

822. *Reactions of n-Butene and Butan-2-ol in Dilute Acid. The Elucidation of the Mechanism and the Intermediate in Elimination from Secondary Alcohols and in the Hydration of Olefins.*

By JOOST MANASSEN and FRITZ S. KLEIN.

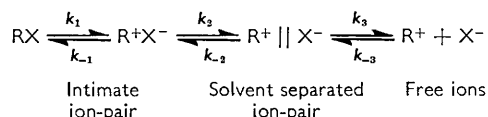
The kinetics of the following competing reactions were studied in aqueous acid at 100° by the isotope dilution method: (1) The conversion of but-1-ene into but-2-ene. (2) The hydration of but-1-ene to butan-2-ol; and by doubly labelling with ¹⁴C and ¹⁸O. (3) The isomerization of [4-¹⁴C]butan-2-ol to its isotopic isomer, [1-¹⁴C]butan-2-ol. (4) The oxygen exchange of butan-2-[¹⁸O]ol with water.

All four reactions could best be explained by a single intermediate which (i) forms but-2-ene by elimination; (ii) combines with solvent to form butan-2-ol; (iii) undergoes reversible elimination to form olefin, whereby the alcohol is isomerized; (iv) is solvolysed reversibly to bring about the oxygen exchange of the alcohol. This intermediate is postulated as a planar carbonium ion, which is partially covalently bound to a water molecule on each side of the plane, the central carbon then being "quinquevalent." This model can best account for the experimental data.

Evidence is presented that the mechanism for the hydration of olefins to secondary alcohols is different from that leading to tertiary alcohols, though the transition state may have some "π-complex character."

HYDRATIONS, dehydrations, and solvolyses are inter-related, yet these three reactions have not been studied under comparable conditions in one system. The considerable work on solvolysis and on olefin-forming eliminations accompanying solvolysis has been reviewed by Ingold.¹ The hydration of olefins has been studied more recently by Taft and his co-workers.^{2,3}

Solvolyses can be classified into those that go by unimolecular (S_N1) or by bimolecular (S_N2) mechanisms. Various criteria have been defined to distinguish between these two mechanisms, but in many reactions these criteria tend to indicate intermediate behaviour. Since the present work represents an example of this type, the existing theories will be briefly indicated. It has been suggested that: (a) Borderline cases are examples of concurrent S_N1 and S_N2 mechanisms and the idea of an intermediate mechanism is rejected. This has been supported recently by Gold.⁴ (b) The solvolysis reaction proceeds by way of ion pairs:



This has been suggested by Winstein and his co-workers in order to explain their results. Substitutions can take place in all three kinds of ion and this may mask many of the criteria earlier used for identification of an ionic mechanism.⁵ (c) S_N1 and S_N2 mechanisms are only the extremes of a whole spectrum of reaction types:⁶ while the group X of the

¹ Ingold, "Structure and Mechanism in Organic Chemistry," Cornell Univ. Press, 1955, Ch. VIII.

² (a) Taft, *J. Amer. Chem. Soc.*, 1952, **74**, 5372; (b) Taft, Lee Purlee, Riesz, and Defazio, *J. Amer. Chem. Soc.*, 1955, **77**, 1584.

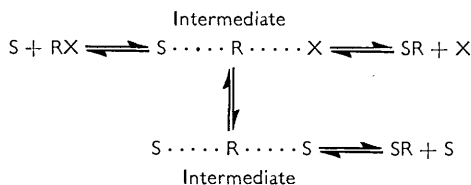
³ Levy, Taft, Aaron, and Hammett, *J. Amer. Chem. Soc.*, 1951, **73**, 3792.

⁴ Gold, *J.*, 1956, 4633.

⁵ Winstein, Clippinger, Fainberg, Heck, and Robinson, *J. Amer. Chem. Soc.*, 1956, **78**, 328.

⁶ (a) Streitwieser, *Chem. Rev.*, 1956, **56**, 571; (b) Dewar, *Ann. Reports*, 1951, **48**, 121.

substrate is leaving, the attacking solvent molecule S approaches, and a metastable intermediate is formed, which can either exchange with the solvent or collapse to form the reagent or the product:

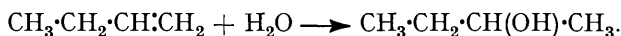


The stronger the bonds between R, S, and X in the intermediate, the more it behaves like the transition state in a classical S_N2 reaction; the looser these bonds, the more it resembles a classical carbonium ion. Several other variations on these theories have been postulated.^{7,8,9,10}

It would be worthwhile to study a chemical system, where these related reactions—hydrations, eliminations, and solvolysis—could be measured simultaneously and to derive a common mechanism connecting them. Such a system was found to be the aqueous acid solution of but-1-ene, but-2-ene, and butan-2-ol. It is well known that both those hydrocarbons are hydrated in hot dilute acid to form butan-2-ol and that under similar conditions the alcohol is dehydrated to an olefin.

