Since the spectrophotometric evidence indicated that copper(II) ion and triethanolamine form complex ions only in the ratio 1:1, it was assumed that the variation of the spectra with *p*H could be accounted for by interaction of the complex with the hydroxyl ion. If this assumption is correct a positive ion, a neutral molecule, and a negative ion should be formed as the *p*H is increased, thus: $Cu(OH)(H_2O)_2N(C_2H_4OH)_3^{+1}$, $Cu(OH)_2(H_2O)N(C_2H_4OH)_3$, and $Cu(OH)_3N(C_2H_4OH)_3^{-1}$. These assumptions were confirmed by a series of migration experiments performed at *p*H values of 8.0, 9.0, 9.5, 9.8 and 10.0. The boundaries moved toward the negative electrode at *p*H values of 8.0, 9.0 and 9.5; they moved toward the positive electrode at a *p*H value of 10.0. The boundaries showed no movement over a period of two hours for the experiment at *p*H 9.8.

For the data obtained at *p*H 8.0 and an ionic strength of 0.03 the dissociation constant of the copper(II) ion–triethanolamine complex was calculated and found to be given by $\log_{10} K_{\text{equilib}} = 4.3 \pm 1$.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Rates and Temperature Coefficients in the Hydration of Two Gaseous Pentenes by Dilute Aqueous Nitric Acid[1]

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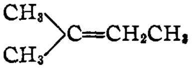
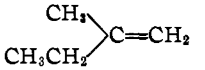
Although the hydrations of the isomeric pentenes trimethylethylene and *as*-methylethylethylene are measurably reversible and lead to the same alcohol, the specific rates of the hydrations may be determined to a useful precision from the decrease with time of the vapor pressure of the olefin over the solution in which the hydration is occurring. These specific rates do not differ largely from that of isobutene, yet the data obtained offer a strong indication that both enthalpies and entropies of activation are significantly lower for the pentenes than for isobutene.

The isomeric olefins trimethylethylene (I) and methylethylethylene (II)


I


II

hydrate in an essentially quantitative fashion to a single product *t*-amyl alcohol.[2] At temperatures of 25° or more the hydration is, we find, measurably reversible, and the reverse reaction must, in the case of at least one, and possibly of both of these olefins, lead to the formation of the isomer. Evidence which we have previously reported[2c] shows that no facile interconversion of the olefins occurs independently of the formation of the alcohol by way, for instance, of the mobile and reversible formation of a single carbonium ion. The reaction system with which we have to deal is therefore

$$\text{Olefin I} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Alcohol} \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} \text{Olefin II}$$

Nevertheless we find with I at 35° and lower and with II at 30° and lower that the quantity $s = -\mathrm{d}\ln(P - P^e)/\mathrm{d}t$ (where P is the partial pressure of gaseous olefin over a solution in which the hydration is proceeding and P^e is the partial pressure at equilibrium) is independent of time to excellent precision up to as much as 80% completion of reaction, just as it was in the simpler cases which we have studied previously.[3]

For this reaction system we have by virtue of a development which closely parallels that of eq. 3 of article I[3a]

$$(h_1 + r/RT)\frac{\mathrm{d}P_1}{\mathrm{d}t} = -k_1P_1 + k_{-1}C_a \quad (1)$$

$$(h_2 + r/RT)\frac{\mathrm{d}P_2}{\mathrm{d}t} = -k_2P_2 + k_{-2}C_a \quad (2)$$

k_1 and k_2 are rates of reaction at unit pressure of olefin (the k_p quantity of articles I and II), P_1 and P_2 are the partial pressures of olefin I and II, r is the ratio (volume of gas phase)/(volume of solution), h_1 and h_2 are the distribution constants of olefin between gas and liquid, C_a is concentration of alcohol. If alcohol and olefin II are absent at time 0 and the partial pressure of olefin I is P^0 at that time we can eliminate C_a by material balance considerations, obtaining after substitution of the definitions

$$k_1' = k_1/(h_1 + r/RT),\ k_2' = k_2/(h_2 + r/RT) \quad (3)$$

and

$$Q = \frac{h_2 + r/RT}{h_1 + r/RT} \quad (4)$$

the equations

$$\frac{\mathrm{d}P_1}{\mathrm{d}t} = -k_1'P_1 + k_{-1}(P^0 - P_1) - k_{-1}QP_2 \quad (5)$$

$$\frac{\mathrm{d}P_2}{\mathrm{d}t} = -k_2'P_2 - k_{-2}P_2 + \frac{k_{-2}}{Q}(P^0 - P_1) \quad (6)$$

