The Exchange of Oxygen between Alcohols and Water. Part II.[*]
The Acid-catalysed Reactions of n-*Butyl Alcohol and* neo*Pentyl Alcohol.*

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The rates of the acid-catalysed oxygen exchange and decomposition of *n*-butyl alcohol and *neo*pentyl alcohol in aqueous media have been measured at 125°. The exchange reaction of *n*-butyl alcohol is some 3 times faster than its decomposition, while the exchange of *neo*pentyl alcohol is some 37 times slower than the decomposition. The decomposition of *n*-butyl alcohol is about 3 times slower than that of *neo*pentyl alcohol, the product being in both cases a rearranged alcohol, olefin, and ether. From these results and from data on the hydration of but-1-ene it is concluded that the exchange reactions proceed by a bimolecular attack of a solvent molecule on the conjugate acid of the alcohol. The same mechanism is probably correct also for other reactions of primary alcohols in acid media such as, for example, ether formation and halogenation. The decompositions proceed, on the other hand, through the initial formation of a carbonium ion by a unimolecular ionisation of the conjugate acid of the alcohol.

IN Part I [*] we reported that the oxygen exchange of *tert.*-butyl alcohol proceeds through the reversible formation of the carbonium ion. Kinetic measurements of the rates of the exchange and of olefin elimination reactions permitted the estimation of rates of carbonium-ion formation and the rate and activation energy of the decomposition of this ion to the olefin. In extending our work to other alcohols we have been guided by the consideration that primary and tertiary alcohols represent the two extremes in the behaviour of aliphatic alcohols. The study of representative alcohols from both classes should make it possible to infer the behaviour of other types of alcohol by interpolation.

n-Butyl and *neo*pentyl alcohol undergo slow acid-catalysed decomposition when heated

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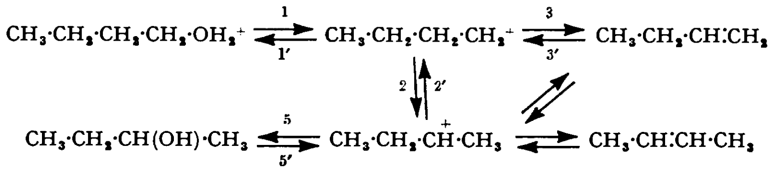
[*] Part I, *J.*, 1955, 791.

in aqueous acidic media. The products from *n*-butyl alcohol are *sec.*-butyl alcohol, di-*n*-butyl ether, and a mixture of butenes. *neo*Pentyl alcohol decomposes to *tert.*-pentyl alcohol and a mixture of pentenes. Polymerisation of the olefins may also occur.

Since both decomposition and exchange are acid-catalysed they probably involve, as a common step, the reversible and rapid formation of the conjugate acid of the alcohol, the oxonium ion : $ROH + H_3O^+ \rightleftharpoons ROH_2^+ + H_2O$.

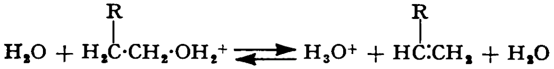
The subsequent reactions of the oxonium compound by one or more of the possible mechanisms detailed below may lead to the exchange and to the formation of the various decomposition products.

(I)



(II) $H_2O^* + R{\cdot}CH_2{\cdot}OH_2^+ \rightleftharpoons H_2O + R{\cdot}CH_2{\cdot}O^*H_2^+$

(III)



$$H_2O + H_2\overset{\overset{\displaystyle R}{|}}{C}{\cdot}CH_2{\cdot}OH_2^+ \rightleftharpoons H_3O^+ + H\overset{\overset{\displaystyle R}{|}}{C}{:}CH_2 + H_2O$$

Oxygen exchange can occur by reactions 1 and 1′ of scheme (I), the recombination of the *n*-butyl ion with water, and by mechanisms (II) and (III). Olefins can be formed by schemes (I) and (III), and *sec.*-butyl alcohol may be formed by reaction 5 of scheme (I), and possibly by mechanism (III). Ethers may be formed by mechanisms 1′ and 5 of scheme (I) and by schemes (II) and (III).

