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Studies on the Mechanism of Olefin–Alcohol Interconversion. The Effect of Acidity on the O^{18} Exchange and Dehydration Rates of *t*-Alcohols

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Evidence from the acidity and temperature dependence of the rates of O^{18} exchange and dehydration of *t*-alcohols has been obtained which indicates that these two reactions proceed by common initial steps but involve different rate-determining steps. The results appear to eliminate a mechanism in which a "free" carbonium ion isomerizes to a π-complex in the rate-determining step of the alcohol–olefin interconversion. However, present results are found to be consistent with mechanisms which involve (in the formation of olefin from alcohol) either a rate-determining reaction of a free carbonium ion with water or the isomerization of an encumbered carbonium ion intermediate, $R^+\ldots OH_2$, to a π-complex. The encumbered carbonium ion classification is proposed for intermediates which possess substantial carbonium ion character and involve measurable interactions between the cationic center and leaving or entering groups of either neutral or various charge types. The mechanism involving the encumbered carbonium ion intermediate is favored.

The effect of acidity in moderately concentrated aqueous mineral acid solutions on the O^{18} exchange rate of *t*-butyl alcohol and the dehydration rate of *t*-amyl alcohol has been determined to provide additional information on the mechanism of carbinol–olefin interconversion.

Dostrovsky and Klein have recently shown that the rate constant for the O^{18} exchange of *t*-butyl alcohol with 0.45 M H_2SO_4 acid at 55° is 27 times greater than the rate constant for the formation of isobutylene from *t*-butyl alcohol under the same conditions.[3] Provided that the mechanism of O^{18} exchange proceeds by a reaction sequence which is common to that of the carbinol–olefin interconversion, this result demonstrates (as indicated by the previous authors) the existence of a reactive intermediate preceding the rate-determining step in the elimination reaction to form olefin.[4] The present study of the effects of acidity and carbinol structure on the rates of the O^{18} exchange and carbinol dehydration reactions has been made to obtain more rigorous evidence for the assumed common reaction sequence.

The present work provides evidence that the mechanisms of the O^{18} exchange and the carbinol dehydration reactions involve common initial steps but have different rate-determining steps. Evidence based upon the effect of carbinol structure on these two reactions will be presented in a subquent paper.

Experimental

Materials.—*t*-Butyl alcohol was Eastman Kodak Co. white label. Distillation from CaH_2 gave b.p. 81.2°, $n^{26.5}_{\mathrm{D}}$ 1.3840. Similar treatment of Fisher *t*-amyl alcohol gave n^{25}_{D} 1.4032. The oxygen-18 water was approximately 1.4 atom per cent., obtained from Stuart Oxygen Co. All mineral acids were Baker C.P. Reagent Grade and were used without further purification.

O^{18} Analysis. The method of Anbar, Dostrovsky, Klein and Samuel[5] was used. It was found desirable to modify the procedure of these authors for removing olefin from the exchanged CO_2. The following procedure was developed.

Into a glass ampoule were placed 100 λ of the purified alcohol to be analyzed, 1 mg. of sulfuric acid and 0.065 mmole of carbon dioxide. The contents were degassed and the ampoule sealed under vacuum, then heated as indicated by the above authors.[5] The carbon dioxide sample was collected by breaking the ampoule inside a tube attached to a vacuum manifold. and then distilling the carbon dioxide from a Dry Ice-bath into a trap designed to introduce gaseous samples into a gas chromatography column. The carbon dioxide was purified (olefin and other gaseous impurities removed) by passing it through a 2-meter gas-phase chromatographic column packed with 30% by weight of Dow-Corning 702 or GE-SF96 silicone oil on C-22 firebrick. This purification proved to be essential in order to obtain precise results with the relatively small oxygen-18 enrichments employed in the present work. At a flow rate of 30 cc./min. of carbon dioxide-free helium and at room temperature, the sample of carbon dioxide appeared in about 2 minutes and was trapped by a liquid nitrogen-bath. The olefin peak appeared in 5 to 20 minutes, depending on the carbinol involved. The carbon dioxide was then analyzed by a mass spectrometer for the 44 to 46 ratio. Duplicate analyses generally agreed to within 2%.

The following experiments were conducted to show that no oxygen-18 exchange occurred when the carbon dioxide was passed through the gas-phase chromatographic column. A sample of pure O^{18}-enriched carbon dioxide was swept through the column and the effluent gas trapped with a liquid nitrogen bath. The oxygen-18 content of this sample was the same, within experimental error, as that of the original sample. A sample containing a normal abundance of oxygen-18 was passed through the column immediately after the one of higher oxygen-18 content. The analysis of the former sample showed normal abundance of oxygen-18. This demonstrated that there was no "hold-up" of carbon dioxide on the column.

Kinetic Procedure.—The reaction mixture was prepared by pipeting 25 ml. of an acid solution containing oxygen-18 water into a 50-ml. heavy-walled erlenmeyer flask and placing the flask into a thermostat at the desired temperature. After this solution had reached the bath temperature a weighed amount of alcohol was added by means of a small beaker placed directly into the flask. After waiting several minutes with the flask immersed in the bath, the reaction was started by tipping over the small beaker and

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(1) This work was supported in part by the Office of Naval Research and carried out in part under the auspices of the United States Atomic Energy Commission.

(2) Eastman Kodak Predoctoral Fellow for 1956–1957.

(3) I. Dostrovsky and F. S. Klein, *J. Chem. Soc.*, 791 (1955); (b) 4401 (1955).

(4) In the present paper the term, rate-determining step, is used to designate that step in the reaction mechanism for which the rate of material transfer is the slowest. In other words, the rate-determining step is that step which has the slowest instantaneous rate of reaction *of the reactants of the step*. Although the term rate-determining step is frequently used explicitly or by implication in this sense, the usage is by no means universal. For example, Dostrovsky and Klein (ref. 3) use the designation to indicate the step with the slowest rate constant (as indicated by Prof. Dostrovsky in a personal communication). We prefer our usage of the term rate-determining step, since the principle of microscopic reversibility is immediately applicable. By this principle, the bottle-neck step for material transfer (which we designate as the rate-determining step) must be the same for the over-all forward and reverse reactions. The point of maximum standard free energy along the reaction coördinate (*the* transition state for the process) is clearly delineated by this usage.

(5) M. Anbar, I. Dostrovsky, F. Klein and D. Samuel, *J. Chem. Soc.*, 155 (1955).

shaking the flask vigorously to ensure complete mixing. In the case of the slower runs (greater than 1 day) prior thermostating of the solution was unnecessary. The acid solutions were prepared with a weighed quantity of reagent grade concentrated acid and sufficient enriched water to bring the solution to the correct volume. The enrichment of the acid solution was in the vicinity of one atom per cent. of oxygen-18. The alcohol concentrations employed were about 0.5 *M*.