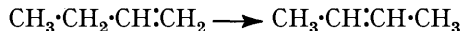
The following reactions were studied in detail:

(1) Hydration of but-1-ene to butan-2-ol:



the formation of [¹⁴C]butan-2-ol from [4-¹⁴C]but-1-ene was measured by the isotopic dilution method; butan-1-ol was present only in negligible amounts.

(2) Conversion of but-1- into -2-ene:



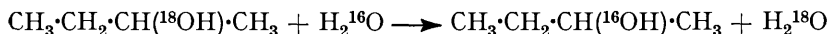
the formation of but-2-ene was followed by gas-chromatography during the hydration of but-1-ene.

(3) Dehydration of butan-2-ol to but-2-ene:



this reaction could be studied by measuring the isomerization rate of [4-¹⁴C]butan-2-ol to [1-¹⁴C]butan-2-ol, where but-2-ene was an intermediate product.

(4) Solvolysis of butan-2-ol. The rate of the oxygen exchange of butan-2-[¹⁸O]ol with water gives a measure of this reaction:



EXPERIMENTAL

Materials.—(1) [4-¹⁴C]But-1-ene was prepared by a slight modification of Regier and Blue's method.¹¹ The butene was purified in a gas-chromatographic column, with a silver nitrate-glycol mixture as solvent.¹² Only ether and methane could be detected as impurities. Yield: 60%, based on methyl iodide.

(2) [4-¹⁴C]Butan-2-ol was prepared from freshly distilled ethyl iodide (3 ml.) mixed with 0.4 mc of [2-¹⁴C]ethyl iodide (from Radiochemical Centre, Amersham) by reaction of the Grignard

⁷ Winstein, Darwish, and Holness, *J. Amer. Chem. Soc.*, 1956, **78**, 2915.

⁸ Huckel and Tomopulos, *Annalen*, 1957, **610**, 78.

⁹ Prévost, *Bull. Soc. chim. France*, 1957, 1489.

¹⁰ Swain and Eddy, *J. Amer. Chem. Soc.*, 1948, **70**, 2989.

¹¹ Regier and Blue, *J. Org. Chem.*, 1949, **14**, 506.

¹² Bednas and Russell, *Canad. J. Chem.*, 1958, **36**, 1272.

reagent with freshly distilled acetaldehyde. The alcohol was purified by gas chromatography at 100° on a tritoyl phosphate column. The purified alcohol contained less than 0.25% of the isotopic isomer [1-¹⁴C]butan-2-ol as shown by the haloform reaction (see below). Yield: 65%, based on ethyl iodide.

(3) Butan-2-[¹⁸O]ol was prepared according to Bunton *et al.*¹³ by exchange between ethyl methyl ketone and H₂¹⁸O and reduction of the ketone by lithium aluminium hydride. The alcohol was purified chromatographically in the same manner as in (2). Yield: 58%, based on the ketone.

(4) *Chromatography of Olefins.*—Most separations of butenes were done on a Burrell Kromotog III apparatus in a 5-m. long 4 mm.-bore copper tube, which had been filled with 50—80 mesh crushed C 22 fire-brick, impregnated by two-fifths of its weight with propylene carbonate. No overlapping of the peaks occurs under these conditions; *cis*- and *trans*-but-2-ene and but-1-ene can be separated at room temperature quantitatively. The flow rate was 25 ml./min. Only the ratios between the different olefins were measured.

(5) *Haloform Reaction.*—The isolation of the methyl carbon next to the hydroxyl group of butan-2-ol was done essentially as described by Roberts *et al.*¹⁴ A reaction time of 3 hr. appeared to be sufficient. If the alcohol consists of a mixture of [4-¹⁴C]- and [1-¹⁴C]-butan-2-ol, only the second alcohol will give rise to radioactivity in the carbon tetrabromide. Only specific activities were measured.

(6) *Radioactivity Measurements.*—The material was combusted according to Wilzbach and Syke's method¹⁵ in a quartz ampoule, and the resulting carbon dioxide introduced into a Geiger counter, which was filled with a 1 : 10 cyclopropane-argon mixture to a pressure of 11 cm. Though the Geiger plateau showed a slope of about 10% per 100 v, no additional purification of the carbon dioxide was undertaken, and the measurements in these circumstances were reproducible within ±2%. The activity measurement was multiplied by the number of carbon atoms in the molecule.

(7) *Tritium and Deuterium Analyses.*—The materials were combusted as described for ¹⁴C analyses. The water was retained instead of the carbon dioxide and reduced in a closed ampoule over zinc dust at 400°. The tritium was measured as hydrogen gas in a Geiger counter under the same conditions as the ¹⁴CO₂, and the deuterium analysed mass-spectrometrically.

(8) ¹⁸O *Measurements.*—These were done essentially as described in ref. 16. The only difference was that the heating time was extended to 24 hr. at 140°.

