The Dependence of the Rate of Hydration of Isobutene on the Acidity Function, H_o, and the Mechanism for Olefin Hydration in Aqueous Acids

By Robert W. Taft, Jr.

The rate, k_p, of hydration of gaseous isobutene at unit pressure by aqueous nitric acid solutions from 0.1 to 5 M and by 1.242 M sulfuric acid has been determined. Values of k_p are far from directly proportional to acid concentration but instead nearly proportional to the acidity function, h_0. Using the Setschenow equation, it is demonstrated that the rate, k_c, of hydration of dissolved isobutene at unit concentration is directly proportional to the acidity function, h_0. By the Hammett theory for the nature of the transition state for a reaction whose rate depends upon the acidity function, these results require that the hydration transition state is isobutene plus a proton, i.e., a "free" carbonium ion. A hydration mechanism is proposed which is consistent with this, the known stereochemical, and other requirements. A comparison of the present results with the rate dependence on acidity for the hydration of crotonaldehyde and β,β-dimethylacrolein indicates that α,β-unsaturated olefins hydrate in aqueous acids by a different mechanism than ordinary aliphatic olefins. Entropies of activation for all of these hydrations and the corresponding reverse reactions furnish strong confirmation of the correctness of the Hammett theory.

Lucas and co-workers[1] have found that the rate, k_c, of hydration of dissolved isobutene (and trimethylene) at unit concentration in mixtures of dilute aqueous nitric acid and potassium nitrate shows a relatively large salt effect. The reaction was investigated in 0.05 to 1 M nitric acid and ionic strengths up to 2. At constant ionic strength, k_c was found under these conditions to be directly proportional to the concentration of acid. However, a recent investigation of the rate, k_p, of hydration of gaseous isobutene at unit pressure by dilute nitric acid solution has indicated that the close equivalence of the effects of added salt and acid on the specific rate of hydration, $k_c/[H_3O^+]$ is probably the result of a compensation of different effects of acid and salt on the activity coefficients of H_3O^+, olefin and the hydration transition state.[2] It is therefore of importance to extend the investigation of rates of hydration of isobutene to more concentrated acid solutions, particularly because of the information obtained concerning the mechanism of olefin hydration in aqueous acids.

Results and Rate Relationships.—In Table I are reported data on the rates, k_p, of hydration of gaseous isobutene at essentially unit fugacity in nitric acid solutions up to 5 M and in 1.242 M sulfuric acid. It is apparent from the marked increase of the $k_p/(H_3O^+)$ ratio with acid concentration that the rate of hydration is far from directly proportional to acid concentration.

TABLE I

Rate Constants, k_p, for the Hydration of Gaseous Isobutene by Aqueous Nitric Acid in 10^4 Mole-l.$^{-1}$-atm.$^{-1}$-min.$^{-1}$ at 25.00°

M	k_p	$k_p/(H_3O^+)$	M	k_p	$k_p/(H_3O^+)$
0.0909	0.114	1.25	2.525	14.35	5.68
.506	.834	1.65	4.03	48.4	12.01
.973	2.21	2.27	5.04	110	21.8
1.515	4.78	3.16			

By aqueous sulfuric acid

1.242	3.83	3.08

(1) (a) H. J. Lucas and W. F. Eberz, This Journal, **56**, 460 (1934); (b) H. J. Lucas and Yun-Pu Liu, ibid., **56**, 2138 (1934).

(2) J. B. Levy, R. W. Taft, Jr., D. Aaron and L. P. Hammett, ibid., **73**, 3792 (1951).

Figure 1 shows a plot of the logarithm of the rate constant, k_p, vs. the Hammett acidity function, H_0.[3] The results indicate that log k_p is nearly (but not exactly) proportional to the acidity function in nitric acid solutions from 0.0909 to 5.04 M.

