and analysed for isopropyl alcohol by a spectrophotometric method based on the oxidation to acetone and conversion into 2,2′-dihydroxydibenzylideneacetone[3] or, as a check in one case, analysed for propene by a bromine-addition method.[4] This check indicated that there was some loss of material, possibly through oxidation, in the course of the experiment. These results are therefore only approximate. They lead to a half-life of *ca.* 7—15 min. for the hydration and indicate that the equilibrium concentration of propene is very small.

Kinetic Measurements of the Dehydration of Cyclohexanol in 3·01M-*Aqueous Perchloric Acid.*—Reaction of cyclohexanol in perchloric acid at 100° (sealed tubes) resulted in some loss of cyclohexanol and formation of olefin. The loss of cyclohexanol could be followed by gas-chromatography of dried (K_2CO_3) ethereal extracts (6 × 5 ml., each diluted to 50 ml.) of a reaction sample, added toluene being used as an internal standard. The formation of olefin, followed by bromine addition,[5] was a more reproducible measure of the progress of the reaction. It was observed by breaking the ampoules by shaking them in a vessel containing cold (0°) water and carbon tetrachloride and a known amount of dissolved bromine, allowing the components to react in the dark for 20 min., and titrating the excess of bromine with thiosulphate after addition of an excess of potassium iodide. The reaction time was found to be important in this estimation. A time of 20 min. at 0° was appropriate to 0·06M-cyclohexene in carbon tetrachloride when 0·05M-bromine was being used. With 0·005M-bromine the time required is 30 min. and the analyses had to be corrected for the consistently low results (92%) obtained with dilute standard solutions. There was no interference by cyclohexanol.

After 22·5 hr. at 100° *ca.* 20% of the cyclohexanol initially present had been converted into cyclohexene, but after this time there was no further increase in the concentration of cyclohexene. Analyses of samples heated for periods up to 160 min. gave an overall first-order rate constant of *ca.* $6{\cdot}5 \times 10^{-5}$ sec.$^{-1}$ for the attainment of the cyclohexanol–cyclohexene equilibrium and hence, account being taken of the proportion of cyclohexene at equilibrium, a value of *ca.* $1{\cdot}3 \times 10^{-5}$ sec.$^{-1}$ for the rate constant of the dehydration.

Tritium Exchange of Cyclohexanol in 3·01M-*Aqueous Perchloric Acid at* 100°.—Sealed ampoules containing 5 ml. of reaction solution (*ca.* 0·1M-cyclohexanol in 3·01M-perchloric acid)

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[3] Neish, " Analytical Methods for Bacterial Fermentations," National Research Council of Canada, Saskatoon, 1952.

[4] Polgár and Jungnickel in " Organic Analysis," Volume III, Interscience Publ., Inc., New York, 1956, p. 232.

[5] Smart, Burrows, Owen, and Quayle, *J. Amer. Chem. Soc.*, 1941, **63**, 3000; ref. 4, p. 234.

were broken in a mixture of water (10 ml.) and cyclohexanol (15—25 g., weighed accurately). The alcohol layer was further extracted with water (6 × 40 ml.) to remove hydroxylic tritium, the layers being separated by centrifuge. After being dried (K_2CO_3), the cyclohexanol was distilled and the radioactivity was determined on 0·192-g. portions of the distillate as described for isopropyl alcohol. Exchange numbers were calculated on the basis of the result that at equilibrium (attained after 22·5 hr.) 80% of the initial amount of cyclohexanol remains in that form and on the assumption that the large b. p. difference between cyclohexene and cyclohexanol ensures absence of cyclohexene in the distilled cyclohexanol samples. Results are given in Table 3.

TABLE 3.

Tritium uptake by cyclohexanol in 3·01M-aqueous perchloric acid at 100°.

Sample volume (5·02 ml.) contains 0·493 g.-atom of exchangeable (*i.e.*, hydroxylic) hydrogen.

Time (hr.)	[Cyclohexanol]$_0$	Activity * of medium (mc)	Activity † of sample (mc)	N	10^7k_1 ‡ (sec.$^{-1}$)
22·5	0·130	4·02	19·50	4·9	77
	0·112	8·04	36·91	4·6	70
48·8	0·130	4·02	31·61	7·9	78
	0·112	8·04	63·59	7·9	78
72·5	0·130	4·02	38·50	9·6	—
95·5	0·112	8·04	74·25	9·2	—
168	0·130	4·02	42·90	10·7	—
387	0·130	4·02	41·77	10·4	—

* Activity per g.-atom of exchangeable (hydroxylic) hydrogen in medium. † Activity per mole of cyclohexanol in solution (the concentration of cyclohexanol being taken as 0·8[cyclohexanol]$_0$). ‡ Calc. as $k_1 = \{\ln (N_\infty - N_0)/(N_\infty - N)\}/t$, where $N_\infty = 10{\cdot}6$.