(9) *Kinetic Measurements.—Hydration experiment.* Into a 65 ml. glass ampoule were run 56 ml. of dilute acid, the contents were frozen by quick immersion in liquid air, and the ampoule was connected to a vacuum line. After degassing, 150 mg. of radioactive butene were distilled in, and the ampoule was sealed. If freezing and warming was done by quick immersion in liquid air and hot water respectively, no breakage of the ampoule occurred owing to expanding ice. The ampoules were shaken six at a time in an aluminium block which was heated thermostatically to 101.4° ± 0.3°.

At various time intervals ampoules were removed and cooled in crushed ice. After immersion in liquid air, they were opened and attached to a vacuum line. By warming with hot water, the olefin which had not reacted could be driven out and sealed into a small ampoule, provided with a break-seal. The liquid phase in the ampoule was neutralized with concentrated sodium hydroxide solution and a fixed amount (2 or 4 ml.) of non-active butan-2-ol was added. After these had been mixed, non-active butene was bubbled through the solution for 5 min. The butanol was then distilled off and dried (K₂CO₃).

(10) *Isomerization-exchange Experiments.*—A typical experiment is described: To 0.555N-perchloric acid (460 ml.) were added 1 ml. of butan-2-[¹⁸O]ol (30 atom % ¹⁸O) and 0.2 ml. of [4-¹⁴C]butan-2-ol (200 μc/ml.), both chromatographically pure. Of this stock solution, 56 ml. were placed in each of eight ampoules identical with those used in the hydration experiments; the contents were frozen, and the ampoules evacuated and sealed. The heating and recovery were done as described under the hydration experiments, except that no olefin had to be recovered here.

(11) *Hydrogen-isotope Experiments.*—These were done with a higher butanol concentration

¹³ (a) Bunton, Konasiewicz, and Llewellyn, *J.*, 1955, 604; (b) Bunton and Llewellyn, *J.*, 1957, 3402.

¹⁴ Roberts, Bennett, and MacMahon, *J. Amer. Chem. Soc.*, 1952, **74**, 4283.

¹⁵ Wilzbach and Sykes, *Science*, 1954, **120**, 494.

¹⁶ Anbar, Dostrovsky, Klein, and Samuel, *J.*, 1955, 155.

(0.7N). Three runs were made: (i) ampoules filled with a solution 0.7N in [4-¹⁴C]butan-2-ol and 0.5N in perchloric acid; (ii) ampoules filled with a solution 0.7N in butan-2-ol and 0.5N in perchloric acid, the total solution having a tritium activity of 16 μc/ml.; (iii) ampoules filled with a solution 0.7N in butan-2-ol and 0.5N in perchloric acid, the total solution containing 9% of deuterium.

The experiments were performed as described under the hydration and isomerization exchange experiments. No extra alcohol-carrier needed to be added, because sufficient alcohol was present in the ampoules. To remove the tritium and the deuterium from the hydroxyl group of the alcohol, it had to be normalized with water, until the water showed no isotope excess.

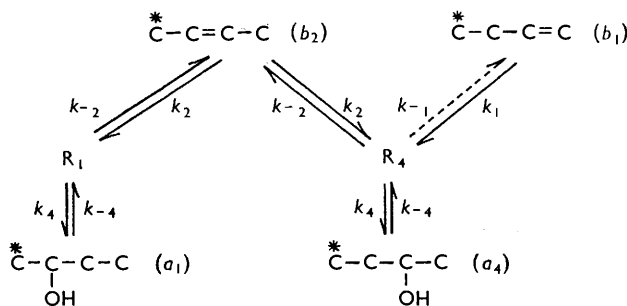
RESULTS

Conversion-Hydration.—[4-¹⁴C]But-1-ene (*b*₁), heated in dilute acid (0.55N) at 100° in a closed vessel, gives the following main reaction products: [4-¹⁴C]but-2-ene (*b*₂) and two isotopic isomers of butan-2-ol, namely, [4-¹⁴C]butan-2-ol (*a*₄) and [1-¹⁴C]butan-2-ol (*a*₁). Fig. 1 shows a scheme with the main reaction steps resulting in these products. The intermediates R₁ and R₄, being isotopic isomers, are as yet undefined. With the aid of the above scheme it is possible (see Appendix I) to derive an expression for the ratio of elimination (*k*₋₂) to substitution (*k*₄) of the proposed intermediate R:

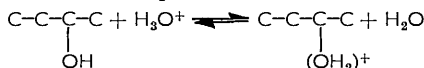
$$k_{-2}/k_4 = \left(\frac{b_2 + 2a_1}{a_4 - a_1} \right)_{\lim t=0} \dots \dots \dots (1)$$

Table 1 gives the results for a typical experiment to measure this ratio. The linear extrapolation of the values of col. 8 to *t* = 0 by the least-mean-squares method, gives the value (see eqn. 1) *k*₋₂/*k*₄ = 0.501 ± 0.008.

FIG. 1. Reaction scheme.



Hydrogen atoms are omitted for simplicity. All rate constants calculated are of first order. The hydrogen-ion and water activities in the appropriate cases are included in these constants. Since the alcohol reagent is actually the alkoxonium ion and not the butanol itself, the rate constants of alcohol reactions contain, in addition, the equilibrium constant of the reaction



and the acidity. Isotope effects of ¹⁸O and ¹⁴C have not been taken into account. To simplify the scheme no distinction has been made between *cis*- and *trans*-but-2-ene (see footnote in Appendix II).

