The Exchange of Oxygen between Alcohols and Water. Part I. Rates of Carbonium-ion Formation and Decomposition in Acidic Aqueous Solutions of tert.*-Butanol.*

By I. Dostrovsky and F. S. Klein.

[Reprint Order No. 5785.]

The rates of oxygen exchange between *tert.*-butanol and water and the rates of the dehydration in the presence of sulphuric acid have been determined at a number of temperatures and acid concentrations. The rate coefficient for the formation of carbonium ion from the alcohol at 55° is $1{\cdot}33 \times 10^{-4}$ sec.$^{-1}$ (for unit activity H^+) and the activation energy associated with the process is 30·1 kcal./mole. The activation energy for the formation of *iso*butene from the *tert.*-butyl carbonium ion is 2·2 kcal./mole. The analysis permits the identification of the rate of hydration of *iso*butene with the rate of formation of the carbonium ion from the olefin. In the dehydration the rate-controlling step is the formation of the carbonium ion *via* the hydroxonium ion, whereas the rate-controlling step of the hydration is the protonation of the olefin. The rates of these reactions are compared with calculated values and with the rates of other similar reactions.

Many reactions of alcohols in aqueous acidic media, and particularly those of tertiary alcohols, are assumed to proceed through the intermediate formation of a carbonium ion. In reactions such as ether formation, acid-catalysed esterification, and dehydration of these alcohols the initial steps are commonly represented as

$$ROH + H_3O^+ \rightleftharpoons ROH_2^+ + H_2O \qquad ROH_2^+ \rightleftharpoons R^+ + H_2O \quad . \; . \; . \quad (1)$$

It is further assumed that the dissociation of the oxonium compound is rate-determining for these reactions.

The purpose of the present series of papers is to determine to what extent the assumption of a carbonium-ion intermediate is justified, and whenever possible to determine its rate of formation and decomposition. We now describe measurements of the rate of oxygen exchange between *tert.*-butanol (a typical tertiary alcohol) and water in the presence of various concentrations of sulphuric acid. Alcohol of normal isotopic composition was dissolved in acidified water enriched with respect to $H_2{}^{18}O$. Samples of alcohol were analysed for ^{18}O content after various intervals of time. The rate constants of the exchange reaction thus obtained are presented in Table 1, together with the rate constants of the dehydration of the alcohol observed under similar experimental conditions.

Table 1. *Rates of oxygen exchange between* tert.*-butanol* (1M) *and water in aqueous sulphuric acid solution, and the rates of the dehydration reaction* (10^5k, *sec.*$^{-1}$).

Acid concn., N	Exchange, 55°	Exchange, 75°	Dehydration, 55°	Dehydration, 75°
0·09	1·33	19·7	0·045	0·95
0·9	15·4	—	0·57	—

In acid aqueous media *tert.*-butanol undergoes a reversible dehydration and this process will lead to an observed oxygen exchange. The question whether the dehydration–hydration reaction proceeds through the carbonium ion or not may be answered by a comparison of the observed rates of their reaction with that of the exchange reaction. The reactions involved may be represented by the general scheme

$$\left.\begin{aligned} ROH + H_3O^+ &\underset{k_2}{\overset{k_1}{\rightleftharpoons}} ROH_2^+ + H_2O \\ ROH_2^+ &\underset{k_4}{\overset{k_3}{\rightleftharpoons}} R^+ + H_2O \\ R^+ + H_2O &\underset{k_6}{\overset{k_5}{\rightleftharpoons}} P + H_3O^+ \end{aligned}\right\} \quad . \; . \; . \; . \; . \; . \quad (2)$$

where P represents the olefin (*iso*butene in this case).

We shall not yet make any assumptions regarding the relative magnitudes of the rate coefficients k_3, k_4, k_5, and k_6, and shall derive them from the experimental data. We can derive for the rate of olefin elimination (and of alcohol dehydration) the equation

$$d[P]/dt = -d[ROH]/dt = k'[ROH] - k''[P]$$

where

$$k' = k_3k_5K[H_3O^+]/(k_4 + k_5)[H_2O]; \qquad K = k_1/k_2 \quad . \quad . \quad . \quad . \quad . \quad (3a)$$

and

$$k'' = k_4k_6[H_3O^+]/(k_4 + k_5) . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3b)$$