Exploratory Measurements with Cyclohexanol in Trifluoroacetic Acid–Perchloric Acid–Water Mixtures.—The hydrogen exchange of cyclohexanol, the dehydration of cyclohexanol (Table 4), and its reversal (Table 5) were briefly examined in these media because the presence of trifluoroacetic acid increased the solubility of cyclohexene.

TABLE 4.

Dehydration of cyclohexanol in ternary acid mixtures.

	Compn. of medium (mole %)					
Temp.	$CF_3\cdot CO_2H$	$HClO_4$	H_2O	[Cyclohexanol]$_0$	Time (min.)	$\frac{[\text{Olefin}]}{[\text{Cyclohexanol}]_0}$
50°	73	7	20	0·178	1380	0·052, 0·062, 0·054
31·6	71	7	22	0·252	20	0
50	64	6	30	0·205	2—78	0
,,	,,	,,	,,	0·185	700	0·0016
,,	,,	,,	,,	0·212	1050	0·0015

TABLE 5.

Disappearance of olefin from a solution of cyclohexene in $CF_3\cdot CO_2H$–$HClO_4$–H_2O (73 : 7 : 20 mole %).

[Cyclohexene]$_0$ = 0·033M.

Time (min.), at 0°	0·8	146	147	2·0	2·1
at 50°	—	—	120	1·5	148
100 [Olefin]/[Olefin]$_0$	26	1	2·4	≤5·9	>2·9

In the measurements of tritium uptake by cyclohexanol in these acid mixtures, 1-ml. samples of reaction solution were removed by pipette and run into water (10 ml.). Inactive cyclohexanol (24·4 g.) was then added. The layers were separated and the removal of hydroxylic tritium and the preparation of a sample for counting were then carried out as in the experiments with aqueous perchloric acid. In acid containing 72 moles % of trifluoroacetic acid and 7 moles % of perchloric acid, the exchange number after complete reaction (>21·5 hr. at 50°) was found to be *ca.* 11. At 50° the half-life of exchange is of the order of 2000 hr. in slightly aqueous trifluoroacetic acid (92 moles % of $CF_3\cdot CO_2H$), of the order of 2 hr. in the ternary acid mixture containing 73 moles % of trifluoroacetic acid and 7 moles % perchloric acid, and of the order of 20 hr. in the ternary mixture containing 64 moles % of trifluoroacetic acid and 6 moles % of perchloric acid.

DISCUSSION

The results quoted indicate that both isopropyl alcohol and cyclohexanol undergo exchange of paraffinic hydrogen atoms in the presence of strong acid and that the isotope exchange occurs without net chemical change.

Calculation of the number of hydrogen atoms per molecule of alcohol that participate in the exchange depends on a knowledge of the distribution coefficient α_T. Values of α_T for aliphatic hydrogen atoms in acidic media do not appear to have been reported and there is also little information concerning deuterium exchange of such systems from which values for tritium might be calculated. However, exchange numbers (after complete reaction, N_∞) of *ca.* 6 for isopropyl alcohol and of *ca.* 11 for cyclohexanol with aqueous perchloric acid at 100° are most reasonably ascribed to exchange of 6 and 11 paraffinic hydrogen atoms, respectively, and thus point to a value of α_T close to unity. Although the participation of other numbers of hydrogen atoms might reasonably be envisaged for the two compounds (*e.g.*, exchange only of α- or β-hydrogen atoms) such assumptions would require grossly different values of α_T for the paraffinic hydrogen atoms in cyclohexanol and isopropyl alcohol, respectively. This is inherently improbable in view of the near-constancy of saturated C–H vibration frequencies and thus of the most important factors of the partition functions.

The value 6 for isopropyl alcohol implies that the six equivalent β-hydrogen atoms are involved; the value of 11 for cyclohexanol points to an isomerisation by which the identity of the ring positions is lost in the course of the reaction.