Isomerization.—If [4-¹⁴C]butan-2-ol (*a*₄) is heated in the same acid medium and under similar conditions to those in the hydration of the but-1-ene, the alcohol concentration at first decreases and but-2-ene is produced until the equilibrium between the alcohol and the olefin is established. The alcohol (*a*₄) isomerizes to [1-¹⁴C]butan-2-ol (*a*₁), as shown by the haloform reaction (p. 4205). It is possible now to derive an expression for the rate of isomerization (*k*_{isom}) at olefin-alcohol equilibrium in terms of the rates of the reaction scheme (Fig. 1) (see Appendix II):

$$k_{\text{isom}} = k_{-4}k_{-2}/(k_{-2} + k_4) \dots \dots \dots (2)$$

Table 2 gives the results of a typical experiment.

The alcohol activity (col. 2) decreases during the first three measurements, owing to formation of olefin. After that the activity becomes constant within the accuracy of the measure-

TABLE 1. Hydration of [4-¹⁴C]but-1-ene in 0.555*N*-perchloric acid at 101.4°.

Time (hr.)	Total butan-2-ol	[1- ¹⁴ C]Butan-2-ol (a ₁)	[4- ¹⁴ C]Butan-2-ol (a ₄)	But-1-ene (b ₁)	But-2-ene		$\frac{b_2 + 2a_1}{a_4 - a_1}$
					<i>trans</i> (b ₂)	<i>cis</i>	
1	10.4	0.97	9.43	87.14	0.84	1.62	0.52
2	21.2	2.25	18.95	74.08	1.56	3.15	0.55
3	29.7	3.32	26.38	62.35	2.92	5.02	0.63
4	38.9	5.06	33.84	53.20	3.10	4.80	0.625
5	46.5	6.70	39.80	44.20	4.22	5.05	0.685
6	55.0	8.15	46.85	35.35	4.70	5.45	0.67
7	62.2	9.95	52.25	27.25	5.00	5.50	0.72
8	65.8	11.20	54.60	23.80	5.45	4.90	0.76
9	75.1	13.80	61.30	15.70	4.85	4.35	0.775
10	78.5	14.90	63.60	12.95	4.55	3.95	0.79
11	81.0	15.95	65.05	10.68	4.60	3.75	0.82
12	83.0	17.40	65.60	8.65	4.90	3.40	0.90

Cols. 2—7 are expressed as percentages of the initial quantity of but-1-ene. Col. 2 is calculated from the specific activity of the alcohol and of the initial but-1-ene. Cols. 3 and 4 are calculated from col. 2 and the ratio of activities of CBr₄ to alcohol. Col. 5 is calculated by subtracting the total of alcohol and but-2-ene from 100%. Cols. 6 and 7 are calculated from col. 5 and the gas-chromatographic results. Col. 8 is calculated from cols. 2, 3, 6, and 7.

TABLE 2. Isomerization and ¹⁸O-exchange of [4-¹⁴C]butan-2-[¹⁸O]ol at 101.4° in 0.555*N*-perchloric acid.

Time (hr.)	Total alcohol (counts/min.)	CBr ₄ (counts/min.)	¹⁸ O-excess (%)	Time (hr.)	Total alcohol (counts/min.)	CBr ₄ (counts/min.)	¹⁸ O-excess (%)
12	11,100	925	1.41	47.5	10,500	3150	0.595
23	11,000	1715	1.09	59	10,500	3600	0.405
				71	10,700	3900	0.283

The numbers in col. 2 and 6 are corrected for the fact that the alcohol contains four carbon atoms (p. 4205).

ment and the alcohol-olefin equilibrium is established. Thus only the last four experimental values were used for calculation of the rate constant:

$$k_{\text{isom}} = 5.18 \pm 0.12 \times 10^{-6} \text{ sec.}^{-1}$$

Oxygen Exchange.—By doubly labelling butan-2-ol with ¹⁸O and ¹⁴C it was possible to measure the oxygen exchange with water and the isomerization to its isotopic isomer at the same time under identical conditions. Table 2 also gives the results of a typical exchange experiment. From the first-order decrease of the ¹⁸O concentration, as given in col. 4 and 8, the rate constant

$$k_{\text{exch}} = 7.49 \pm 0.155 \times 10^{-6} \text{ sec.}^{-1}$$

was calculated. Analogously to the method of Grunwald, Heller, and Klein¹⁷ (see Appendix III) the rate of exchange (*k*_{exch}) can be expressed as

$$k_{\text{exch}} = k_{-4}(1 - 1/n) \dots \dots \dots (3)$$

where *n* is the number of solvent water molecules attached to the reaction intermediate (R₁ or R₄) in nearest-neighbour sites.