The correct and unambiguous assignment of the various pathways cannot be made on the basis of the study of the exchange reaction of *n*-butyl alcohol alone. Additional evidence was obtained from the study, in sealed tubes at 125°, of the oxygen exchange of*neo* pentyl alcohol, from the rate of decomposition of both *n*-butyl alcohol and *neo*pentyl alcohol, and from the hydration of but-1-ene. Solutions of the alcohols were made up in aqueous sulphuric acid (*ca.* 1N). The medium was enriched with ^{18}O in the exchange reactions, and was of normal isotopic composition in the decomposition. Otherwise conditions were identical for the two reactions. The kinetics of the exchange reactions were followed by observing the increase in the ^{18}O-enrichment of the undecomposed alcohol as a function of time. Since the alcohols produced in the decomposition, *sec.*-butyl alcohol and *tert.*-pentyl alcohol, exchange oxygen rapidly under our conditions, they will have the isotopic composition of the medium. To avoid errors from the presence of these materials in the final samples it was necessary to adopt a careful and elaborate purification and decontamination technique before subjecting the samples to isotopic analysis.

The kinetics of the total decomposition were followed by estimating the amount of alcohol remaining unchanged as a function of time. The analysis was made by the isotopic dilution technique. Known amounts of enriched alcohol were added to samples of the reaction mixture, the alcohol was separated and purified, and its isotopic composition determined. From the amount and composition of the added tracer and the composition of the isolated alcohol the amount of unchanged alcohol originally present was calculated.

The rates of the exchange and decomposition reactions for both alcohols are presented in Table 1.

The mechanistic interpretation of the observed rate of decomposition of *n*-butyl alcohol can be derived from a comparison with the similar reaction of *neo*pentyl alcohol. The rearrangement of the *neo*pentyl skeleton is known to follow immediately upon the formation of the carbonium ion (cf. Ingold, " Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, 1953, p. 511 *et seq.*). The decomposition of *neo*pentyl alcohol in acidic media is, therefore, almost irreversible and its rate measures the rate of heterolysis of the oxonium ion.* Measurements in formic acid solutions have shown that the rate of ionisation

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* In the present paper, the heterolysis of the oxonium compound is taken to mean the reaction : $-C{-}CH_2^+ \longrightarrow -C^+ + H_2O$ and not the reaction involving the splitting of hydrogen.

of *neo*pentyl bromide to give carbonium ions is typical of all primary aliphatic bromides (Dostrovsky and Hughes, *J.*, 1946, 171). From theoretical considerations, involving the operation of the inductive effect, this rate of ionisation of *neo*pentyl compounds should be somewhat higher than that of analogous *n*-alkyl compounds. The same relationship is probably maintained with respect to heterolysis in aqueous media of the oxonium compounds. We conclude, therefore, that the rate of heterolysis of the oxonium compound of *n*-butyl alcohol will be equal to or somewhat smaller than that of *neo*pentyl alcohol. The observed rate constants (Table 1) are not the true constants of the various reactions summarised in schemes (I)—(III) but are composite rate coefficients having the form: $k_{\text{obs.}} = kK[\text{H}^+]$, where K is the equilibrium constant defined by $K = [\text{ROH}_2{}^+]/([\text{ROH}][\text{H}^+])$. Since values of K for the various alcohols are not available, it is difficult to compare the true rate constants for two alcohols in terms of the observed rate constants. However, for the primary alcohols under discussion it is not likely that the values of K differ greatly. It may be expected further than the difference, if any, will be in the direction of a higher value of K for *neo*pentyl alcohol (*i.e.*, this alcohol will be slightly more basic than *n*-butyl alcohol).

TABLE 1. *Rate constants for the exchange and decomposition of* n-*butyl alcohol and* neo*pentyl alcohol in aqueous acid at* 125°.