The slope of Fig. 1 shows an upward drift with increasing H_0, and its average value is not integral as is usually the case.[4] The rate constant, k_p, for the hydration of gaseous isobutene at unit fugacity by the Brönsted relation is[2,5]

$$k_p = k_p° \frac{(H_3O^+)\gamma_{H_3O^+}}{a_{H_2O}\gamma_\pm} = k_p'° a_{H^+} \frac{1}{\gamma_\pm} \quad (1)$$

where

k_p and $k_p'°$ are thermodynamic rate constants

(H_3O^+) is the concentration of hydronium ion (stoichiometric acid concentration)

$\gamma_{H_3O^+}$ the activity coefficient of hydronium ion

$\gamma_\pm$ the activity coefficient of the likewise positively charged transition state

a_{H_2O} is the activity of water

a_{H^+} is the activity of H$^+$

Since h_0 (the antilog of H_0) is given by $h_0 = a_{H^+}\gamma_B/\gamma_{BH^+}$, where γ_B and γ_{BH^+} are activity coefficients of a basic indicator and its conjugate acid, respectively, the condition for proportionality between k_p and h_0 (or log k_p and H_0) is

$$\gamma_{BH^+}/\gamma_\pm\gamma_B = \text{constant} \quad (2)$$

This is not the condition which normally leads to proportionality between k and h_0, but rather the relationship

$$\gamma_{BH^+}\gamma_0/\gamma_B\gamma_\pm = \text{constant} \quad (3)$$

(where γ_0 is the activity coefficient for dissolved olefin) would be expected providing that the transition state is effectively the substrate plus a proton.[4] The rate constant, k_c, for the hydration of dissolved isobutene at unit concentration is given by the equation

$$k_c = k_c° \frac{(H_3O^+)\gamma_{H_3O^+}\gamma_0}{a_{H_2O}\gamma_\pm} = k_c'° a_{H^+} \frac{\gamma_0}{\gamma_\pm} \quad (4)$$

(3) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 167–169.

(4) Reference 3, pp. 273–278.

(5) Note that the failure of direct proportionality between k_p and (H_3O^+) indicates by equation (1) that for this system the approximation that ratio of activity coefficients $\gamma_{H^+}/\gamma_\pm$ of the hydrogen ion to the likewise positively charged reaction transition state is unity is an extremely poor one. For further information on this point see ref. 8a.
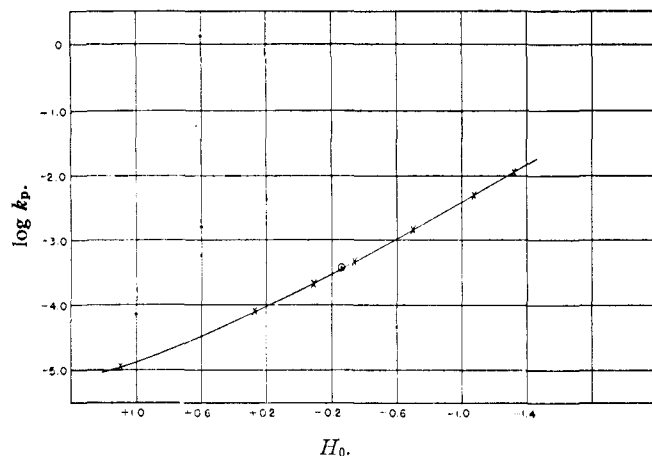
Fig. 1.—The dependence of the rate, k_p, of hydration of gaseous isobutene at unit pressure on the acidity function. H_0: ✕, aqueous nitric acid solutions; ⊙, aqueous sulfuric acid.

Since proportionality between k_c and h_0 would result if equation (3) holds, one is lead to suspect that it is the rate of hydration, k_c, of dissolved olefin at unit concentration rather than the rate, k_p, of gaseous olefin at unit pressure which should exactly parallel h_0. Fortunately this may be tested to a good approximation. Equations (2) and (3) differ by the term, γ_0, the activity coefficient of dissolved olefin, and this may be evaluated from available rate data (up to 1 M HNO_3) by the relationship which follows from equations(1) and (4)

$$\frac{(k_c/(H_3O^+))M_1}{(k_c/(H_3O^+))M_2} \Big/ \frac{(k_p/(H_3O^+))M_1}{(k_p/(H_3O^+))M_2} = \frac{(\gamma_0)M_1}{(\gamma_0)M_2} \quad (5)$$

where M_1 and M_2 refer to the appropriate terms at different acid concentrations. In Table II are given values of the activity coefficient of olefin, γ_0, at the given acid molarity. One-tenth molar nitric acid has been taken as the standard state in calculating these values from the rate data of Table I and references 1a and 2.