Combining equations (1), (2), and (3) and introducing the results of Tables 1 and 2, we find

$$n = 1 / \left(1 - \frac{k_{\text{exch}}}{k_{\text{isom}}} \cdot \frac{1}{1 + k_{-2}/k_4} \right) = 1.93 \pm 0.11$$

This result means that the number of water molecules in nearest-neighbour sites to the reaction intermediate is 2; *i.e.*, the intermediate common to the four reactions described above, as postulated in the scheme Fig. 1, is found to be bound to two water molecules.

¹⁷ Grunwald, Heller, and Klein, *J.*, 1957 2604

In calculating the rate of alcohol isomerization, k_{isom} , this reaction was assumed to go only by way of reversible olefin formation. However, we cannot at first exclude the possibility of an isomerization by the following alternative reactions: (1) Isomerization of the intermediate R without the intervention of the olefin; (2) direct isomerization of the alkoxonium ion, with neighbouring-group assistance. Both types of isomerization are not frequently encountered in systems of the type in question,^{6a} and, if found,¹⁴ they account for only a few units % of the total reaction.

In our calculations of k_{isom} , the inclusion of a direct isomerization of the intermediate ions R_1 and R_4 could not affect the final result for the number of water molecules in nearest neighbour sites. It can easily be shown that the effect of this inclusion on the ratio k_{-2}/k_4 (eqn. 1) cancels exactly the effect on the rate constant of the isomerization (eqn. 2), and the rate of oxygen exchange k_{exch} (eqn. 3) will not be affected at all.

The second alternative of direct alkoxonium isomerization would be in contradiction with the results of Bunton *et al.*¹³ (see p. 4209).

In order further to elucidate the mechanism of the isomerization of butan-2-ol, the following considerations led to the measurement of the hydrogen exchange of butan-2-ol with solvent, which showed a hydrogen-isotope effect in the hydration of but-2-ene (see p. 4210).

Isomerization by either mechanism (1) or (2) will be accompanied by a hydrogen-shift from $C_{(3)}$ to $C_{(2)}$. It has been shown¹⁸ that in shifts like these no hydrogen exchange with the solvent takes place. If, on the other hand, the alcohol isomerization occurs by way of the olefin, every isomerization will give rise to hydrogen exchange with the solvent. So the isomerization of [4-¹⁴C]butan-2-ol was compared kinetically with the hydrogen-isotope exchange of butan-2-ol under identical conditions in tritium- and deuterium-containing solvents (see p. 4205). The results are given in Table 3.

TABLE 3. Results of butanol-isomerization measurements in hydrogen-, deuterium-, and tritium-containing solvents.

Time (hr.)	Alcohol isomerized (%)	Tritium exchanged $\times 0.5$ (%)	Deuterium exchanged $\times 0.5$ (%)
24	8.2	1.5	3
48	17.0	3.0	5.9
72	22.5	—	8.9

Col. 2 is calculated by comparing carbon tetrabromide activity with the total alcohol activity. The results of cols. 3 and 4 were corrected by a factor 2, since but-2-ene on hydration has equal chances to form both $*C-C(OH)-CT-C$ and $*C-CT-C(OH)-C$ (other H atoms omitted).

The difference between the deuterium and the tritium experiments shows an appreciable isotope effect, which can be calculated as follows:

$$\text{Ratio between the numbers of cols. 2 and 3 gives } k_{\text{isom}}/k_T = 5.7$$

$$\text{Ratio between the numbers of cols. 2 and 4 gives } k_{\text{isom}}/k_D = 2.7$$

These results show clearly that hydrogen exchange takes place; the ratio of deuterium- to tritium-isotope effect is of the expected magnitude and no evidence for isomerization by either mechanism (1) or (2) can be found in these experiments. Further experiments on the hydrogen-isotope effect are in progress.

DISCUSSION

Summarizing the above results, we found that the ratio of elimination to substitution of the intermediate R is $k_{-2}/k_4 = 0.501$, and that, from the measured rates of alcohol isomerization (k_{isom}) and of ¹⁸O exchange (k_{exch}), the number n of water molecules in nearest-neighbour sites to the proposed reaction intermediate is 2.

The various reaction mechanisms to be considered are: a common carbonium-ion intermediate, different intermediates for each reaction, no intermediate at all, or a mixture of any of the above (such as concurrent unimolecular and bimolecular reactions). From the reaction scheme (Fig. 1), the only postulate to fit all experimental facts is a common reaction intermediate with two molecules of water in nearest-neighbour sites.

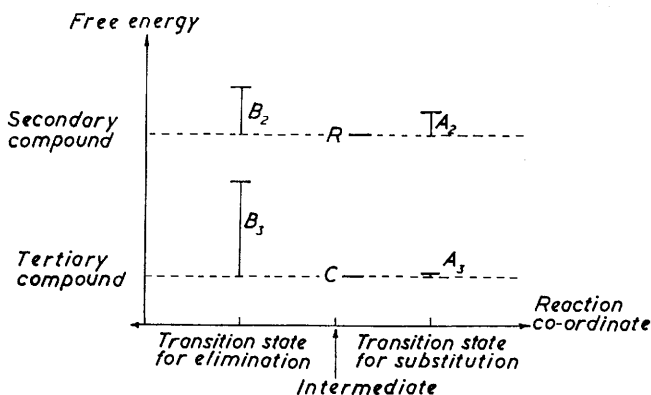
¹⁸ Cannell and Taft, *J. Amer. Chem. Soc.*, 1956, **78**, 5812.