These may be integrated by the method of Rakowski[4] to yield

$$P_1 - P_1^e = \frac{\lambda_1(P^0 - P_1^e - \lambda_2P_2^e)}{\lambda_1 - \lambda_2}e^{-\rho_1t} - \frac{\lambda_2(P^0 - P_1^e - \lambda_1P_2^e)}{\lambda_1 - \lambda_2}e^{-\rho_2t} \quad (7)$$

$$P_2 - P_2^e = -\frac{P^0 - P_1^e - \lambda_2P_2^e}{\lambda_1 - \lambda_2}e^{-\rho_1t} + \frac{(P^0 - P_1^e - \lambda_1P_2^e}{\lambda_1 - \lambda_2}e^{-\rho_2t} \quad (8)$$

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[1] The work reported herewith was carried out as project NR 056-062 under contract N6onr-271 between the Office of Naval Research and Columbia University. Reproduction in whole or in part permitted for any purpose of the United States Government.

[2] (a) H. J. Lucas and Yun-Pu Liu, THIS JOURNAL, **56**, 460 (1934); (b) Yun-Pu Liu and Tien-Chi Wei, *J. Chinese Chem. Soc.*, **4**, 297 (1936); (c) J. B. Levy, R. W. Taft, Jr., and L. P. Hammett, THIS JOURNAL, **75**, 1253 (1953).

[3] (a) J. B. Levy, R. W. Taft, Jr., D. Aaron and L. P. Hammett, THIS JOURNAL, **73**, 3792 (1951); (b) R. W. Taft, Jr., J. B. Levy, D. Aaron and L. P. Hammett, *ibid.*, **74**, 4735 (1952).

[4] Rakowski, *Z. physik. Chem.*, **57**, 321 (1907).

with P_1^e and P_2^e the partial pressures of olefins I and II at equilibrium, ρ_1 and ρ_2 given by the expression

$$\tfrac{1}{2}\{k_1' + k_{-1} + k_2' + k_{-2} \pm \sqrt{(k_1' - k_2' + k_{-1} - k_{-2})^2 + 4k_{-1}k_{-2}}\} \quad (9)$$

with the plus and minus signs, respectively, and λ_1 and λ_2 given by substitution of ρ_1 and ρ_2, respectively, in the equations

$$-\lambda = \frac{k_{-1}Q}{k_1' + k_{-1} - \rho} = \frac{(k_2' + k_{-2} - \rho)Q}{k_{-2}} \quad (10)$$

It follows from eq. 7 and 8 that

$$s = -\frac{\mathrm{d}\ln(P - P^e)}{\mathrm{d}t} = \rho_1 \frac{1 - \dfrac{\rho_2(1 - \lambda_1\pi)(\lambda_2 - 1)}{\rho_1(1 - \lambda_2\pi)(\lambda_1 - 1)}e^{-(\rho_2 - \rho_1)t}}{1 - \dfrac{(1 - \lambda_1\pi)(\lambda_2 - 1)}{(1 - \lambda_2\pi)(\lambda_1 - 1)}e^{-(\rho_2 - \rho_1)t}} \quad (11)$$

with

$$\pi = P_2^e/(P^0 - P_1^e) \quad (12)$$

P being the total pressure of olefin, P^e the corresponding value at equilibrium, and P^0 the value at time 0. Setting $\mathrm{d}P_2/\mathrm{d}t = 0$ and $P_1 + P_2 = P^e$ in eq. 6 we have also

$$\pi = k_{-2}/Q(k_2' + k_{-2}) \quad (13)$$

In the cases with which we have worked the reversibility of the hydration is small, which means that k_{-1} and k_{-2} are considerably smaller than k_1' and k_2'; further the fact that the value of the slope s is decidedly different when the initial system contains only I from its value when II alone is initially present shows that the difference between k_1' and k_2' is considerable. Under such conditions the last term under the radical in expression (9) is a small quantity of the second order and we have to the first order of small quantities

$$\rho_1 = k_1' + k_{-1} \quad (14)$$

$$\rho_2 = k_2' + k_{-2} \quad (15)$$

By eq. (10) then we have

$$\lambda_1 = -\infty \quad (16)$$

$$\lambda_2 = 0 \quad (17)$$

to the same precision. Equation (11) then reduces to

$$s = \rho_1 \frac{1 + \pi(\rho_2/\rho_1)e^{-(\rho_2 - \rho_1)t}}{1 + \pi e^{-(\rho_2 - \rho_1)t}} \quad (18)$$