The reaction was stopped by removing the flask from the thermostat and immediately plunging it into a Dry Ice-acetone-bath accompanied by rapid agitation. Neutralization of the acid was accomplished by bubbling ammonia gas into the solution while stirring rapidly, using extreme care to keep the temperature below −10°. Toward the completion of the neutralization, the formation of a frozen salt solution made this inconvenient, and the temperature was allowed to approach zero. For reactions done at greater than 40°, the temperature during neutralization was held below zero. If the ammonium sulfate formed was not sufficient to yield the saturated solution necessary to salt out the alcohol, reagent grade ammonium sulfate was added slowly with stirring until a saturated solution was obtained. The alcohol layered out of the saturated salt solution and was collected with a fine capillary pipet. It was dried over several charges of potassium carbonate and distilled from calcium hydride, a procedure which removed all detectable amounts of oxygen-18 enriched water. The 0.2 to 0.5 ml. of alcohol collected was then analyzed as described above.

In all of the experiments with *t*-butyl alcohol the elimination rate to form olefin was very small compared to the exchange rate so that the amount of exchange occurring through the recombination of the liberated olefin with enriched water during the first two half-times of exchange (upon which the rate constants were based) was so small that this correction was less than experimental error. It was also unnecessary to make a correction for oxygen exchange between water and sulfuric acid. The exchange rate of sulfuric acid is accurately known under all of the conditions employed and it is negligible compared to the rate of oxygen exchange of *t*-butyl alcohol.[6]

In all oxygen-18 experiments the temperature was controlled to ±0.02° and was measured by a thermometer calibrated by the Bureau of Standards. The times were measured to ±0.15 minute.

Kinetic Analysis.—The oxygen exchange reaction is one of the general type $MA + A^* \rightleftarrows MA^* + A$, and accordingly follows the first-order law[7,8]

$$\ln\left(\frac{A_\infty - A_0}{A_\infty - A}\right) = kt \qquad (1)$$

where

A_0 = normal abundance of oxygen-18

A_∞ = oxygen-18 content of alcohol at equil. with respect to exchange

A = oxygen-18 content of alcohol at time t

Accurate evaluations of the terms $(A_\infty - A_0)$ and $(A_\infty - A)$ are obtained from the results of the mass spectrometric analysis of carbon dioxide (obtained as described above). The atom fraction, n, of oxygen-18 in a carbon dioxide sample is given by the expression

$$n = \frac{r}{2(r + 1)}$$

where r is the 46/44 mass ratio.

The oxygen-18 content of the alcohol is calculated assuming a statistical distribution of oxygen-18 among the species in the heated ampule, which is represented by the expression

$$(A - A_0) = \frac{(n - n_0)(m_1 + m_2 + m_3)}{m_1} \qquad (2)$$

Where

$(A - A_0)$ = atom fraction of excess oxygen-18 in the alcohol

n = atom fraction of oxygen-18 in the carbon dioxide

n_0 = normal abundance of oxygen-18 in the alcohol determined by analyzing unreacted alcohol

m_1 = equivalents of oxygen in the alcohol

m_2 = equivalents of oxygen in the carbon dioxide

m_3 = equivalents of oxygen in the sulfuric acid

The validity of this equation has been demonstrated by Anbar, Dostrovsky, Klein and Samuel.[5]

To obtain an accurate value of $(A_\infty - A_0)$, *t*-butyl alcohol was allowed to react for longer than ten half-times and analysis was then carried out as described. In general, an accurate value of $(A_\infty - A_0)$ may be difficult to determine directly, especially if the exchange reaction is inconveniently slow or if side reactions assume major proportions.

The equilibrium oxygen-18 content of the alcohol can be obtained, however, in another fashion.[7] The amount of isotope appearing in the alcohol will be proportional to the ratio of oxygen atoms that are heavy to those that are normal in the water, assuming no isotope effect.[8] A simple extension of this implies that at the exchange equilibrium the ratio of oxygen-18 to oxygen-16 in the alcohol will be equal to the ratio of oxygen-18 to oxygen-16 in the water (again assuming a statistical distribution of the isotopes). It is known that a completely statistical distribution is not usually the case, but that the heavier isotope tends to concentrate to a small degree in the heavier molecule. If it is assumed that dilution of oxygen-18 in the water by the exchange reaction is negligible, the value of A_∞ can be calculated from the oxygen-18 content of the water in the original acid solution. Since the ratio of the moles of alcohol to moles of water was of the order of 10^{-2}, this assumption is not in error by more than 1%. The oxygen-18 content of the water in the acid solution was determined by shaking a small sample of the water with carbon dioxide for about 12 hours, and then analyzing the carbon dioxide in the mass spectrometer.

The oxygen-18 content of the aqueous acid solution was calculated using the expression

$$(W - W_0) = \frac{(n - n_0)(m_4 + m_2)}{m_4}$$

where

$(W - W_0)$ = atom fraction of excess oxygen-18 in the water

$(n - n_0)$ = atom fraction of excess oxygen-18 in the analyzed carbon dioxide

m_4 = equivalents of oxygen in the water

m_2 = equivalents of oxygen in the carbon dioxide

t-Butyl alcohol with its relatively rapid exchange rate and much slower elimination rate (*ca.* 1/50 the exchange rate) provided a good opportunity of checking both methods of obtaining the equilibrium oxygen-18 content.

In Table I are listed the "infinity" values calculated by both methods and the percentage difference. The value of $(W - W_0)$ was divided by 1.01 to compensate for the 1% dilution of the oxygen-18 by the alcohol, and the resulting number is labeled $(W - W_0)_\infty$.

TABLE I

COMPARISON OF INFINITY VALUES FOR *t*-BUTYL ALCOHOL AT 25.0°

Number of half-times	$(A_\infty - A_0)$	$(W - W_0)_\infty$	Difference, %
11.7[a]	0.01324	0.01333	0.7
30.5[b]	0.01301	0.01299	0.2

[a] 3.00 *M* sulfuric acid. [b] 4.00 *M* sulfuric acid.

As shown in Table I, the agreement between the two methods is within experimental error (2%). Consequently, the equation which has been used in all subsequent work to calculate the rate constant for oxygen exchange (hereafter labeled k_{ex}) is the following modification of eq. 1

$$k_{ex} = \frac{1}{t}\ln\left[\frac{(W - W_0)_\infty}{(W - W_0)_\infty - (A - A_0)}\right] \qquad (1')$$

In Table II are given the rate constants obtained from the oxygen-18 exchange reaction between *t*-butyl alcohol and water at 25° in aqueous acid media. Table II illustrates the precision of the exchange rate constant, k_{ex}, obtained from experiments with varying percentage exchange.

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[6] T. C. Hoering and J. W. Kennedy, THIS JOURNAL, **79**, 56 (1957).

[7] E. Grunwald, A. Heller and F. S. Klein, *J. Chem. Soc.*, 2604 (1957).

[8] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 178.