In order to decide on the configuration of the intermediate and on the type of bonding between the water molecules and the carbon skeleton, the measured value of the elimination to substitution ratio k_2/k_4 (eqn. 1) has to be considered. The bonds, it will be shown in the following, are of a covalent character and thus the intermediate is not a typical free-carbonium ion.

Levy *et al.*¹⁹ found that on hydration of 2-methylbut-1- or -2-ene no interconversion of the olefins, but only formation of alcohol is observed. This shows that the elimination to substitution ratio for the intermediate—a carbonium ion in this reaction—is much smaller than that in the hydration of but-1-ene, where interconversion has been observed. More recent measurements by Boyd²⁰ show that the order of magnitude for the elimination to substitution ratio for the tertiary pentyl system is the same as that for the tertiary butyl system. From the values given for the latter system by Dostrovsky and Klein,²¹ one calculates that the elimination to substitution ratio for the tertiary butyl ion at 100° and in 0.555*N*-acid is 0.08. This result is appreciably smaller than the experimental value found in the present work for the secondary butyl intermediate.

It has been shown by Ingold¹ that secondary carbonium ions should have a smaller elimination to substitution ratio than their "methyl-substituted" tertiary carbonium

FIG. 2.



ions. This was confirmed by experiment. Since in our experiments we find a higher elimination to substitution ratio, we conclude that the mechanism for the secondary butyl compound is different from that of the tertiary pentyl compound, and therefore does not involve a free carbonium ion as intermediate.

Calculating the free energies of formation for the carbonium ions in question, Moiseev and Syrkin²² have pointed out that, while the assumption of a carbonium ion for the hydration to tertiary compounds can be considered possible, this would lead in the case of secondary compounds to activation energies which are not in accordance with experimental results. This leads us to the assumption of an intermediate mechanism similar to those discussed by Doering and Zeiss,²³ Dewar,^{6b} and Streitweiser.^{6a} Here the two water molecules are attached symmetrically to each side of the plane of the carbon skeleton, and the bonds between the water molecules and the central carbon atom in the reactive intermediate are of a partially covalent character. Bunton *et al.*¹³ found that the rate of racemization of optically active butan-2-ol is twice its rate of ¹⁸O exchange with water; each act of exchange therefore is accompanied by an inversion of configuration. This fact points to the symmetrical position of the two water molecules.

¹⁹ Levy, Taft, and Hammett, *J. Amer. Chem. Soc.*, 1953, **75**, 1253.

²⁰ Boyd, Thesis, 1959, Pennsylvania State University, U.S.A.

²¹ Dostrovsky and Klein, *J.*, 1955, 791.

²² Moiseev and Syrkin, *Doklady Akad. Nauk U.S.S.R.*, 1957, **115**, 541.

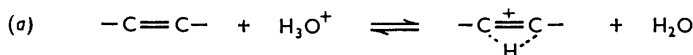
²³ Doering and Zeiss, *J. Amer. Chem. Soc.*, 1953, **75**, 4733.

The relative free energies and the respective energies of activation for the secondary intermediate compared to a tertiary carbonium ion are indicated in Fig. 2. The tertiary carbonium ion C is more stable than the secondary intermediate R . The formation of tertiary alcohol is brought about by the combination of an ion and a polar molecule, which is considered²⁴ to need almost no energy of activation A_3 . The formation of the secondary alcohol is a unimolecular decomposition of the symmetrical intermediate, which can be considered to need some energy of activation A_2 . This will tend to make A_2 greater than A_3 .

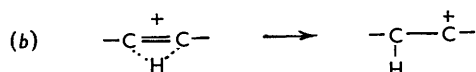
The elimination of the tertiary ion will, since water is not covalently bonded in the transition state,^{2,3} be a unimolecular elimination of a proton from the ion. The elimination of a proton from the secondary intermediate can, however, be expected to receive some help from the neighbouring water molecule (see inset). This would lower the activation energy B_2 for the latter process, which can be expressed as $B_2 < B_3$, the activation energy of the tertiary carbonium ion to the elimination transition state. Both conditions, $A_2 > A_3$ and $B_2 < B_3$, tend to give a greater elimination to substitution ratio for the secondary intermediate than for the tertiary ion, as was borne out by the experiment. This gives support to our assumption of covalently bonded water molecules.