Alcohol	Normality of sulphuric acid	10^8k (sec.$^{-1}$)	
		Exchange	Decomp.
n-Butyl	0·917	56	16·4
n-Butyl	0·092	7	—
*neo*Pentyl	0·960	1·4	51

Turning now to the data of Table 1 we see that the decomposition of *n*-butyl alcohol is some three times slower than that of *neo*pentyl alcohol, a factor which may be easily accounted for by the expected differences in rates of heterolysis of the oxonium compounds and the values of K. This indicates, not only that the decomposition of *n*-butyl alcohol is a consequence of such an ionisation, but also that the contribution of the reaction of scheme (III), *i.e.*, β-olefin elimination, is negligible. It follows further that the reverse reaction 1′ in scheme (I) cannot be appreciable as compared with reaction 1, or the rate of disappearance of *n*-butyl alcohol would have been much smaller than that of *neo*pentyl alcohol.

The fact that oxygen exchange in *n*-butyl alcohol is faster than the decomposition would mean that at least part of the reaction proceeds by another mechanism, probably the bimolecular one shown in scheme (II). The final decision as to the extent of exchange contributed by (I) and (II) can only be made if more precise information is available regarding the reversibility of the ionisation of the oxonium compound, the first step of scheme (I). To this end we have studied the hydration of [^{14}C]but-1-ene under the conditions of our exchange experiments (Dostrovsky and Klein, to be published). Both but-1-ene and but-2-ene are formed in the acid decomposition of *n*-butyl alcohol but but-2-ene is known to be hydrated solely to *sec.*-butyl alcohol. The composition of the products formed by the hydration of [^{14}C]but-1-ene were determined by examining the radioactivity of the alcohols produced. The radioactive but-1-ene was sealed in tubes together with aqueous sulphuric acid and heated at a temperature and for times identical with those used in the exchange reactions. The analysis of the products of hydration was made by adding both *n*- and *sec.*-butyl alcohol carriers to the mixture after reaction. After elaborate separation and decontamination it was found that the amount of *n*-butyl alcohol formed on hydration of but-1-ene is not more than 1 part in 1000 of the hydrated product. The dehydration of the normal alcohol is, therefore, essentially irreversible. This result is a consequence of the minute proportion of the primary carbonium ion present in equilibrium with the secondary ion and not because of any inherent slowness of the reaction of the first ion with water.

The essential irreversibility of the first step precludes the participation of this mechanism in the oxygen-exchange reaction. We may, therefore, conclude that oxygen exchange proceeds almost entirely by the bimolecular reaction scheme (II).

A check of this conclusion may again be obtained by reference to the results of the oxygen exchange of *neo*pentyl alcohol. Dostrovsky, Hughes, and Ingold (*J.*, 1946, 173) have shown that steric hindrance causes *neo*pentyl compounds to be particularly resistant to bimolecular attack on the α-carbon atom. If oxygen exchange of primary alcohols proceeds by a bimolecular attack on the α-carbon of the oxonium compound we should find that the rate of exchange of *neo*pentyl alcohol is greatly suppressed compared with that of a normal alcohol. Table 1 shows that this is so, *neo*pentyl alcohol exchanging at least 37 times slower than *n*-butyl alcohol, thus supporting the bimolecular mechanism (II). While this depression of the rate of exchange of *neo*pentyl alcohol is considerable, analogy with the corresponding bromides (Dostrovsky and Hughes, *loc. cit.*) would have predicted a much greater effect. It is possible that some of the observed exchange of this alcohol is due to a unimolecular reaction. This point is now being investigated further. Since the reacting entity is the oxonium compound and not the free alcohol the observed rate coefficient is composite and includes the concentration (or, better, the activity) of hydrogen ion and the equilibrium constant for the formation of the oxonium compound.

$$k_{\text{obs.}}(\text{exchange}) = k_2K[\text{H}^+]$$

As the value of the equilibrium constant K is unknown it is impossible to estimate the true bimolecular rate constant k_2. Similarly for the unimolecular ionisation of *neo*pentyl and *n*-butyl oxonium compounds the rate of decomposition of the alcohol is given by $k_{\text{obs.}}(\text{decomp.}) = k_1K[\text{H}^+]$ and here again we cannot find the value of k_1. Therefore the rates of ionisation and of bimolecular reactions of oxonium compounds cannot be compared with the rates of similar reactions of the corresponding bromides and sulphonium compounds.