TABLE II

RATE CONSTANTS, k_{ex}, FOR OXYGEN-18 EXCHANGE BETWEEN *t*-BUTYL ALCOHOL AND WATER IN AQUEOUS ACID MEDIA AT 25.0° IN UNITS OF 10^4 MIN.$^{-1}$

Time, min.	Exchange, %	k_{ex}
A. Rate constants in 0.96 *M* sulfuric acid		
600	14.7	2.64[a]
1505	32.7	2.63[a]
2602	51.4	2.77[a]
6945	82.3	2.51[a]
	Av.	2.64
	Av. error	0.08
B. Rate constants in 2.00 *M* sulfuric acid		
256.0	25.3	11.4[a]
458.0	44.0	12.6[a]
	Av.	12.0
	Av. error	0.8
C. Rate constants in 3.00 *M* sulfuric acid		
80.1	36.7	57.0
140.0	55.4	57.5
220.0	71.2	56.5
	Av.	57.0
	Av. error	0.4
D. Rate constants in 4.00 *M* sulfuric acid		
30.0	45.9	205[a]
30.0	47.4	214
54.5	65.0	192[a]
60.0	73.5	221
80.0	83.3	224
	Av.	211
	Av. error	11
E. Rate constant in 3.00 *M* perchloric acid		
114.0	62.5	85.9
F. Rate constant in 3.00 *M* hydrochloric acid		
181.0	37.8	26.2

Rate constant was calculated (eq. 1) using the equilibrium oxygen-18 content of an alcohol sample. All other rate constants have been calculated (eq. 1′) using the oxygen-18 content of the aqueous acid solution as the equilibrium oxygen-18 content of the alcohol.

Dehydration Procedure.—The dehydration of *t*-amyl alcohol at 25° was performed in an apparatus of the type described by Levy, Taft, Aaron and Hammett[9] (see Fig. 1 of this reference). The apparatus after S was eliminated. The procedure for the dehydration was that of Taft, Levy, Aaron and Hammett,[10] except that the alcohol solution (0.80 molar) and the dilute acid were added to a round-bottom flask of about 100-ml. capacity without an internal compartment.

The acid solution was introduced first and then chilled. The alcohol solution was added on top of this and a two-layered system was formed. The resulting solution, when thoroughly mixed, was 0.50 *M* with respect to alcohol and varied from 1.50 to 4.00 *M* with respect to acid. After the solution was degassed twice, the apparatus was sealed at L and immersed in a constant-temperature bath.[10] After a few minutes, when the contents of the flasks had completely melted, shaking was started. With rapid and vigorous shaking (a shaking rate of 305 r.p.m. was used in all experiments) the layers became uniformly mixed and the solution came to bath temperature within a few minutes.[10] Zero time was taken at the start of the shaking, and the time was recorded for about each 0.30 cm. pressure rise. It was assumed that little or no reaction had taken place in the cold layered solution prior to mixing.

The dehydration of *t*-amyl alcohol at 50° was done in an apparatus modified by the inclusion of a 20-ml. cylindrical cup inside a 130-150-ml. reaction flask.[10] This was done to permit the contents of the flask to approach bath temperature without the occurrence of any reaction. The procedure described in reference 10 was modified by reversing the positions of the acid and alcohol solutions. The alcohol molarity was lowered to 0.25 *M* due to the large quantity of olefin evolved from a 0.50 *M* alcohol solution, more than could be measured conveniently by this apparatus.

The slope of the log $(P^e - P)$ *vs.* time plot was in each case linear, with no deviation from first-order kinetics observed even to 90% completion of the reaction. The rate constants were based on a pressure rise of olefin of about 14 cm. at 25° and 32 cm. at 50°. The reactions were generally followed to 70–80% completion. The only exceptions to the above statements were the dehydrations performed in perchloric acid. The pressure of olefin generated was about 6 cm. for the dehydrations of *t*-amyl alcohol at 25° in 1.86 *M* perchloric acid solution, and the reactions were followed to 50% completion. For sulfuric acid solutions, the value of *h* used in the rate equation was 0.003 mole-l.$^{-1}$ -atm.$^{-1}$. A value of *h* of 0.00368 mole-l.$^{-1}$-atm.$^{-1}$ has been reported for trimethylethylene at 30° in 1 *M* sulfuric acid.[11] In perchloric acid solution the value of *h* used was 0.005 mole-l.$^{-1}$-atm.$^{-1}$ (0.00583 is reported for *h* at 30° in 1 *M* perchloric).[11] The knowledge of these distribution constants need not be highly accurate since *h* was in all cases small compared to r/RT. At no time did *h* account for more than 2% of the term $(r/RT + h)$. This knowledge of *h* permits the calculation of a rate constant from each kinetic run.[12] Equilibrium pressures were calculated by extrapolating the plot of log $(P^e - P)$ *vs.* time to zero time.

In Table III are listed some typical results illustrating the precision of the dehydration rate constants.

TABLE III

RATE CONSTANTS, k_{-1}, FOR THE DEHYDRATION OF *t*-AMYL ALCOHOL IN 4.10 *M* AQUEOUS SULFURIC ACID AT 25.0° IN UNITS OF 10^4 MIN.$^{-1}$

r/RT	Alcohol, *M*	k_{-1}
0.150	0.50	37.9
.150	.25	37.7
.200	.50	36.7
.250	.50	38.7
	Av.	37.8
	Av. error	0.6

Results

Table IV list the oxygen exchange rate constants, k_{ex}, obtained in mineral acid solutions for *t*-butyl alcohol. Similar results for *t*-amyl alcohol are given in Table V.

TABLE IV

OXYGEN-18 EXCHANGE RATE CONSTANTS, k_{ex}, FOR *t*-BUTYL ALCOHOL IN AQUEOUS SULFURIC ACID SOLUTIONS (UNLESS OTHERWISE INDICATED), IN UNITS OF 10^4 MIN.$^{-1}$

Alcohol, *M*	Acid, *M*	Temp., °C.	k_{ex}	Av.[a] error
0.25	0.96	25.01	2.29	. .
.53	.96	25.01	2.64	0.1
.75	.96	25.01	2.46	. .
.53	2.00	25.01	12.0	0.8
.53	3.00	25.01	57.0	0.4
.53	4.00	25.01	211	11
.53	3.00[b]	25.01	85.9	. .
.53	3.00[c]	25.01	26.2	. .
.53	0.96	44.87	72	. .
.53	0.96	50.01	157	2

[a] An average error is listed if two or more values of the rate constant were determined by separate experiments. [b] Perchloric acid. [c] Hydrochloric acid.

The dehydration of *t*-butyl alcohol in aqueous acid solutions at 25° proceeds to such a slight extent that the rate of dehydration is difficult to determine by direct means.[13,14] Therefore, *t*-amyl

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[9] J. B. Levy, R. W. Taft, Jr., D. Aaron and L. P. Hammett, THIS JOURNAL, **73**, 3792 (1951).

[10] R. W. Taft, Jr., J. B. Levy, D. Aaron and L. P. Hammett, *ibid.*, **74**, 4735 (1952).

[11] R. W. Taft, Jr., E. L. Purlee and P. Riesz, *ibid.*, **77**, 899 (1955).