TABLE II

THE ACTIVITY COEFFICIENT OF ISOBUTENE AS A FUNCTION
OF NITRIC ACID CONCENTRATION AT 25°.

HNO_3, M	γ_0
0.10	(1.00)
.50	0.91
1.00	.85

The results in Table II indicate that the isobutene is "salted in" solution with increasing acid concentration. However, the effect is only a small one and follows, within the limits of accuracy of the γ_0 values, the Setschenow equation

$$\log \gamma_0 = -0.090\, c \quad (6)$$

where c = stoichiometric acid concentration.

If one assumes the Setschenow equation (6) to apply up to five molar nitric acid, as has previously been demonstrated for similar cases,[6a,b] it is possible to calculate values of log k_c from the data of Table I by the relationship[2]

(6) (a) G. Akerlöf, THIS JOURNAL, 57, 1196 (1935); (b) M. Randall and C. F. Failey, Chem. Rev., 4, 271 (1927). (c) This value of $10^3 h^0$ is in reasonably good agreement with that (5.18 ± 0.06) obtained by direct measurement (unpublished data).

$$\log k_c = \log \frac{k_p}{h^0} + \log \gamma_0 \quad (7)$$

where h^0 is the distribution ratio of isobutene between the standard 0.1 M nitric acid solution and the gas phase in mole-l.$^{-1}$-atm.$^{-1}$. A value of 10^3 h^0 = 5.4, obtained from the k_p/k_c ratio for 0.1 M nitric acid, was used in the calculations.[6c] In Fig. 2 the calculated log k_c values for acidities greater than 1 M as well as values of log k_c obtained by Lucas and Eberz[1a] and Ciapetta and Kilpatrick[7] in HNO_3, HCl and $HClO_4$ solutions of 1 M and less, are plotted against the acidity function, H_0. A single point for 1.242 M H_2SO_4 is included in Fig. 2; the log k_c value used was obtained by equation (7) taking γ_0 as unity.

The resulting linear relationship of very good precision and with a slope (1.07) very near to integral value confirms the validity of equations (1), (3) and (4). The dashed line in Fig. 2 is a curve through log k_c values plotted $vs.$ log (H_3O^+). This illustrates the failure of k_c to parallel the acid concentration, as well as showing the acidity region (above H_0 = 0) in which H_0 is diagnostic. The fact that log k_c directly parallels H_0 indicates that the near proportionality between log k_p and H_0 (Fig. 1) is the result of a nearly constant activity coefficient for dissolved isobutene and its small decrease with increasing acid concentration causes the upward drift in Fig. 1.
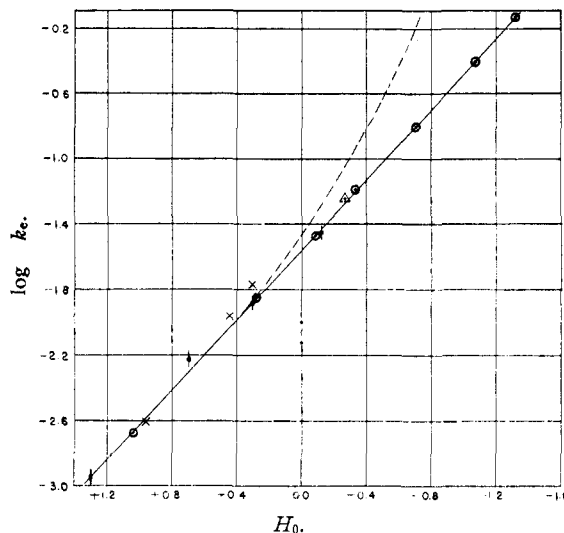

Fig. 2.—The dependence of the rate, k_c, of hydration of dissolved isobutene at unit concentration on the acidity function, H_0: ⊙, present results, nitric acid solutions; △, present results, sulfuric acid solution; ⬥, Lucas and Eberz, nitric acid solutions (ref. 1a); ✕, Ciapetta and Kilpatrick, hydrochloric acid and perchloric acid solutions (ref. 7).