and, since π is a small quantity, to

$$s = \rho_1\{1 + \pi(\rho_2/\rho_1 - 1)e^{-(\rho_2 - \rho_1)t}\} \quad (19)$$

Since s is in fact independent of time to good precision in all our experiments the term involving time in eq. (19) must be negligible compared with unity and we have to the same precision

$$s = \rho_1 = k'_1 + k_{-1} = \frac{k_1}{h_1 + r/RT} + k_{-1} \quad (20)$$

If the initial system contains olefin II instead of olefin I the slope obviously is given by

$$s = \frac{k_2}{h_2 + r/RT} + k_{-2} \quad (21)$$

When a solution of *t*-amyl alcohol of known initial concentration C_a° is allowed to react to equilibrium the equations

$$K_1 = \frac{k_{-1}}{k_1} = \frac{P_1}{C_a} = \frac{P_1}{C_a^\circ - (h_1 + r/RT)P_1 - (h_2 + r/RT)P_2} \quad (22)$$

$$K_2 = \frac{k_{-2}}{k_2} = \frac{P_2}{C_a} = \frac{P_2}{C_a^\circ - (h_1 + r/RT)P_1 - (h_2 + r/RT)P_2} \quad (23)$$

will apply. Combining these we have

$$\frac{1}{K_1 + K_2} = \frac{C_a^\circ}{P_e} - \frac{r}{RT} - \frac{h_1P_1 + h_2P_2}{P_1 + P_2} \quad (24)$$

In our experiments the last term was never more than 1% of the total value of the right hand side and the sum $K_1 + K_2$ may therefore be calculated to satisfactory precision from the experimentally accessible value of P^e, the total pressure of olefin at equilibrium, and the known ratio r. From reported[5] standard free energy values the ratio K_2/K_1 may be estimated to be 0.13 at 35°, and there is indeed ample experimental evidence[6] that it is considerably smaller than 1. If we took it to be 0 we should alter our values of k_1 or k_2 by no more than 1% in the least favorable case. Substituting K_1k_1 for k_{-1} we may convert eq. (20) to the form

$$\frac{RT}{r(s - K_1k_1)} = \frac{1}{k_1} + \frac{h_1}{k_1}\frac{RT}{r} \quad (25)$$

and obtain the value of k_1 from the experimental values of s and r by successive approximations which converge rapidly because K_1k_1 is considerably smaller than s. We have used least squares methods to obtain the best value of the intercept $1/k_1$. The quantity K_1k_1 was negligible compared with s for trimethylethylene at 15°, and K_2k_2 was negligible for methylethylethylene at all temperatures involved.

Experimental

The method was that described as Procedure A in article I. Extensive studies of the kind described in that article on the effect of shaking rate led to the same conclusion, namely, that saturation equilibrium is maintained under the conditions employed. The solution was in all cases 0.973 *M* nitric acid.

Trimethylethylene was prepared from *t*-amyl alcohol with concentrated sulfuric acid,[6] and was twice distilled through a column filled with glass helices. The fraction boiling between 37.5 and 37.8° in the second distillation was used in the rate measurements; $n^{21.6}\mathrm{D}$ 1.3865. *as*-Methylethylethylene was Phillips Petroleum Co. technical grade reported to contain 95 mole per cent. of this hydrocarbon. It was fractionated through the same column and a middle fraction boiling between 30.3 and 30.7° at 759 mm. was used in the rate measurements; $n^{20}\mathrm{D}$ 1.3770.

Constancy of the Slope s.—In a typical case involving the hydration of trimethylethylene at 35°, 27 observations of pressure were made over a period of 224 minutes which corresponded to 80% completion of the hydration reaction. Least squares determination of the slope of the plot of ln $(P - P^e)$ against time gave a slope of -2.624×10^{-3} with a maximum deviation of 0.010 and a median deviation of 0.0043. Using only the first 9 points the best slope was 2.64 $\times 10^{-3}$, for the middle 9 it was 2.74×10^{-3}, and for the last 9 it was 2.78×10^{-3}. The value of s was always computed by least squares methods and the probable errors were always of this order of magnitude. The plots which were always made never showed any visual indication of curvature.

Determination of the Quantity $K_1 + K_2$.—Solutions of *t*-amyl alcohol of 0.031 *M* concentration were prepared in

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[5] "Selected Values of the Properties of Hydrocarbons," Circular of the National Bureau of Standards C461.