For the isotopic exchange reaction we can similarly obtain the equation

$$dN/dt = (N_\infty - N)\{([ROH] + [H_2O])/[H_2O]\}\{k_4[H_3O^+]/(k_4+k_5)\}\{k_3K/[H_2O] + k_6[P]/[ROH]\} \quad (4)$$

where N is the mole-fraction of $R^{18}OH$ in the alcohol at any time and N_∞ is the value at isotopic equilibrium. In this equation [P] and [ROH] are time-variable, and the integration leads to equations which are not particularly useful. If, however, we start with a system containing water, olefin, and alcohol at their equilibrium total concentrations but with the water and alcohol differing in their isotopic compositions, equation (4) can be integrated readily since now [P] and [ROH] are constant and their ratio is determined by the equilibrium constant of the dehydration–hydration reaction :

$$[P_\infty]/[ROH_\infty] = k_3k_5K/k_4k_6[H_2O] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The rate coefficient for the exchange reaction then becomes

$$k_{exch.} = \{([ROH]_\infty + [H_2O])/[H_2O]\}k_3K[H_3O^+]/[H_2O] \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Comparing equations (3) and (5), we note that

$$k' = k_{exch.}\{[H_2O]/[(H_2O] + [ROH]_\infty)\}k_5/(k_4 + k_5) \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Since $[H_2O]/([H_2O] + [ROH])$ is very nearly unity, it follows that k' will be always smaller than $k_{exch.}$. A comparison of the experimentally determined coefficients $k_{exch.}$ and k' permits therefore the computation of the ratio k_4/k_5. Once this ratio is available it can be substituted in equation (3*b*) to obtain a value for $k_6[H_3O^+]$. Under our experimental conditions the equilibrium of the dehydration–hydration reaction is reached much sooner than that of the isotopic exchange. Therefore it is sufficient to delay the measurement of the exchange reaction by several half-lives of the olefin reaction to ensure that it is proceeding under conditions of chemical equilibrium.

In the equations derived above, concentrations are used rather than activities. The errors introduced by this simplification cannot affect the arguments presented below and therefore no attempt was made to determine, by separate experiments, the appropriate activity coefficients.

Values for k' and k'' for the dehydration and hydration reactions have been reported by Lucas and Eberz (*J. Amer. Chem. Soc.*, 1934, **56**, 460), Eberz and Lucas (*ibid.*, p. 1234), and by Levy, Taft, Aaron, and Hammett (*ibid.*, 1951, **73**, 3792). All these values have been obtained in essentially aqueous media and with nitric acid as catalyst. Since in our case the exchange reactions were carried out in a medium which contained an appreciable amount of alcohol (about 10 vols. %), considerable corrections are necessary in comparing the data. These corrections have to allow for the effect of solvent on the rate of the reaction and on the activity of the catalyst. To avoid such corrections, which are at best approximations, we have carried out independent measurements of the dehydration reaction under conditions as close as possible to those used in the exchange reactions. These are the values presented in Table 1. Our value for k' at 55° and 0·09N-acid, $0·45 \times 10^{-6}$ sec.$^{-1}$, may be compared with that of Levy, Taft, Aaron, and Hammett (*loc. cit.*), $1·67 \times 10^{-6}$ sec.$^{-1}$, and that calculated from Eberz and Lucas's lower-temperature experiments (*loc. cit.*), *viz.*, $1·63 \times 10^{-6}$ sec.$^{-1}$. The approximately four-fold rate coefficient in the highly aqueous solvent as compared with the more alcoholic medium (1M-*tert.*-butanol) is in reasonable agreement with the expected solvent effects on these reactions (cf. Ingold, " Structure and Mechanism in Organic Chemistry," Cornell, 1953, p. 453) and with our experiments in 0·1M-butanolic solutions ($1·1 \times 10^{-6}$ sec.$^{-1}$ as calculated from data of Table 5.

Using the results of Table 1 and equation (6), we calculate for the ratio k_4/k_5 the value 29 in 0·1N-acid and 26 in 1N-acid at 55°, and 20 in 0·1N-acid at 75°. The decrease in the ratio k_4/k_5 with increasing temperature would indicate a slightly higher activation energy for process 5 as compared with process 4 [see equations (2)]. If one assumes that process 4, involving the recombination of a carbonium ion with a water molecule, possesses no activation energy, then it is possible to calculate an activation energy of about 2·2 kcal./mole for the decomposition of the carbonium ion to olefin. The ratio k_4/k_5 determines the proportion of olefin formed in other reactions involving carbonium ions, such as unimolecular solvolysis of *tert.*-butyl halides and sulphonium salts. It is therefore of some interest to compare the proportion of olefin elimination reported for such reactions with the values of k_4/k_5. No values are available for olefin elimination in highly aqueous solvents as used in our work, but making extreme extrapolation from media of lower water content (cf. Ingold, *op. cit.*, p. 459) and correcting our results to 25° by using the temperature coefficient as determined above, we estimate the proportion of olefin formed in the solvolysis of *tert.*-butyl bromide in "90%" ethanol as 3%, compared with 2·8% as calculated from the value of k_4/k_5 at 25°.