[12] E. L. Purlee, R. W. Taft, Jr., and C. A. DeFazio, *ibid.*, **77**, 837 (1955).

[13] W. F. Eberz and H. J. Lucas, *ibid.*, **56**, 1230 (1934).

[14] R. W. Taft, Jr., and P. Riesz, *ibid.*, **77**, 902 (1955).

Table V

Oxygen-18 Exchange Rate Constants, k_{ex}, for *t*-Amyl Alcohol in Aqueous Sulfuric Acid Solutions in Units of 10^4 Min.$^{-1}$

Alcohol, *M*	Acid, *M*	Temp., °C.	k_{ex}	Av. error
0.50	0.96	25.01	7.72	0.1
0.50	0.96	38.02	58.4	0.8

alcohol has been employed to determine the effect of acid on the dehydration rate. Table VI lists the rate constants, k_{-1}, obtained from the dehydration of *t*-amyl alcohol in aqueous acid media at 25°. Each value of k_{-1} is based upon two to four experiments with r/RT values varying from 0.15 to 0.25. The results of Table III show that a decrease from 0.50 to 0.25 *M* alcohol concentration produces no measurable effect on the rate constants.

Table VI

Rate Constants, k_{-1} for the Dehydration of *t*-Amyl Alcohol in Aqueous Acid Media at 25.0° in Units of 10^4 Min.$^{-1}$

Acid, *M*	k_{-1}	Av. error
1.50[a]	1.59	0.06
3.00[a]	14.2	.01
4.10[a]	37.8	.6
1.86[b]	2.78	.01
0.97[c]	1.38	..

[a] Sulfuric acid. [b] Perchloric acid. [c] Nitric acid, calcd. from data of ref. 16.

The dehydration of *t*-amyl alcohol performed at 50.03° in 1.50 *M* sulfuric acid yielded an average k_{-1} of $7.56 \pm 0.12 \times 10^{-3}$ min.$^{-1}$.

The rate constants, k_{-1}, of Table VI are gross dehydration constants. It has been shown[15] that the rate constant for the dehydration of *t*-amyl alcohol to trimethylethylene is $^5/_6$ of the gross constant ($^1/_6$ is the dehydration rate constant for the formation of 2-methyl-1-butene). Consequently, the rate constants for the hydration of gaseous trimethylethylene at unit pressure, k_p, were calculated from the results of the reversible dehydration by the expression developed previously[10,11] ($k_p = (r/RT + h)(s - 5k_{-1}/6)$). Values of k_p are listed together with corresponding values of the apparent equilibrium constant, $K_p = C_a^e/p_o^e$ (C_a^e = equilibrium concentration of *t*-amyl alcohol, and p_o^e = equilibrium pressure of trimethylethylene), in Table VII.

Table VII

Rate Constants, k_p, and the Apparent Equilibrium The Constants, K_p, for the Reversible Hydration of *t*-Amyl Alcohol in Aqueous Acid Media at 25.0° (k_p in Units of 10^4 Moles-l.$^{-1}$ Atm.$^{-1}$-min.$^{-1}$ and K_p in Units of Moles-l.$^{-1}$-atm.$^{-1}$)

Acid, *M*	k_p	Av. error	K_p[c]	Av. error
1.50[a]	4.45	0.16	3.4	0.2
3.00[a]	29.4	0.6	2.5	.1
4.10[a]	93.8	2.4	2.8	.2
1.86[b]	14.5	0.1	6.0	.1

[a] Sulfuric acid. [b] Perchloric acid. [c] The values of k_{-1} have been corrected for dehydration to trimethylethylene only.

Purlee[16] has previously obtained values for the rate of dehydration of *t*-amyl alcohol in nitric acid solutions (0.97 to 4.9 *M*) at 30°. These k_{-1} values were obtained from the small residual pressures in the reversible hydration of trimethylethylene. Purlee's results pertain to very dilute alcohol solutions and are consequently not strictly comparable with the present results. Table VIII lists the k_{-1} values obtained by Purlee.

Table VIII

Rate Constants, k_{-1}, for the Dehydration of *t*-Amyl Alcohol in Nitric Acid Solutions at 30.00° Obtained by Purlee from the Reversible Hydration of Trimethylethylene (k_{-1} in Units of 10^4 Min.$^{-1}$)

Acid, *M*	k_{-1}	Acid, *M*	k_{-1}
0.973	1.38	3.00	12.4
1.500	3.09	4.00	20.2
2.01	5.13	4.94	30.9

Discussion

Hydration and Dehydration Rates.—The rates of hydration of gaseous tertiary olefins at unit pressure, k_p, have been studied extensively in moderately concentrated aqueous nitric acid solutions.[17] The data show the following dependence on acidity: $\log k_p = -\rho H_0 +$ constant, where H_0 is the Hammett acidity function. The mean value of ρ for olefins of various sizes and shapes was found[18] to be +1.25.

The hydration rate constants of Table VII for sulfuric acid solutions at 25.0° follow the equation $\log k_p = -(1.00)H_0 - 3.92$. The value of k_p for trimethylethylene in 0.973 *M* HNO_3 at 25.0° obtained from results of Purlee[19] also follows this equation (av. deviation of the four data is ±0.02 log unit). The value of $\rho = 1.00$ is somewhat different from that given[18] earlier (1.20) for the hydration of trimethylethylene in one to five molar nitric acid solutions at 30.0°. The difference is in the direction expected from the equation[18] $\log k_c = -(0.98) \cdot H_0 +$ constant (where k_c is the rate constant for the olefin at unit concentration), and the greater salting-out effect of sulfuric than nitric acid.[11] The value of $\log k_p + H_0$ for the hydration of trimethylethylene in 1.86 *M* perchloric acid (Table VII) is larger (−3.55) than for the sulfuric acid solutions (−3.92) presumably for a similar reason. Further, small departures from unit slope are known to be normal behavior.[20]

Using the Zucker–Hammett hypothesis[20,21] to interpret the fit of olefin hydration rates to the H_0 function, Taft formulated the mechanism shown (A) for the *t*-alcohol–olefin interconversion.[22]

The effect of acidity on the dehydration rates of *t*-amyl alcohol (Tables VI and VIII) is of especial interest from the standpoint of the Zucker–Hammett hypothesis and its application to the mechanism of the alcohol–olefin interconversion, since this

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[15] *Cf.* P. Riesz, R. W. Taft, Jr., and R. H. Boyd, This Journal, **79**, 3724 (1957).

[16] E. L. Purlee, Ph.D. Thesis, The Pennsylvania State University, June, 1954, p. 20.

[17] A summary of literature references is given in ref. 15.

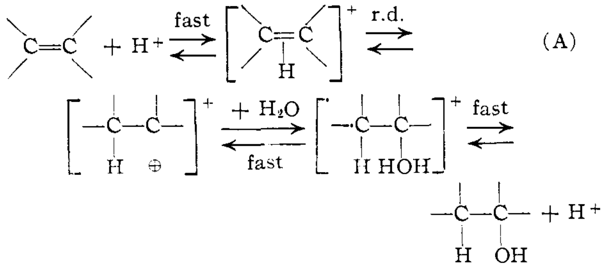
[18] R. W. Taft, Jr., E. L. Purlee, P. Riesz and C. A. DeFazio, This Journal, **77**, 1584 (1955).