Mechanism of Exchange in Isopropyl Alcohol.—It is improbable that exchange occurs in the alcohol molecule itself through attack by acid. For example, the rules of exchange for saturated hydrocarbons [6] argue against direct exchange in methyl groups, and so does experience with aliphatic acids [7] and with primary alcohols.[8]

Provided it is permissible to neglect secondary isotope effects (as is the case with tracer concentrations of tritium) an exchange involving *n* equivalent positions within a molecule may formally be represented as an exchange reaction of *n* independent molecular fragments with one exchangeable hydrogen atom each. The exchange of each of the equivalent hydrogen atoms can thus be regarded as an independent process and is characterised by the same rate constant as the overall exchange of the group of *n* atoms.[9] This simplified treatment is applicable to the six β-hydrogen atoms of isopropyl alcohol.

Two main views have been expressed concerning the exchange mechanism in related systems. The first of these envisages the exchange as a rapid process involving reaction between carbonium ions and the medium.[10] However, it is not easy to rationalise why the presence of the positive charge should endow the carbonium ion with greater reactivity (towards an electrophilic reagent!) than is possessed by the alcohol molecule itself. The polar effect of the positive charge would suggest the reverse influence and indeed it is known that some carbonium ions do not exchange hydrogen in acidic media.[11] It has therefore been proposed that exchange reactions of this type go through an olefin which may or may not be formed *via* the carbonium ion.[2] We now examine whether the observed rate of olefin formation from isopropyl alcohol is compatible with this view.

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[6] Otvos, Stevenson, Wagner, and Beeck, *J. Amer. Chem. Soc.*, 1951, **73**, 5741; 1952, **74**, 3269.

[7] Keston, Schoenheimer, and Rittenberg, *J. Amer. Chem. Soc.*, 1937, **59**, 1765; Ives, *J.*, 1938, 81; Bell, Hill, Macdonald, Reed, and Macdonald, *J.*, 1953, 3456.

[8] Gold and (R. S.) Satchell, following paper.

[9] Block and Gold, *J.*, 1959, 966.

[10] Setkina and Kursanov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1959, 433.

[11] *E.g.*, Collins, Rainey, Smith, and Kaye, *J. Amer. Chem. Soc.*, 1959, **81**, 460; Smith, Bowman, and Kmet, *ibid.*, p. 997; Cram and Tadanier, *ibid.*, p. 2737; Stewart, Gatzke, Mocek, and Yates, *Chem. and Ind.*, 1959, 331.

For a scheme

$$\mathrm{ROH} \underset{-a}{\overset{a}{\rightleftharpoons}} \mathrm{P} \underset{-b}{\overset{b}{\rightleftharpoons}} {}^{*}\mathrm{ROH}$$

the exchange velocity is given by

$$\mathrm{d}N/\mathrm{d}t = \lambda(N_\infty - N) \qquad (1)$$

(with $\lambda = k_{-b}$ or, if the distribution coefficient α_T is unity, $\lambda = k_a k_b / k_{-a}$) provided that there is no significant accumulation of the olefin (P). The coefficients k_a, k_b, etc., are functions of the chemical composition of the medium but not of the isotopic composition, *i.e.*, $v_B = k_B[\mathrm{P}]N_\infty$. If tritium uptake proceeds only by the addition of water to the olefin and not also by other exchange reactions at the olefin stage (an assumption rendered probable by the absence of exchange during the hydration of olefins in deuterium oxide [12]), k_a relates to the elimination of one specified β-hydrogen atom. Since the equilibrium concentration of olefin is very small in the solutions considered, it follows that $k_{-a} \gg k_a$ or, since k_{-a} and k_b differ only to the extent of a small factor corresponding to the tritium isotope effect in olefin hydration, $k_{-a} \gg k_a k_b / k_{-a}$. Thus the above scheme requires the hydration of propene in a given medium to be much faster than the hydrogen exchange. In 3·08M-perchloric acid this requirement is certainly satisfied, the half-life of the hydration being of the order of 10 min. and that for exchange *ca.* 25,000 min. The exchange constant approximately represents one-sixth of the rate of dehydration of isopropyl alcohol (the additional factor k_b / k_{-a} being the isotope effect in olefin hydration). It should be noted that k_a is one-sixth of the rate constant of dehydration of isopropyl alcohol because only one-sixth of all dehydrations will eliminate any given single hydrogen atom.

Mechanism of Exchange in Cyclohexanol.—For cyclohexanol the process may be described in terms of two reactions, namely, (1) the exchange (without isomerisation) involving a group of equivalent exchangeable hydrogen atoms of the substrate and (2) the above-mentioned isomerisation which produces no net chemical change but results in an isotopically rearranged molecule of cyclohexanol.