The fact that the rate constant for the exchange reaction is considerably greater than that of the dehydration reaction is sufficient to exclude the mechanism of exchange involving direct olefin elimination from the oxonium ion, *viz.*, $ROH_2^+ \rightleftharpoons P + H_3O^+$. Had this been the correct mechanism the rate coefficient of the exchange and dehydration reactions would be identical. Recently Levy, Taft, and Hammett (*J. Amer. Chem. Soc.*, 1953, **75**, 1253, 3955) showed that there is little or no *as*-ethylmethylethylene (2-methylbut-1-ene) formed when trimethylethylene is hydrated to *tert.*-amyl alcohol. From this observation they concluded that . . . "The reaction scheme consisting in the rapid and reversible addition of a proton to the olefin, followed by a rate-determining reaction of the ion with a water molecule, is definitely excluded as the mechanisms of the hydration reaction." In other words, in equation (2), k_4 cannot be smaller than k_5 or k_6, in complete agreement with our findings. Levy, Taft, and Hammett (*loc. cit.*), however, were led to assume the direct elimination of olefin from the oxonium ion. From the arguments presented above it will be seen that this conclusion is not warranted and that all that is necessary to explain the failure to observe the interconversion of the olefins is that k_4 be sufficiently greater than k_5 (for each olefin).

Although the evidence presented in this paper does not rigorously exclude the possibility of exchange by a bimolecular attack of a water molecule on the oxonium ion, $H_2{}^{18}O + ROH_2^+ \rightleftharpoons R^{18}OH_2^+ + H_2O$, we consider that for a tertiary alcohol in a highly aqueous medium this is an unlikely mechanism. The operation of this mechanism in other alcohols is discussed in a subsequent paper.

Accepting the mechanism depicted in equation (2), we may identify the observed rate coefficient for the exchange reaction, as determined under gross chemical equilibrium conditions, as approximately equal to

$$k_{\text{exch.}} \approx k_3K[H_3O^+]/[H_2O] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Similarly, using equation (3*b*), we may identify k'', the rate constant of the hydration reaction, with $k_6[H_3O^+]$.

The observed activation energies for the exchange and hydration reaction can also be identified with the corresponding steps. The value of 30·5 kcal./mole, calculated from the rates of exchange at 55° and 75°, corresponds to the heat of activation of the ionisation step 3 plus the difference in the heat of activation of steps 1 and 2. Our value should be compared with 34·8 kcal./mole, as determined by Eberz and Lucas (*loc. cit.*), and 34·1 kcal./mole, as calculated by Franklin (*Trans. Faraday Soc.*, 1952, **48**, 443). The hydration reaction (6) possesses the lower activation energy of 23·4 kcal./mole (Lucas and Eberz, *loc. cit.*). The relatively high activation energy of the ionisation step can be compared with the activation energy of the unimolecular decomposition of sulphonium ions. Thus *tert.*-butyldimethylsulphonium ion decomposes in water with an activation energy of 33 kcal./mole, a value close to that observed above for the decomposition of the oxonium ion.

The values of the various rate coefficients and activation energies determined in the present work are collected in Table 2, where they are compared with those from Franklin's calculation (*loc. cit.*).

TABLE 2. *Rate coefficients of the various steps in the acid-catalysed dehydration of* tert.*-butanol in aqueous media.*

Reaction	k (obs.)	E_A (obs.), kcal./mole	k (calc.) *	E_A (calc.),* kcal./mole
3	$1{\cdot}33 \times 10^{-4}$ †	30·1	$3{\cdot}1 \times 10^{-4}$ †	34·1
4	$(3{\cdot}8 \times 10^{14})$	0	$3{\cdot}8 \times 10^{14}$	0
5	$1{\cdot}3 \times 10^{13}$	2·2	$3{\cdot}8 \times 10^{14}$	0
6	—	—	$1{\cdot}45 \times 10^{-1}$	21·3

* Values calculated by Franklin corrected to 55° and expressed as bimolecular rate constants; k_4 and k_5 include the concentration of water (55·5 moles/l.).