[19] Reference 16, p. 14.

[20] F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 935 (1957).

[21] L. Zucker and L. P. Hammett, *ibid.*, **61**, 2791 (1939).

[22] R. W. Taft, Jr., *ibid.*, **74**, 5372 (1952).



reaction is the reverse of the hydration reaction studied initially. The data of Table VI are satisfactorily fitted (average deviation = ±0.04 log unit) by the equation: $\log k_{-1} = -(1.00)\ H_0 - 4.30$ as illustrated in Table IX. The unsatisfactory fit of the dehydration rates to the equation, $\log k_{-1} = \log (H_3O^+) +$ constant, is also illustrated in Table IX. The dehydration rates of Purlee in nitric acid solutions at 30.0° follow the H_0 function ($\log k_{-1} = -(1.00)H_0 - 3.99$) to the same precision, as shown in Table X. The unsatisfactory fit of the dehydration rates to the equation[23] $\log k_{-1} = -(1.00)H_R +$ constant, is illustrated in Table X. The rates of a number of acid-catalyzed reactions which presumably involve the formation of R^+ from ROH in a step preliminary to the rate-determining step follow the H_R function.[23]

TABLE IX

CORRELATION OF THE EFFECT OF ACIDITY ON THE RATE CONSTANT, k_{-1}, FOR THE DEHYDRATION OF *t*-AMYL ALCOHOL IN AQUEOUS ACID MEDIA AT 25.0° WITH THE H_0 FUNCTION

Acid	Molarity	$-H_0$	$\log k_{-1}$	$\log k_{-1} + H_0$	$\log k_{-1} - \log (H_3O^+)$
HNO_3	0.97	0.16	−4.19	−4.35	−4.19
H_2SO_4	1.50	.56	−3.80	−4.36	−3.98
$HClO_4$	1.86	.71	−3.56	−4.27	−3.83
H_2SO_4	3.00	1.38	−2.85	−4.23	−3.33
H_2SO_4	4.10	1.89	−2.42	−4.31	−3.03

TABLE X

CORRELATION OF THE EFFECT OF ACIDITY ON THE RATE CONSTANT, k_{-1}, FOR THE DEHYDRATION OF *t*-AMYL ALCOHOL IN AQUEOUS NITRIC ACID SOLUTIONS AT 30.0° WITH THE H_0 FUNCTION

Molarity	$-H_0$	$\log k_{-1} + H_0$	$\log k_{-1} + H_R$	Molarity	$-H_0$	$\log k_{-1} + H_0$	$\log k_{-1} + H_R$
0.973	0.16	−4.02	−4.53	2.96	1.00	−3.91	−5.17
1.500	.45	−3.96	−4.66	4.00	1.32	−4.01	−5.60
2.01	.67	−3.96	−4.85	4.94	1.56	−4.01	−5.90

It has been recognized[18,24] that the carbonium ion intermediate represented in the mechanism above may not be a "free" cation, *i.e.*, that the leaving water molecule (in the formation of olefin from alcohol) may be held by a lingering interaction with the cationic center. The present results are consistent with such an interaction.

It is probable that the activity coefficient behavior of the transition state for the isomerization of a completely free carbonium ion to a π-complex (over-all reaction: $ROH + H^+ \rightleftarrows$ "$R^{+}_{\ddagger}$" $+ H_2O$) would closely resemble that of "open-sextet" species which are known to display unique behavior.[23,25] This behavior has been shown by Deno, *et al.*,[23a,26] to be the essential ingredient leading to acid-catalyzed reaction rates which follow (in the region of acidity with which we are presently concerned) the equation, $\log k = -H_R +$ constant. *The fact that the acid-catalyzed dehydration and hydration rates do not follow this relationship may be interpreted as indicating that with regard to its activity coefficient behavior (but not with respect to internal electronic factors*[15]*) the transition state for the alcohol-olefin interconversion is not of "free" R^+ character.*[27]

It seems reasonable, however, that the transition state for the general reaction, $RR'OH^+ \rightleftarrows R^+ + R'OH$ (where R' is either H or alkyl) would exhibit activity coefficient behavior closely resembling that of normal conjugate acids of primary bases.[28] The structure of the transition state for such reactions must be represented as $(RR'OH)^+$ with a somewhat elongated C–O bond, so that with respect to the surrounding media such a state will appear very similar to the oxonium ion.[28a]

By the same line of reasoning, the activity coefficient behavior for the transition state of a reaction between an entering nucleophile and an *intermediate* which possesses both a high degree of carbonium ion character (as judged by internal electronic effects) and a small but measurable interaction with a departing water or alcohol molecule is expected to resemble that of an oxonium ion.

These ideas find support in the fact that a great many reactions of the above kinds in both the aromatic and aliphatic series all follow H_0,[29] whereas

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(23) (a) N. C. Deno, H. E. Berkheimer, W. L. Evans and H. J. Peterson, THIS JOURNAL, **81**, 2344 (1959), and earlier references given therein; (b) A. M. Lowen, M. A. Murray and G. Williams, *J. Chem. Soc.*, 3321 (1950); (c) F. H. Westheimer and M. S. Kharasch, THIS JOURNAL, **68**, 1871 (1946); (d) P. D. Bartlett and J. D. McCollum, *ibid.*, **78**, 1441 (1956); (e) H. Ladenheim and M. L. Bender, *ibid.*, **82**, 1895 (1960).

(24) E. L. Purlee and R. W. Taft, Jr., *ibid.*, **78**, 5807 (1956).

(25) There are limitations to this statement which are unfortunately not well defined at present. N. C. Deno and W. L. Evans, *ibid.*, **79**, 5804 (1957), have observed that the cations derived from *p*-acetylamino and *p*-benzoylamino substituted arylcarbinols do not show this unique behavior but instead resemble usual conjugate acids in their activity coefficient behavior. The spectral properties of these ions, however, are closely similar to those of the other aryl cations which display the unique activity coefficient behavior.

(26) N. C. Deno and C. Perizzolo, THIS JOURNAL, **79**, 1345 (1957).

(27) This conclusion, although more explicit, does bear a certain distinct resemblance to the earlier notions expressed along these lines by N. C. Deno, T. Edwards and C. Perrizolo, *ibid.*, **79**, 2111 (1957).

(28) M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957).

(28a) NOTE ADDED IN PROOF.—Evidence has been discussed recently (R. W. Taft Jr.,) THIS JOURNAL, **82**, 2965 (1960) which suggests that an important if not the critical feature in the different activity coefficient behaviors of ROH_2^+ and R^+ is the hydrogen bonding interaction of the former with proton accepting solvents.