Intermediate formation of cyclohexene would provide a route for isomerisation since the re-hydration of an olefin molecule can regenerate either a cyclohexanol molecule in which the hydroxyl group is attached to its original position or a molecule in which the hydroxyl group is displaced one position along the ring. In addition, rearrangement may conceivably occur at the carbonium-ion stage through hydride shifts between adjacent positions. Transannular hydride shifts which are known to occur, in, for example, cyclodecyl derivatives,[13] are less likely in a six-membered ring.

In the dehydration–hydration mechanism, exchange and isomerisation are interconnected. During each dehydration one-eleventh of the alicyclic hydrogen atoms of a given cyclohexanol molecule is lost and on rehydration will contain a tracer proportion of the tritium label. Since multiply-tritiated species will not occur in experiments with tritium in tracer concentrations this is equivalent to saying that one-eleventh of all dehydrations of a given cyclohexanol molecule will introduce, on rehydration, a tracer proportion of tritium label into *all* positions. In macroscopic terms—if kinetic isotope effects are for the moment ignored—the rate of tritium exchange will be one-eleventh of the rate of dehydration of cyclohexanol (on the assumption that the equilibrium proportion of cyclohexene is negligible). It follows that, in this case also, equation (1) may be applied, but k_a now represents about one-eleventh of the rate constant for the formation of cyclohexene from cyclohexanol.

This formulation of the exchange reaction requires the alcohol–olefin equilibrium to be attained more rapidly than the exchange, since the rate constant for the attainment of chemical equilibrium is the sum of the rate constants for dehydration and hydration which,

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[12] Purlee and Taft, *J. Amer. Chem. Soc.*, 1956, **78**, 5807; Riesz, Taft, and Boyd, *ibid.*, 1957, **79**, 3724.

[13] Prelog, *Experientia*, Suppl. VII, p. 261, Basle, 1957.

for an equilibrium lying mainly on the alcohol side, will greatly exceed the rate constant for dehydration alone. These requirements are satisfied by the experimental results. In the ternary acid system the hydration of cyclohexene has been found to be much faster than the exchange of cyclohexanol, and the experiments with aqueous perchloric acid show the alcohol–olefin equilibration (starting from cyclohexanol) to be complete before the half-time of exchange. The experiments with the aqueous acid are quantitatively perhaps less significant owing to the low solubility of cyclohexene and therefore its possible accumulation in another liquid or vapour phase. The apparent equilibrium concentration of olefin detected (20%) probably exceeds the equilibrium concentration in the aqueous phase and is a value distorted by the distribution coefficient of cyclohexene between the phases.

The assumed mechanism of the reaction is therefore adequate and the results do not require the postulation of processes outside this scheme, such as exchange in the carbonium ion or the occurrence of hydride shifts in that ion.

The Transition State.—In the case of isopropyl alcohol the acidity-dependence of the exchange has been studied over a wide range of acidity. The rate increases only slightly less rapidly than the first power of Hammett's acidity function h_0, the rate constant being given by $\lambda = kh_0^{0 \cdot 90}$. The reaction is therefore clearly acid-catalysed.

It seems unlikely that in aqueous perchloric acid the protonated alcohol $Me_2CH{\cdot}OH_2^+$ would go over into olefin without intermediate formation of the carbonium ion Me_2CH^+ in a substantially free form. The dehydration is therefore represented by the sequence

$$ROH + H_3O^+ \underset{-1}{\overset{1}{\rightleftharpoons}} ROH_2^+ + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (A)$$

$$ROH_2^+ \underset{-2}{\overset{2}{\rightleftharpoons}} R^+ + H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (B)$$

$$R^+ + H_2O \underset{-3}{\overset{3}{\rightleftharpoons}} P + H_3O^+ \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (C)$$