† These rate coefficients are multiplied by the unknown equilibrium constant K. They represent therefore the rate of formation of carbonium ion from the alcohol according to the equation

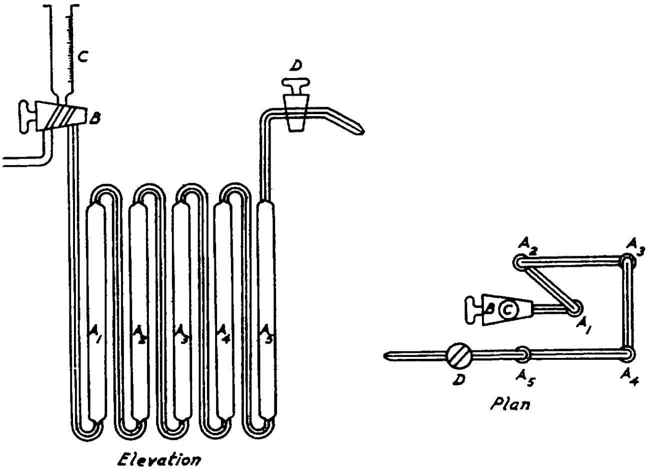
$$\mathrm{ROH} + \mathrm{H_3O^+} \rightleftharpoons \mathrm{R^+} + 2\mathrm{H_2O}.$$

From the constants collected in Table 2 it is seen that the rate-determining step, in the sense of the slowest step in a series of reactions, for the dehydration reaction is the ionisation of the oxonium ion, and for the hydration reaction it is the protonation of the olefin (k_6).

EXPERIMENTAL

Materials.—Water containing about 2·8% of $H_2{}^{18}O$ was used throughout. It was purified by distillation from alkaline potassium permanganate.

tert.*-Butanol.* The commercial product was purified by refluxing it over sodium and fractionation through a 20-plate column. The distillate (m. p. 24·5°) was free from olefin. All other reagents were of analytical grade.



Isotopic Exchange Reactions.—The apparatus used was similar to that of Lucas and Eberz (*loc. cit.*) and is shown in the Fig. The reaction system consisted of five vertical glass tubes ($A_1 \ldots A_5$), 18 cm. long and 15 mm. in inside diameter, connected in series by glass capillaries of 1·5 mm. inside diameter. One end of the apparatus is closed by a two-way capillary stopcock B, carrying a graduated separation funnel C (100 ml. capacity). The other end of the apparatus is closed with a capillary stopcock D with a drawn-out tip. The volume of the apparatus between stopcocks B and D was about 120 ml.

Stock solutions of sulphuric acid (1N and 0·1N) were prepared by adding a weighed quantity of the concentrated acid to ^{18}O-enriched water. Reaction mixtures for the exchange runs were prepared by adding a known weight of *tert.*-butanol to a weighed amount of the sulphuric acid stock solutions. The densities of the mixtures were measured in separate experiments, and their values used in calculating the molarities of the alcohol and acid.

The apparatus was filled by introducing the mixture through funnel C and stopcock B until all the air had been displaced and surplus solution appeared at the tip of stopcock *D*, which was then closed. Mercury (50 ml.) was then poured into funnel *C* and a small amount was allowed to fill the capillary below *B* by manipulation of stopcock *D*. The whole apparatus was then submerged in a thermostat regulated to 0·01°. After an interval of at least six times the half-life for olefin formation, sampling was started. Samples (7 ml.) were withdrawn through stopcock *D* at intervals of time suitable for the application of Guggenheim's method of kinetic analysis (cf. *Phil. Mag.*, 1926, **2**, 538). The samples were run into test tubes containing enough 10N-potassium hydroxide to neutralise the solution; anhydrous potassium carbonate (2 g.) was then added, and the mixture shaken vigorously, and then allowed to settle for 15 min. The bottom (aqueous) layer was removed with a fine pipette, and the alcohol layer dried with more anhydrous potassium carbonate. After 2 hr. over the desiccant, the alcohol was vacuum distilled. An equal volume of anhydrous potassium carbonate was again added, and the mixture shaken vigorously for 2 hr. at 50° and left overnight. The alcohol was finally separated by centrifuging and analysed for its ^{18}O content by Anbar, Dostrovsky, Klein, and Samuel's method (*J.*, 1955, 155). As an illustration of our method one run is represented in full in Table 3. where N_t represents the atom % of ^{18}O in alcohol at time *t*.

From the slope of a plot of log $(N_{t+300} - N_t)$ against *t*, the value of $19·7 \times 10^{-5}$ sec.$^{-1}$ was obtained for $k_{\text{exch.}}$.

TABLE 3. ^{18}O *Exchange between* tert.*-butanol* (1·04M) *and water in aqueous sulphuric acid* (0·0913N) at 75·0°. *Initial* ^{18}O *content of aqueous reaction medium* 2·5 *atom* % $H_2{}^{18}O$.