(29) *Cf.* for example, ref. 27 and 31b; N. C. Deno and C. Perizzolo, *J. Org. Chem.*, **22**, 836 (1957); J. B. Ley and C. A. Vernon, *J. Chem. Soc.*, 2987 (1957); D. P. N. Satchell, *ibid.*, 3524 (1957); M. M. Kreevoy and R. W. Taft, Jr., THIS JOURNAL, **77**, 3146 (1955); D. S. Noyce and L. R. Snyder, *ibid.*, **80**, 4324 (1958); D. S. Noyce and W. L. Reed, *ibid.*, **80**, 5539 (1958); P. Salomaa, *Acta Chem. Scand.*, **11**, 132 (1957); M. M. Kreevoy and F. R. Kowitt, THIS JOURNAL, **82**, 739 (1960).

The racemization of 1-phenylethanol in 0.02 to 0.8 *M* $HClO_4$ has d log *k* values between $-dH_0$ and $-dH_R$ (ref. 7). Although a decisive conclusion in this instance cannot be drawn because of the low acid concentration range involved, it is worthy of note that as the stability of a carbonium ion intermediate increases the more the transition state of the reaction, $R^+ + R,OH \rightarrow RR,OH^+$, will come to resemble (probably by all criteria) the oxonium ion (A. Streitwieser, Jr., *Chem. Revs.*, **56**, 639 (1956); M. M. Kreevoy and R. W. Taft, Jr., THIS JOURNAL, **79**, 4020 (1957)). Consequently, if H_R dependence on rate is ever to be observed for this kind of reaction, it will occur for the most unstable "free" carbonium ions.

none of the existing reaction rates which follow H_R (*cf.* ref. 23) involve a rate-determining reaction of oxonium ion to give R^+ and a water or alcohol molecule (or the reverse of such a reaction). The nature of entering and leaving groups in acid-catalyzed reactions involving electronically deficient intermediates apparently plays a very strong role in determining the nature of the observed dependence of rate on acidity.[30]

According to the argument presented above, one may eliminate from consideration for the *t*-alcohol-olefin interconversion a transition state which consists of "alcohol plus a proton minus a water molecule" on the grounds that such a transition state would lead to dehydration and hydration rates which follow H_R. Reasonable remaining mechanisms consequently must all be of the type which lead (because the reaction involves addition of water to olefin) to transition states containing "olefin plus a proton plus one (or more) water molecules." Two mechanisms consistent with this requirement (as discussed in detail in a later section) are those in which in the rate-determining step an intermediate, $R^+ \ldots OH_2$, isomerizes to a π-complex, or a "free" R^+ intermediate forms olefin by a β-proton fission reaction with a water molecule. The activity coefficient behavior for the transition states for either of these two processes according to the ideas expressed above would be expected to lead (as observed) to hydration and dehydration rates which both rather closely follow H_0.[31]

Inasmuch as the Zucker-Hammett hypothesis apparently anticipates that the formation of a transition state which consists of "substrate plus a proton plus a water molecule" should give rise to rates which follow the stoichiometric acid concentration (rather than H_0), the hypothesis fails as a criterion of mechanism for the olefin-alcohol interconversion. That is, according to the Z.-H. hypothesis and the above conclusion regarding the composition of the transition state, the olefin hydration rate is expected to (but does not) follow the stoichiometric acid concentration.

It must be emphasized that the present results and interpretations place on tenuous grounds the original basis[22] for Taft's mechanism for the olefin-alcohol interconversion. However, support for this mechanism has been obtained subsequently from a number of other independent lines of evidence,[15,17,24] none of which are invalidated by the present results. The O^{18} exchange rates studied in the present work provide a valuable new line of evidence consistent with this mechanism.

O^{18} Exchange Rates.—In Table XI the dependence on acidity of the rate constants for O^{18} exchange of *t*-butyl alcohol in sulfuric acid solutions at 25° is shown. These rate constants follow the equation $\log k_{ex} = (-1.20)H_0 + \text{constant}$, as is illustrated by the fourth column in Table XI. Two additional experiments at 25° in 3.00 *M* hydrochloric acid and 3.00 *M* perchloric acid gave $\log k_{ex} + (1.20)H_0$ values of -3.84 and -3.55, respectively. The faster rate in perchloric acid than that predicted by the correlation in Table XI is probably to be attributed to a specific electrolyte effect.[20] The result in hydrochloric acid is in good agreement with the results in sulfuric acid solutions.

TABLE XI

THE EFFECT OF ACIDITY OF THE RATE CONSTANT, k_{ex}, FOR OXYGEN-18 EXCHANGE BETWEEN WATER AND *t*-BUTYL ALCOHOL IN SULFURIC ACID SOLUTIONS AT 25.0°

Acid, *M*	$-H_0$	$\log k_{ex}$	$\log k_{ex} + (1.20) H_0$	$\log k_{ex} - \log (H_3O)^+$
0.96	0.23	−3.58	−3.86	−3.56
2.00	0.84	−2.92	−3.93	−3.22
3.00	1.38	−2.24	−3.90	−2.72
4.00	1.85	−1.68	−3.90	−2.28
		Av.	−3.90	

The ρ-values (in the equation $\log k = -\rho H_0 + \text{const.}$) for the elimination rate constants of *t*-amyl alcohol and (apparently) *t*-butyl alcohol are close to unity. Since small differences in ρ from unity are to be expected, it can be said that the effect of acidity is of essentially the same kind on both the exchange rate and the elimination rate. This result and the similar demonstration for *sec*-butyl alcohol[32] supports the obvious possibility that both reactions go by the same or similar routes.

Activation Parameters.—In 1.0 *M* H_2SO_4 solution, the ratio of the rate constants k_{ex}/k_{-1} for *t*-butyl alcohol is 30 at 50° and 50 at 25°. The activation energy difference, $E_a^{elim} - E^{exch} = 3.1 \pm 0.6$ kcal., is of interest for it represents (as a consequence of the common reactant state) the difference in the enthalpies of the elimination and substitution transition states.

The present results for the k_{ex}/k_{-1} rate ratio and its activation energy for *t*-butyl alcohol are in good

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(30) An important corollary of these conclusions is that the dependence of rate on acidity for a reaction mechanism in which R^+ is formed in preliminary equilibria preceding the rate-determining step is determined to good approximation by the nature of the nucleophilic reagent and the type of reaction which R^+ undergoes with it. Thus, for example, the acid-catalyzed reaction

$$(C_6H_5)_2CHOH + C_2H_5OH \xrightarrow{H^+} (C_6H_5)_2CH_2 + CH_3CHO$$

follows the H_R function (ref. 23d), but the reaction

$$(C_6H_5)_2CHOH + C_2H_5OH \xrightarrow{H^+} (C_6H_5)_2CHOC_2H_5 + H_2O$$

is predicted to follow the H_0 function.

A second (perhaps less obvious) corollary is that the leaving group can exert an important influence on the form of the dependence of rate on acidity. This follows from the fact that kinetic processes will frequently proceed through encumbered rather than free carbonium ion intermediates (*cf.* later discussion) and thus, for example, leaving groups such as H_2O or alcohols can cause the reaction transition state to show activity coefficient behavior which closely resembles that of oxonium ions.