The conclusions regarding the mechanism of the exchange reaction are applicable to other acid-catalysed reactions in aqueous media. For example, the acid-catalysed formation of *n*-alkyl ethers may now be assumed to proceed by the bimolecular attack of an alcohol molecule on the oxonium compound. From the quantities of ether formed (essentially an irreversible reaction in our conditions) compared with the exchange reaction, it appears that *n*-butyl alcohol is a somewhat more effective nucleophilic reagent than water. An analogous conclusion regarding the relative nucleophilic reactivity of ethanol and water was derived from the study of the solvolytic reactions of the phosphorochloridates (Dostrovsky and Halmann, *J.*, 1953, 505).

The halogenation of alcohols by the halogen acids provides another example. Our results confirm the conclusion of Grunwald and Winstein (*J. Amer. Chem. Soc.*, 1947, **69**, 2051) regarding the mechanism of the bromination of ethyl alcohol by hydrogen bromide, the proof of which has been inconclusive (cf. Ingold, *op. cit.*, p. 340).

EXPERIMENTAL

neo*Pentyl Alcohol.*—Ethyl trimethylacetate (18 g.) in dry ether (60 ml.) was added dropwise to a suspension of lithium aluminium hydride (30 g.) in ether (70 ml.). After the excess of hydride had been decomposed with water–alcohol–ether the solution was poured on ice–sulphuric acid and the *neo*pentyl alcohol was isolated as usual. It was fractionated through a 20-plate column (yield 60%, m. p. 54·9°; purity, estimated from freezing-point depression, better than 99·6%).

neo*Pentyl* [^{18}O]*Alcohol.*—Trimethylacetic acid was allowed to exchange with ^{18}O-enriched water by heating them in a sealed tube to 70° for 5 days with occasional shaking. The enriched acid obtained was esterified with ethyl alcohol, sulphuric acid being used as catalyst. The ester was reduced to the alcohol as described above. The product contained 1·23 mol.% of *neo*pentyl [^{18}O]alcohol.

n-*Butyl* [^{18}O]*Alcohol.*—Sodium *n*-butyl sulphate (38 g.) was added to 10N-sodium hydroxide solution (30 ml.) enriched in ^{18}O. The mixture was refluxed for 2 days in an apparatus arranged for continuous removal of the alcohol–water azeotrope. The azeotrope was saturated with anhydrous potassium carbonate and the alcoholic layer dried and fractionated through a 20-plate column (b. p. 116—117°, 5·62 mol.% of *n*-butyl [^{18}O]alcohol).

sec.-Butyl [^{18}O]alcohol was prepared by the lithium aluminium hydride reduction of ethyl methyl ketone which had previously been allowed to exchange with ^{18}O-enriched water. It had b. p. 99·1—99·5°, 5·3 mol.% of *sec.*-butyl [^{18}O]alcohol.

Exchange Reaction of n-*Butyl Alcohol.*—Portions (55 ml.) of a solution of *n*-butyl alcohol (0·729M) in aqueous sulphuric acid (0·917N) enriched in ^{18}O (2·58 atom %) were vacuum-sealed in glass tubes and placed in an oil thermostat at 125° ± 0·2°. Tubes were withdrawn at intervals, chilled, and opened. The small upper layer (containing about 75% of di-*n*-butyl ether and 25% of *n*-butyl alcohol) was removed and the aqueous layer neutralised with 10N-potassium hydroxide solution enriched to 2·58 atom % with respect to ^{18}O. The solution was fractionally distilled and the azeotrope collected. The upper layer of the distillate was separated and the aqueous layer saturated with potassium carbonate to salt out more alcohol. The combined alcoholic layer was dried (K_2CO_3) and fractionally distilled. When the temperature at the top of the column reached the b. p. of *n*-butyl alcohol the distillation was interrupted and pure *sec.*-butyl alcohol (0·5 ml.) was added to the top of the column and allowed to flow into the flask. The distillation was resumed and continued until the b. p. of the pure normal alcohol was again reached. Separate experiments using *sec.*-butyl [^{18}O]alcohol and *n*-butyl alcohol showed that the fractionation alone left about 0·5% of the secondary alcohol in the *n*-butyl alcohol and after the decontamination with added *sec.*-butyl alcohol no trace of the *sec.*-butyl [^{18}O]alcohol could be detected.