Time (min.)	20	30	50	60	80	100	120
N_t	0·370	0·408	0·684	0·757	0·920	1·030	1·113
N_{t+200}	1·389	1·393	1·403	1·409	1·419	1·427	1·435
log $(N_{t+200} - N_t)$ ...	0·0082	$\bar{1}$·9663	$\bar{1}$·8570	$\bar{1}$·8141	$\bar{1}$·6981	$\bar{1}$·5985	$\bar{1}$·5076

Dehydration Experiments.—The apparatus used in this experiment was similar to that described by Levy, Taft, Aaron, and Hammett (*J. Amer. Chem. Soc.*, 1951, **73**, 3792) except that the manometer had a total length of 100 cm. The total volume of the apparatus was 110·5 ml. The experimental procedure differed somewhat from that described by the above authors in that the starting material in our experiments was a dilute solution of the alcohol and not the olefin, and therefore the rate of pressure increase with time was observed. The reaction mixture was prepared by the method described for the exchange reactions. After being placed in the reaction vessel the solution was degassed by repeated freezing, evacuating, melting, and refreezing. The reaction vessel was then sealed under vacuum, and the apparatus placed in a thermostat. Pressure readings were taken at predetermined intervals. Experiments were repeated for various ratios of vapour space to liquid volume. For such conditions, and following the procedure of Levy, Taft, Aaron, and Hammett (*loc. cit.*), the following equation can be derived:

$$C^{\circ}_{a}/k_{\text{obs.}}p_{\infty} = r/RTk' + h/k' \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (8)$$

where $C_a{}^{\circ}$ and p_{∞} are the initial alcohol concentration and final olefin partial pressure, respectively; *r* is the ratio of vapour space to solution volume; h = concentration of olefin/partial pressure of olefin; k' is the rate coefficient for the dehydration reaction (cf. p. 792) and $k_{\text{obs.}}$ is the observed rate coefficient as determined from the rate of pressure rise in the experiments described above. Plotting $C_a{}^{\circ}/k_{\text{obs.}}p_{\infty}$ against *r*, we obtain the values of k' presented in Table 1. As an illustration of our method one run is presented in full in Table 4.

TABLE 4. *Dehydration of* tert.*-butanol* (1·04M) *in aqueous sulphuric acid* (0·0858N) *at* 55°.

Time (min.)	7	17	27	52	67	87	122	147	192	207
P_t	198·0	208·3	217·8	239·0	250·2	264·1	284·7	296·9	314·9	320·8
P_{t+1320}	377·5	377·9	378·1	379·7	380·3	381·1	381·8	382·9	383·8	384·2
log $(P_{t+1320} - P_t)$ ...	2·2541	2·2294	2·2049	2·1483	2·1143	2·0682	1·9872	1·9345	1·8382	1·8021

Vol. of liquid phase 74·5 ml.; $r = 0·483$; $P_0 = 192·9$ mm. (from the linear extrapolation to zero time); P_{∞} (observed at 11 half-lives) = 384·2 mm.; p_{∞} = 191·3 mm. Loss of alcohol from liquid phase = 0·38%.

From the plot of log $(P_{t+1320} - P_t)$ against time the value of $k = 8·7 \times 10^{-5}$ sec.$^{-1}$ was obtained.

Two further runs on the same mixture at the same temperature but with r = 1·225 and 1·862 gave values of k of 3·7 × 10^{-5} and 2·4 × 10^{-5} sec.$^{-1}$ and had p_∞ of 194·5 and 191 mm., respectively. From the slope of this straight line obtained on plotting $C_a{}^\circ/k_{\text{obs.}}p_\infty$ against r, the value of 4·17 × 10^{-7} sec.$^{-1}$ was obtained for k'.

Our experiments on the dehydration of *tert.*-butanol in media containing different amounts of the alcohol are summarised in Table 5.

TABLE 5. *Rate coefficients* (× 10^5, *sec.*$^{-1}$) *of dehydration of* tert.*-butanol in aqueous sulphuric acid.*

Normality of acid, N	0·858	0·858	0·0858
Molarity of alcohol	0·104	1·04	1·04
Temperature 55·0°	1·03 *	0·528	0·0417
„ 75·0°	—	—	0·870

Temp. coeff. = 4·57 per 10°. Energy of activation = 34·5 kcal.

* Corrected value from observations in 0·952N-acid.

ISOTOPE DEPARTMENT, THE WEIZMANN INSTITUTE OF SCIENCE,
REHOVOTH, ISRAEL.

[*Received, October 7th,* 1954.]