A further argument for this difference in mechanisms is the active part the water plays in the elimination of the secondary intermediate and, by the rule of microscopic reversibility, in the transition state of the hydration step as well. This is also shown by the absence of π -complexing in the solubility studies of ethylene and propene.²⁵

The relatively high deuterium- and tritium-isotope effects found in our experiments (Table 3) lend further support to the suggested mechanism and the hydration transition state for the secondary compound discussed above. Taft *et al.*²⁶ found only a small isotope effect (either positive or negative) in the hydration of olefins to tertiary alcohols. To explain a transition state without covalently bonded water in the hydration of olefin, they suggest the preliminary formation of a π -complex:

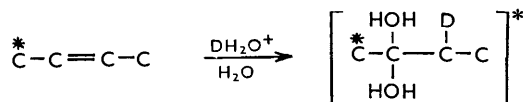


followed by a rate-determining rearrangement to a carbonium ion:



The small observed isotope effect is the result of compensating opposing effects in reactions (a) and (b).

For the hydration leading to secondary alcohol, as in our case, no pre-equilibrium has to be assumed, and only the step where the C-H bond is formed has to be considered for the isotope effect:



This is the rate-determining step in the hydration of the olefin.

Some indication of the structure of the transition state in the hydration reaction of but-2-ene (above) (*i.e.*, the transition state in the elimination reaction of the secondary intermediate) may also be derived from the fact that the thermodynamically less stable *cis*-but-2-ene is formed in preference to the *trans*-isomer on elimination of the intermediate

²⁴ Franklin, *Trans. Faraday Soc.*, 1952, **48**, 443.

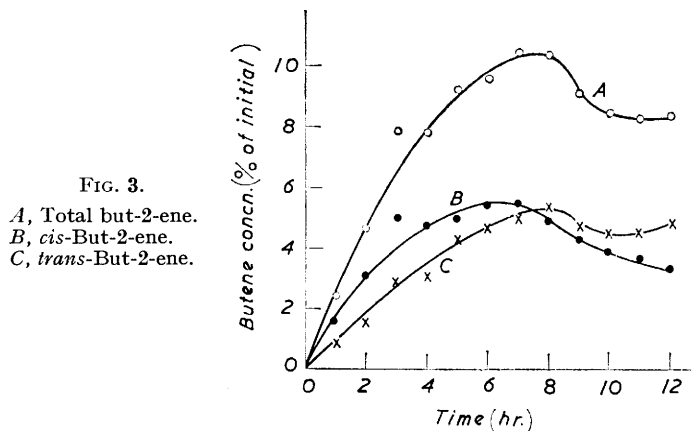
²⁵ Lee Purlee and Taft, *J. Amer. Chem. Soc.*, 1956, **78**, 5811.

²⁶ Lee Purlee and Taft, *J. Amer. Chem. Soc.*, 1956, **78**, 5807.

(see Fig. 3). A similar result was reported for the interconversion of normal butene on an acidic heterogeneous catalyst.^{27*}

If a mixture of *cis*- and *trans*-but-2-ene is separated on a chromatographic column, which contains as solvent a saturated solution of silver nitrate in ethylene glycol,¹² the *trans*-butene emerges appreciably earlier than the *cis*-butene. Since the glycol alone does not cause this separation, the silver ion is considered responsible by the formation of a π -complex with the double bond. The fact that the *trans*-butene emerges from the column earlier than means that its π -complex with silver is less stable than that of silver with *cis*-butene. If the transition state in the elimination reaction of the butene intermediate resembles a π -complex between butene and hydroxonium ion, a parallel with the silver complexes could be drawn. The transition state for the *cis*-butene would then be more stable than for the *trans*-butene, resulting in a greater formation rate for the former.

By comparing rates of conversion, hydration, isomerization, and oxygen exchange in an aliphatic system of interrelated olefins and alcohols, we have thus been able to describe a



common mechanism, similar to "the merged bimolecular displacement and elimination," as observed by Winstein *et al.*⁷ in an alicyclic system. This mechanism connects all observed reactions by a single type of a "quinquevalent" carbonium-solvent complex

APPENDIX I

From reaction scheme (Fig. 1) one can derive:

$$(1) \quad db_2/dt = k_{-2}(R_1 + R_4) - 2k_2b_2$$

$$(2) \quad da_4/dt = k_4R_4 - k_{-4}a_4$$

$$(3) \quad da_1/dt = k_4R_1 - k_{-4}a_1$$

Assuming stationary-state conditions for R_1 and R_4 we have

$$R_1 = (k_2b_2 + k_{-4}a_1)/(k_{-2} + k_4) \quad R_4 = (k_2b_2 + k_{-4}a_4 + k_1b_1)/(k_{-2} + k_4)$$

Combination of eqns. (1) and (3) and substitution for R_1 and R_4 gives

$$(4) \quad d(b_2 + 2a_1)/dt = [k_{-2}k_1b_1 + k_{-2}k_{-4}(a_4 - a_1)]/(k_{-2} + k_4)$$

* Note added in proof. The same preferential *cis*-but-2-ene formation in concentrated phosphoric acid and on a solid catalyst has been observed by Waag and Pines (Abs. 135th Meeting Amer. Chem. Society, Boston, Mass., April, 1959, 18 Q), and an identical explanation was given [personal communication].