[6] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith and W. E. Vaughan, This Journal, **58**, 140 (1936).

0.973 *M* nitric acid in the apparatus and under the conditions described in article II under the heading "Dehydration Procedure" and were allowed to react to equilibrium. At 35° the partial pressure of olefin at equilibrium was found to be 0.0234 atm. for $r/RT = 0.0494$ and 0.0224 for $r/RT = 0.0542$. At 25° the values were 0.008 for $r/RT = 0.060$ and 0.007 for $r/RT = 0.064$. From these data we obtain for $K_1 + K_2$ 0.77 at 35° and 0.24 at 25°.

Results and Discussion

The specific rates obtained are tabulated in Table I along with the probable errors which measure their precision. The enthalpies and entropies of activation are reported in Table II together with probable errors computed from the probable errors of the specific rates. The constancy of $\Delta H\ddagger$ over the temperature range involved was tested by computing the value of *k* at the intermediate temperature from the values at the extreme temperatures assuming $\Delta H\ddagger$ to be constant. For I the value thus calculated is 16.7×10^{-5}, for II it is 20.5×10^{-5}. Our values of the distribution coefficient *h* of the olefin between gas phase and solution, valid to order of magnitude precision only are: for I, 12.4, 9.7 and 6.5 at 15, 25 and 35°, respectively; for II, 8.1, 8.1 and 5.9 at 10, 20, and 30°, respectively. These values are all in units of 10^3 mole l.$^{-1}$ atm.$^{-1}$.

TABLE I

SPECIFIC RATES, k_p IN 10^5 MOLE L.$^{-1}$ATM.$^{-1}$MIN.$^{-1}$ FOR THE HYDRATION OF GASEOUS OLEFINS IN 0.973 *M* NITRIC ACID

Temp., °C.	Trimethylethylene	Temp., °C.	Methylethylethylene
15	6.62 ± 0.095	10	7.58 ± 0.02
25	16.9 ± 0.9	20	19.84 ± 0.28
35	39.7 ± 2.1	30	48.4 ± 0.66

TABLE II

ENTHALPIES OF ACTIVATION, $\Delta H\ddagger$, IN KCAL. AND ENTROPIES OF ACTIVATION, $\Delta S\ddagger$, IN CAL./DEG. FOR THE HYDRATION OF GASEOUS OLEFINS

	Trimethylethylene	Methylethylethylene
$\Delta H\ddagger$	15.22 ± 0.56	15.22 ± 0.37
$\Delta S\ddagger$	−32.9 ± 1.9	−31.6 ± 1.4

As Table III shows the two pentenes with which we are here concerned hydrate at rates not very different from the rate for isobutene, yet there is a strong presumption that the small effect of the methyl group upon the rates derives from near compensation of significant decreases in both enthalpy and entropy of activation. The effects are in the same direction, although not as pronounced and therefore not as certain, as those concerned in the comparison of methylcyclopentene with isobutene which we reported in article II. As in that case these effects appear to derive largely from the fact that the larger molecules lose more in enthalpy and in entropy in the transfer from the gas state to a condensed phase than does a smaller one. The heat of evaporation at 25° of olefin I is 1.6 kcal. greater than that of isobutene, that of olefin II is 1.3 kcal. greater than that of isobutene.[7] The entropy of gaseous olefin I is 10.7 cal./deg. greater than that of isobutene, that of gaseous olefin II is 11.5 cal./deg. greater.

TABLE III

RELATIVE RATES OF HYDRATION AND RELATIVE ENTHALPIES AND ENTROPIES OF ACTIVATION

	Isobutene	Trimethylethylene	Methylethylethylene
k/k_0	(1)	0.77	1.42
$\Delta H\ddagger - \Delta H_0\ddagger$ (kcal.)	(0)	−1.49 ± 0.57	−1.49 ± 0.39
$\Delta S\ddagger - \Delta S_0\ddagger$ (cal./deg.)	(0)	−5.6 ± 1.9	−4.3 ± 1.5

No exact comparison is possible between our relative enthalpies and entropies of activation for the reaction of *gaseous* olefins and those of Lucas, *et al.*,[2] for the hydration of *dissolved* olefins. The two sets of values must differ by the uncertain differences in enthalpy and entropy of vaporization of the olefins from the dilute nitric acid.

NEW YORK 27, N. Y.

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[7] D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, THIS JOURNAL, **71**, 2767 (1949). *Cf.* ref. 5, p. 139.