(31) In the region of acidity involved in present considerations, $\log a_{H_2O}$ is to a good approximation invariant (if greater accuracy is required, the correction for this term can readily be applied). Consequently, *any hydration reaction* ($R + H_2O \rightleftarrows R\text{–}OH_2$) for which the *activity coefficient behavior of the product and reactant are closely similar* must necessarily (by thermodynamic requirements) have forward and reverse reaction rate constants which have essentially the same dependence on acidity, *irrespective of the reaction mechanism.* This is the situation which prevails in the olefin–alcohol interconversion as shown by the nearly invariant values of equilibrium constants, $K_p = C_a^e/p_0^e$ (see earlier definition) given in Table VII and the small salting-out effect of sulfuric acid on trimethylethylene.[11] In view of earlier demonstrations that the activity coefficient behaviors of organic substrates in concentrated mineral acid solution are remarkably similar (ref. 24a, 26, F. A. Long and W. F. McDevit, *Chem. Revs.*, **5**, 119 (1952), and F. A. Long and D. McIntyre, THIS JOURNAL, **76**, 3243 (1954)), this situation may be expected to prevail rather generally.

(32) C. A. Bunton and D. R. Llewellyn, *J. Chem. Soc.*, 3402 (1957).

accord with the results obtained by Dostrovsky and Klein.[3] The value of k_{ex}/k_{-1} at 25° calculated by the Arrhenius equation from Dostrovsky and Klein's measurements at 55 and 75° in 0.45 M H_2SO_4 agrees with our value within experimental error.

For *t*-amyl alcohol, the rate ratio k_{ex}/k_{-1} in 1 M H_2SO_4 solution at 25° is 10.4. The activation energy difference, $E_a^{elim} - E_a^{exch} = 1.0 \pm 0.6$ kcal.

Table XII summarizes values of the enthalpies and entropies of activation obtained in the present study.

TABLE XII

ENTHALPIES AND ENTROPIES OF ACTIVATION FOR ALCOHOL DEHYDRATION AND O¹⁸ EXCHANGE RATES. ENTROPIES OF ACTIVATION ARE BASED UPON UNIT ACID CONCENTRATION

	Dehydration		O^{18} Exchange	
Alcohol	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.
t-Butyl	33.9 ± 0.3^a	$+19 \pm 2^a$	30.7 ± 0.3^c	$+15 \pm 2^c$
t-Amyl	29.1 ± 0.5^b	$+12 \pm 2^b$	28.1 ± 0.3^d	$+13 \pm 2^d$

[a] Cf. ref. 3, 13, 14, and 18. [b] Obtained from data in 1.50 M H_2SO_4 at 25.01 and 50.03°. A value of 29.5 ± 1.3 kcal. was obtained previously in 0.973 M HNO_5 (ref. 16). [c] Obtained from data in 0.96 M H_2SO_4 at 25.01 and 50.03°; Arrhenius equation followed within experimental error. [d] Obtained from data in 0.96 M H_2SO_4 at 25.01 and 38.02°.

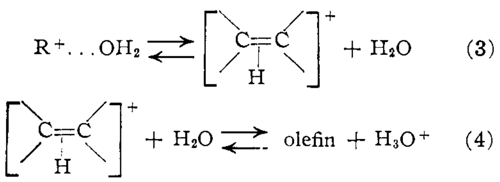
The entropies of activation given in Table XII are of interest. The entropies of activation for alcohol dehydration and O^{18} exchange are nearly the same with experimental error. Both are large positive values indicating that substantial ionization of the C–O bond is involved in both reactions.[18,22,33]

Conclusions.—We believe the facts that the O^{18} exchange and dehydration rates both follow H_0 and that the transition states for the two reactions have closely similar entropies provide substantial evidence that the two reactions proceed through the same initial steps but involve different rate-determining steps. The appreciably faster exchange rates are accounted for on the basis of the formation of a reaction intermediate.[3,7,32]

The evidence presented in this work is consistent with either of the mechanisms (or some appropriate combination of the two)

I $$ROH + H_3O^+ \rightleftarrows ROH_2^+ + H_2O \qquad (1)$$

$$ROH_2^+ \rightleftarrows R^+ \ldots OH_2 \qquad (2)$$



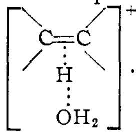
II $$ROH + H_3O^+ \rightleftarrows ROH_2^+ + H_2O \qquad (1)$$

$$ROH_2^+ \rightleftarrows R^+ + H_2O \qquad (2)$$

$$R^+ + H_2O \rightleftarrows \text{olefin} + H_3O^+ \qquad (3)$$

In mechanism I, steps 1, 2 and 4 are fast and step 3 is rate determining in the dehydration reaction.[34] In the exchange reaction, step 1 is fast and step 2 is rate determining. It is assumed that the intermediate $R^+ \ldots OH_2$ undergoes very rapid exchange with water.[35] In mechanism II, steps 1 and 2 are fast in the dehydration reaction and 3 is rate determining. The O^{18} exchange reaction by mechanism II involves a fast step (1) and a rate-determining step (2). Either reaction by either mechanism involves transition states whose activity coefficient behavior is expected (as described above) to closely resemble that of oxonium ions, a relationship apparently required by the fact that both the olefin hydration rate and the alcohol dehydration rates as well as the O^{18} exchange rates follow the H_0 function.

In mechanism I the molecularity of step 3 with respect to water has not been indicated and may be greater than zero, provided that the added water molecule does not become *firmly* attached to carbon.[15] Further, the π-complex structure may be alternately given as



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The evidence previously presented[15] concerning the effect of ring size on rates and equilibria in olefin–alcohol interconversion is considered to be equally consistent with mechanisms I and II. Solvent isotope effect evidence has been previously presented[24] which favors mechanism I over II, although this evidence presently cannot be considered to be highly critical.[20] Mechanism I, however, is the favored mechanism for reasons to be discussed more fully in subsequent work.

The encumbered carbonium ion classification is proposed to give description to all intermediates having substantial carbonium ion character and measurable interactions between the leaving group and the cationic center. This classification includes ion-pairs such as the intimate and solvent-separated ion pairs for which extensive definitive evidence has been obtained by Winstein and students.[36] Further included are any neutral leaving groups,

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[33] F. A. Long, J. G. Pritchard and F. E. Stafford, THIS JOURNAL, **79**, 2362 (1957).

[34] When k_{ex}/k_{-1} becomes less than approximately 10, there is no single effective rate-determining step; *cf.* in this connection M. L. Bender, R. D. Ginger and J. P. Unik, *ibid.*, **80**, 1044 (1958).