where R^+ represents the (classical) isopropyl cation. Either step 2 or step 3 may be rate-controlling and would provide a transition state of the composition $\{ROH,H^+\}$, as required by the Zucker–Hammett hypothesis for an H_0-dependent dehydration. If step 2 were rate-controlling in dehydration, then step —2 would be rate-determining in hydration. Reasons have been given against assuming reaction —2 to be the rate-controlling step in the hydration of other olefins [12,14] and accordingly reactions 3 and —3 are perhaps more likely to be rate-controlling. Measurements of oxygen-isotope exchange of isopropyl alcohol in an acidic medium [15] offer strong support for this view. According to the scheme given, which is identical with that put forward by Dostrovsky and Klein for t-butyl alcohol,[16] the rate constant for oxygen exchange is k_1k_2/k_{-1} and therefore it would equal the hydrogen exchange rate if step 2 is rate-controlling in hydrogen exchange, but it would exceed the hydrogen exchange rate if the latter had reaction 3 as rate-controlling step. The only experimental value available for oxygen exchange of isopropyl alcohol relates to aqueous 1·06M-perchloric acid containing 1·0M-sodium hydrogen sulphate (for which H_0 is expected to be in the range —0·2 to —0·6) at 100°. The observed rate constant ($1{\cdot}5 \times 10^{-5}$ sec.$^{-1}$) is to be compared with an extrapolated rate constant of *ca.* 1×10^{-7} sec.$^{-1}$ (or slightly less) for hydrogen exchange at the same acidity. According to this scheme and for a rate-controlling step 3, the rate constant for hydrogen exchange is $\lambda = k_1k_2k_3/k_{-1}(6k_{-2} + k_3)$. Therefore the ratio of the rate constants for oxygen and tritium exchange should equal $(6k_{-2} + k_3)/k_3$ whence we obtain a ratio of *ca.* 25 for k_{-2}/k_3. The corresponding ratio for t-butyl alcohol, extrapolated to 100° from Dostrovsky and

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[14] Levy, Taft, and Hammett, *J. Amer. Chem. Soc.*, 1953, **75**, 1253.

[15] Batts, personal communication.

[16] Dostrovsky and Klein, *J.*, 1955, 791.

Klein's measurements[16] of oxygen exchange and dehydration in 0·09M-perchloric acid at 55° and 75°, is *ca.* 12. The effect of methyl-substitution in the isopropyl cation to produce the t-butyl cation is expected to reduce the acidity of the ion and to lower the rate constant for proton detachment from it (k_3). The fact that k_{-2}/k_3 is nevertheless smaller for the t-butyl cation than it is for the isopropyl cation indicates a large difference between the velocities of the reactions

$$\mathrm{Me_2CH^+ + H_2O \longrightarrow Me_2CH{\cdot}OH_2^+}$$

and

$$\mathrm{Me_3C^+ + H_2O \longrightarrow Me_3C{\cdot}OH_2^+}$$

We conclude that these reactions, which are sometimes described as the collapse of a solvation shell, are activated processes.

The foregoing discussion is barely affected by considering these processes in terms of the scheme recently described by Boyd, Taft, Wolf, and Christman.[17] This description differs from the mechanism contained in equilibria (A)—(C) only in two details. First, it is explicitly stated (and this in no way conflicts with the views or evidence given above) that the water molecule is never quite detached from R^+ as a result of step 2, and that this same loosely bonded water molecule acts as base in step 3. Step 3 is itself considered to take place in two stages, but this sub-division has no kinetic consequences since the second stage [labelled step (4) by Boyd *et al.*] is not rate-controlling. It will obviously require somewhat sophisticated work to establish an experimental distinction between the two schemes.

We have noted that the alternative transition states both have the composition required by the application of the Zucker–Hammett hypothesis to the H_0-dependence of the dehydration of isopropyl alcohol. However, the hydration of several olefins has also been shown[18] to follow H_0 and if, as seems likely, the same result applies to propene, it conflicts with the Zucker–Hammett hypothesis. The dilemma that either the forward or the backward reaction must be opposed to the Zucker–Hammett hypothesis is not remedied by attributing unorthodox structures to the transition state. In view of the fact that the oxygen exchange of t-butyl alcohol[17] and s-butyl alcohol[19] also follows H_0 and is highly unlikely to involve a transition state of composition $\{P,H\}^+$, we conclude that it is a reaction which conforms to the Zucker–Hammett principle and, therefore, that reactions starting from alcohols are more likely to follow the Zucker–Hammett principle than those starting from olefins. Possible solutions of the problem raised thereby in relation to acid-catalysed reactions of olefins (and aromatic hydrocarbons) have been discussed by several authors.[17,20]

The Basicity of Isopropyl Alcohol.—We direct attention also to the observation that the rate increase of hydrogen exchange with acidity continues unabated up to high acidities ($H_0 = -4$). Bartlett and McCollum[21] have deduced from the acidity-dependence of the rate of reaction between isopropyl alcohol and triarylcarbonium ions that the pK_a value of the alcohol is $-3{\cdot}2$. Accordingly, the alcohol should be extensively protonated at the highest acidities studied by us, and the exchange velocity should tend to an asymptotic value corresponding to complete protonation, but it does not. The apparent contradiction could be reconciled by the assumption of what would appear to be an improbably large temperature coefficient for ($H_0 - pK_a$).

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[*Received, July 2nd,* 1962.]

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