The purified *n*-butyl alcohol was fractionated and the various fractions analysed for ^{18}O by Anbar, Dostrovsky, Klein, and Samuel's procedure (*J.*, 1955, 155). The constancy of the ^{18}O content of the various fractions confirmed the completeness of the decontamination from *sec.*-butyl [^{18}O]alcohol. A typical run is shown in Table 2. The values of N represent mole fractions of labelled alcohol. The rate constant was calculated by the method of least squares.

Decomposition of n-*Butyl Alcohol.*—Solutions of *n*-butyl alcohol in aqueous sulphuric acid were made up as in the previous experiment, except that all materials had normal isotopic compositions and were sealed in tubes. The tubes were placed in the thermostat together with the tubes used in the exchange experiments. After removal from the thermostat the tubes were chilled and opened, and to 50 ml. of the solution was added 0·300 ml. (3·28 mol.) of *n*-butyl [^{18}O]alcohol (5·62 mol. % ^{18}O). The rest of the procedure was identical with that used in the exchange experiments except that the decontamination step with *sec.*-butyl alcohol was omitted. The ^{18}O-content of the resulting butyl alcohol was used in calculating the percentage of the alcohol decomposed, by use of the isotopic dilution formula:

TABLE 2. *Exchange of* ^{18}O *between* n-*butyl alcohol* (0·729M) *and water in the presence of sulphuric acid* (0·917N) *at* 125·0°.

Time (days)	0	2	4	6	8	12	18	18	24	∞
$10^2 N_t$	0·40	1·085	1·76	2·105	2·195	2·825	3·31	3·285	3·54	4·841
$\log (N_\infty - N_0)/(N_\infty - N_t)$	—	0·0725	0·1585	0·1965	0·2250	0·3430	0·4625	0·4555	0·5335	—

$k_{obs.}$ (exchange) = $0·56 \times 10^{-6}$ sec.$^{-1}$.

$$\text{Fraction undecomposed} = f = [(N-N_t)(N_0-N_s)]/[(N_t-N_s)(N-N_0)]$$

where N and N_s are the mole fraction of butyl [^{18}O]alcohol in the tracer and normal *n*-butyl alcohol, and N_t and N_0 are similar quantities measured at times t and 0 respectively. The rate coefficient for the decomposition reaction was calculated, first-order kinetics being assumed, from the equation $kt = 2·303 \log 1/f$. A typical run is shown in Table 3.

TABLE 3. *Decomposition of* n-*bulyl alcohol* (0·729M) *in aqueous sulphuric acid* (0·917N) *at* 125·0°.

$N_s = 0·0020$; $N_\infty = 0·04198$.

Time (days)	0	12	18	24	36
$10^2 N_t$	0·566	0·602	0·669	0·686	0·761
f	—	0·902	0·758	0·728	0·617
$\log 1/f$	—	0·0448	0·1203	0·1379	0·2097

$k = 0·16 \times 10^{-6}$ sec.$^{-1}$ (by least squares).

Exchange Reaction of neo*Pentyl Alcohol.*—Portions (55 ml.) of a solution of *neo*pentyl alcohol (0·242M) in aqueous sulphuric acid (0·960N) enriched in ^{18}O were vacuum-sealed in glass tubes and heated in an oil-thermostat at 125°. At intervals the tubes were withdrawn and treated as described for *n*-butyl alcohol. The crude *neo*pentyl alcohol was purified as follows: Concentrated hydrochloric acid (10 ml.) was added to the dry alcohol and after being thoroughly shaken was allowed to stand. The upper layer (containing mainly *tert.*-pentyl chloride) was removed, the aqueous layer diluted with 2 volumes of water, and the alcohol distilled off. The upper alcoholic layer was dried (K_2CO_3) then fractionally distilled. Several fractions boiling at the same temperature (118°) were collected and analysed for ^{18}O content. The constancy of the isotopic composition of the various fraction indicated the purity of the alcohol.