[35] Mechanism I with the assumption of certain rate relationships is capable of explaining the striking stereochemical studies of Hammond and students (G. S. Hammond and T. D. Nevitt, THIS JOURNAL, **76**, 4121 (1954); C. H. Collins and G. S. Hammond, *ibid.*, submitted; *cf.* also P. von R. Schleyer, *ibid.*, **82**, submitted (1960). In non-aqueous solvent, stereospecific *trans* addition of HCl and HBr to tertiary olefins has been found. The hydration of the same olefin in aqueous acid media is non-stereospecific. These results may be explained by assuming the following rate relationships in the aqueous solution. The first formed *trans*-encumbered carbonium ion undergoes exchange to give the *cis*-encumbered carbonium ion more rapidly than collapse to the reaction product (alcohol or halide). In non-aqueous solution, the exchange rate of the *trans*- to the *cis*-encumbered carbonium ion intermediate is slow compared to the *rate* of collapse, thus leading to the observation of *trans* addition. The stereospecific *trans* addition provides especially compelling evidence for the π-complex intermediate. Mechanism II appears incapable of accounting for stereospecific *trans* addition.

[36] S. Winstein, E. Clippinger, A. H. Fainberg, R. Heck and G. C. Robinson, *ibid.*, **78**, 328 (1956); S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958), and earlie rreferences. *Cf.* also N. Kornblum *et al.*, *ibid.*, **77**, 6269 (1955); G. S. Hammond, *et al.*, *ibid.*, **82**, 704 (1960).

such as the H_2O molecule of present concern. We believe this classification also has the utility that the encumbrance of the carbonium ion (bonding to it) may be more completely specified if known. Thus, for example, the Doering–Zeiss intermediate[37] is classified as having front and back-side encumbrances.

The encumbered carbonium ion intermediate $R \ldots OH_2^+$ has been previously invoked (in somewhat different forms) to explain the results of stereochemical investigations of the mechanism of the O^{18} exchange reaction of *sec*-butyl alcohol[32,38] and 1-phenyl ethanol.[7]

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(37) W. von E. Doering and H. H. Zeiss, THIS JOURNAL, **75**, 4733 (1953); *cf.* Also A. Streitwieser, Jr., *Chem. Revs.*, **56**, 573 (1956).

(38) C. A. Bunton, A. Konasiewicz and D. R. Llewellyn, *J. Chem. Soc.*, 607 (1955).

UNIVERSITY PARK, PENNA.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY OF NEW JERSEY]

Concerning the Mechanism of the Reaction of Trisubstituted Phosphines with Episulfides[1]

BY DONALD B. DENNEY AND MARVIN J. BOSKIN

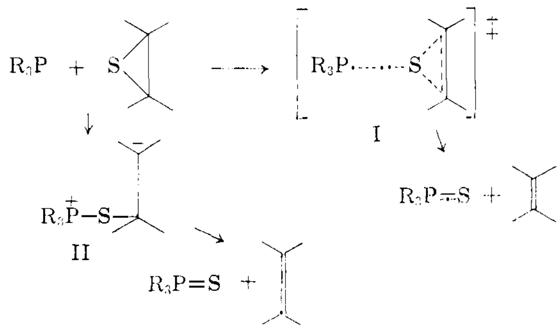
RECEIVED FEBRUARY 22, 1960

Triphenylphosphine and tributylphosphine react with *cis*-2-butene episulfide and *trans*-2-butene episulfide to give *cis*-2-butene and *trans*-2-butene, respectively. The kinetics of the reaction of triphenylphosphine with these two episulfides and 1-butene episulfide have been measured in several solvents of different dielectric constants. The rates of the reactions are relatively insensitive to large changes in dielectric constant of the medium. These data indicate that the desulfurization reaction proceeds by a nucleophilic attack by the phosphine on the sulfur to give the phosphine sulfide and olefin in one step. This process is envisioned as a smooth displacement on sulfur with little or no charge separation in the transition state.

The reactions of episulfides with many nucleophilic reagents such as lithium diethylamide,[2] primary and secondary amines[3] and mercaptide ions[3,4] proceed with ring opening and formation of a mercaptide ion or a mercaptan. With organolithium compounds,[5] triphenylphosphine[6] and triethyl phosphite,[6-8] the respective products are the alkyl or aryl lithium mercaptides, triphenylphosphine sulfide, triethyl thiophosphonate and in each case the olefin resulting from desulfurization of the episulfide.

Quite recently Neureiter and Bordwell[8] have shown that the desulfurization reaction is stereospecific. They treated *cis*-2-butene episulfide and *trans*-2-butene episulfide with phenyllithium and triethyl phosphite. In every case the *cis*-episulfide gave essentially pure *cis*-olefin, and the *trans*-episulfide gave essentially pure *trans*-olefin. These results have been confirmed by work in this Laboratory. It has been found that triphenylphosphine and tributylphosphine react with *cis*-2-butene episulfide to give *cis*-2-butene, and with *trans*-2-butene episulfide to give *trans*-2-butene.

As Neureiter and Bordwell[8] pointed out, these results are most easily explained by a mechanism which involves direct attack by the nucleophile on the sulfur atom of the episulfide ring. Such an attack could give rise to the products by proceeding through a transition state, I, which yields the olefin and the phosphine sulfide in one step. Another less likely possibility involves displacement on sulfur to give the intermediate II. If II is formed it must decompose to the products faster than rotation about the central carbon–carbon bond can occur. Rotation would ultimately lead to a mixture of olefins.



Since these reactions are rather novel, it seemed of interest to investigate in more detail the exact nature of the desulfurization process. In order to do this a kinetic study was initiated. The general kinetic procedure was modeled closely after that employed by Bartlett and Meguerian[9] in their study of the reaction of sulfur with triarylphosphines.

The rates of the reactions of *cis*-2-butene episulfide and *trans*-2-butene episulfide with triphenylphosphine were measured in several solvents. The rate data are summarized in Table I. The reaction is bimolecular, first order in each reactant. It can easily be seen that varying the dielectric constant of the solvent by a factor of *ca.* 16 has only a small effect on the rate of the reaction. Bartlett and Meguerian[9] have found that the rate of the reaction of triphenylphosphine with sulfur is markedly affected by small changes in the dielectric

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(1) Some of this work has been presented in preliminary form, *Chemistry & Industry*, 330 (1959).

(2) H. Gilman and L. A. Woods, THIS JOURNAL, **67**, 1843 (1945).

(3) H. R. Snyder, J. M. Stewart and J. B. Ziegler, *ibid.*, **69**, 2672 (1947).

(4) C. C. J. Culvenor, W. Davis and N. S. Heath, *J. Chem. Soc.*, 282 (1949).

(5) F. G. Bordwell, H. M. Anderson and B. M. Pitt, THIS JOURNAL, **76**, 1082 (1954).

(6) R. E. Davis, *J. Org. Chem.*, **23**, 1767 (1958).

(7) R. D. Schuetz and R. L. Jacobs, *ibid.*, **23**, 1799 (1958).

(8) N. P. Neureiter and F. G. Bordwell, THIS JOURNAL, **81**, 578 (1959).

(9) P. D. Bartlett and G. Meguerian, *ibid.*, **78**, 3710 (1956).