²⁷ Lucchesi, Baeder, and Longwell, *J. Amer. Chem. Soc.*, 1959, **81**, 3235.

and from eqns. (2) and (3):

$$(5) \quad d(a_4 - a_1)/dt = [k_4 k_1 b_1 - k_{-2} k_{-4} (a_4 - a_1)] / (k_{-2} + k_4)$$

Combination of (4) and (5) gives

$$(6) \quad d(b_2 + 2a_1)/d(a_4 - a_1) = [k_{-2} + k_{-2} k_{-4} (a_4 - a_1) / k_1 b_1] / [k_4 - k_{-2} k_{-4} (a_4 - a_1) / k_1 b_1]$$

At $t = 0$, where a_1 and $a_4 = 0$, by Hopital's rule,

$$[F(t)/G(t)]_{t=0} = [dF(t)/dt / dG(t)/dt]_{t=0},$$

equation (6) becomes

$$\left[\frac{d(b_2 + 2a_1)}{d(a_4 - a_1)} \right]_{t=0} = \left(\frac{b_2 + 2a_1}{a_4 - a_1} \right)_{t=0} = \frac{k_{-2}}{k_4}$$

In most of the calculations k_{-1} was neglected, because of its small value. Accurate calculations including k_{-1} show that it affects results only to a negligible extent, if it does not cancel out entirely.

APPENDIX II

From Fig. 1 we define the rate of formation of [$4\text{-}^{14}\text{C}$]butan-2-ol as (3); after the but-2-ene (b_2) * reaches equilibrium concentration $db_2/dt = 0$,

$$(b_2)_e = k_{-2}(R_1 + R_4) / 2k_2$$

Using the expressions for R_1 and R_4 of Appendix I, b_1 in the present experiment being zero, we find

$$(b_2)_e = k_{-2} k_{-4} (a_1 + a_4) / 2k_2 k_4$$

substituting R_1 and $(b_2)_e$ in eqn. (3) and rearranging, we have

$$(7) \quad \frac{da_1}{dt} = \frac{k_{-4} \cdot k_2}{k_{-2} + k_4} \cdot \frac{a_4 - a_1}{2} = \frac{k_{-4} \cdot k_{-2}}{k_{-2} + k_4} \cdot \left(\frac{a_0}{2} - a_1 \right)$$

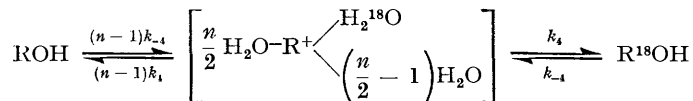
$a_0 = a_1 + a_4$, a_0 being corrected for equilibrium olefin content.

Since the experimental rate of isomerization of alcohol is given by the equation $da_1/dt = k_{\text{isom}}(\frac{1}{2}a_0 - a_1)$ one obtains for the rate constant of isomerization

$$k_{\text{isom}} = k_{-4} k_{-2} / (k_{-2} + k_4)$$

APPENDIX III

Analogously to Fig. 1 and ref. 17, we write the scheme for the oxygen-isotope exchange with n nearest-neighbour site solvent molecules:



isotope effects being neglected. Assuming isotope tracer concentrations, $\text{R}^{18}\text{OH} = a^*$, $\text{H}_2^{18}\text{O} = w^*$, and R = concentration of intermediate, including the alcohol-oxonium and acidity in k_{-4} , we derive:

$$-da^*/dt = k_{-4}a^* - k_4R$$

$$dR/dt = k_{-4}[a^* + (n-1)\text{ROH } w^*/\text{H}_2\text{O}] - nk_4R$$

* $(b_2)_e$ is the sum of the equilibrium concentrations of *cis*- and *trans*-butene; k_{-2} is the sum of the dehydration rates forming these olefins, and k_2 is the rate of hydration at butene equilibrium:

$$k_2 = (k_{2\text{trans}}b_{2\text{trans}} + k_{2\text{cis}}b_{2\text{cis}}) / (b_2)_e$$

It can easily be shown that the above simplified notation does not introduce any approximations in the final result.

At steady state of R , $dR/dt = 0$, hence

$$k_4 R = \frac{k_{-4}}{n} \left[a^* + (n-1) \frac{\text{ROH}}{\text{H}_2\text{O}} w^* \right]$$

since at isotope equilibrium: $w_\infty^*/\text{H}_2\text{O} = a_\infty^*/\text{ROH}$ and $w^* + a^* = w_\infty^* + a_\infty^* = \text{const.}$

$$\begin{aligned} \frac{-da^*}{dt} &= k_{-4} a^* - \frac{k_{-4}}{n} \left[a^* + (n-1) \frac{\text{ROH}}{\text{H}_2\text{O}} w^* \right] \\ (8) \qquad &= k_{-4} \left(1 - \frac{1}{n} \right) \frac{\text{ROH} + \text{H}_2\text{O}}{\text{H}_2\text{O}} (a^* - a_\infty^*) \end{aligned}$$

we find

$$k_{\text{exch}} = k_{-4} (1 - 1/n)$$

Eqn. (8) in its integrated form was used for the evaluation of the exchange data.

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