The efficiency of the purification procedure was tested in the following experiment: *tert.*-Pentyl alcohol (2 ml.) was dissolved in ^{18}O-enriched water (10 ml.; 9·4 atom % $H_2{}^{18}O$) to which concentrated sulphuric acid (0·25 ml.) had been added. The mixture was heated at 55° with frequent shaking for 4 hr; this time is sufficient for the complete exchange of oxygen between *tert.*-pentyl alcohol and water. *neo*Pentyl alcohol (2 g.) was then added and the mixture subjected to the purification described above. In the step involving concentrated hydrochloric acid, material enriched in ^{18}O was used (7 atom % ^{18}O) and the dilution was made with 2·5 atom % $H_2{}^{18}O$. The *neo*pentyl alcohol recovered was analysed and found to contain 0·00023 atom % excess of ^{18}O. The maximum error introduced in the kinetic runs by the purification procedure is, therefore, not more than 3%. A typical exchange run is presented in Table 4. In a duplicate run a value of 1·3 × 10^{-8} sec.$^{-1}$ was obtained.

TABLE 4. *Exchange of* ^{18}O *between* neo*pentyl alcohol* (0·242M) *and water in the presence of sulphuric ocid* (0·960N) *at* 125°.

Time (days)	0	18	30	∞
$10^2 N_t$	0·200	0·253	0·279	2·500
$\log [(N_\infty - N_0)/(N_\infty - N_t)]$	—	0·0101	0·0152	—

$k_{obs.}$ (exchange) = 1·4 × 10^{-8} sec.$^{-1}$.

Decomposition of neo*Pentyl Alcohol.*—The procedure was identical with that described for the exchange reaction, except that materials of normal isotopic composition were used. The amount of undecomposed *neo*pentyl alcohol was determined by the isotopic dilution technique using ^{18}O-labelled *neo*pentyl alcohol. A typical run is shown in Table 5.

TABLE 5. *Decomposition of* neo*pentyl alcohol* (0·242M) *in aqueous sulphuric acid* (0·960N) *at* 125°.

$N_s = 0{\cdot}0020$. $N_\infty = 0{\cdot}01227$.

Time(days)	0	12	18
Tracer added (mg./50 ml.)	433	141	109
$10^2 N_t$	0·371	0·390	0·389
f	—	0·588	0·453
$\log 1/f$	—	0·2306	0·3439

$k_{obs.}$ (decomp.) = 0·51 × 10^{-6} sec.$^{-1}$.

Formation of Ether in the Reactions of n-*Butyl Alcohol.*—The ether layer formed in some of the reaction tubes during the exchange and decomposition runs was separated and weighed. The partition coefficient of *n*-butyl alcohol between di-*n*-butyl ether and aqueous sulphuric was determined in separate experiments to be 5 at room temperature. This value was used in correcting the weight of the ether isolated for dissolved alcohol. The corrected values are: 2·6 mmols. per 50 ml. after 18 days and 3·7 mmols. per 50 ml. after 24 days. A linear increase in ether formation with time being assumed, the approximate rate constant of 6 × 10^{-8} l. mole^{-1} sec.$^{-1}$ was found. Since the rate of exchange under these conditions is about 1 × 10^{-8} l. mole^{-1} sec.$^{-1}$, the ratio of the rate of ether formation to the rate of exchange is about 6.

Composition of Olefin produced in the Reactions of n-*Butyl Alcohol.*—The gas produced in some of the reaction tubes was analysed mass-spectrometrically and found to contain but-1-ene and but-2-ene in the ratio 1 : 10.

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