The Mechanism of Olefin Hydration.—Hammett has presented evidence that for those acid-catalyzed reactions in aqueous solution for which *rates parallel* the stoichiometric *acid concentration*, the reaction transition state consists of substrate, a proton, and a water molecule; but for those reactions

(7) F. G. Ciapetta and M. Kilpatrick, THIS JOURNAL, 70, 639 (1948).

whose *rates parallel* H_0, the transition state does not contain the added water molecule. That is, the type of dependence of rate on acidity should be diagnostic of the presence or absence of an added water molecule in the transition state. The correctness of this theory is strongly supported by the recent work of Long and co-workers,[8] and it is consistent with other recent data.[9]

The present results therefore have important consequences concerning the mechanism of hydration of ordinary aliphatic olefins. The solubility of isobutene in aqueous nitric acid solutions is very considerably less than that calculated on the basis of ideal solubility. This indicates that dissolved isobutene is not present as a hydrate. The fact that k_c parallels H_0 requires by the Hammett theory, then, that the hydration transition state be simply olefin plus a proton, that is, a "*free*" carbonium ion. By "*free*" carbonium ion is meant an ion hydrated only by ion–dipole interaction without any strong covalent interactions between the ion and a water molecule. The steps usually considered as rate determining in olefin hydration are those involving either (1) a proton transfer from water to olefin with the formation of an unstable carbonium ion intermediate; (2) the reaction of a carbonium ion with water forming the conjugate acid of the resulting alcohol (preceded by a fast reversible step as in (1)); or (3) a concerted process involving an electrophilic attack by H_3O^+ at one of the unsaturated carbons and a nucleophilic attack by H_2O at the other carbon. All of these mechanisms must, however, be eliminated because the presence of at least one molecule of water is required in the "half reacted" or transition state.

The following mechanism is proposed as being consistent with the rate data and theory.
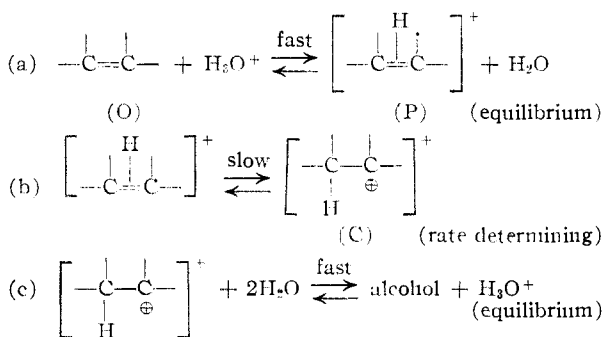
(P) and (C) are both unstable carbonium ion intermediates. (P) is a π-complex of the type considered by Dewar and others[10a,c] in which the proton is embedded in the π-orbitals which extend above (or below) the plane of the C–C double bond. (P) is of such nature that the stereochemistry of the olefin is preserved in the fast reversible step (a). In (C) the proton is covalently bonded by a σ sp^3 hybrid bond with the H–C–C tetrahedral

angle. The positive charge in (P) is probably nearly equally shared by the two unsaturated carbon atoms, while in (C) one of these bears a greater portion of the charge. The stereochemistry of the positive carbon in (C) is probably not preserved.[9] It is to be noted that the rate-determining step is the isomerization of the carbonium ions (P) to (C) and the transition state, intermediate between the two, is essentially the conjugate acid of the olefin (olefin plus proton)—a "free" carbonium ion. Dewar has indicated that there are theoretical reasons for believing that the isomerization from (P) to (C) requires activation.[10b]

The proposed mechanism is consistent with the rate equations (1) and (4). By the Brönsted relation, the rate of step (b) is

$$\text{vel.} = k(P)\frac{\gamma_P}{\gamma_{\ddagger}}, \text{ but, by the fast reversible step (a)}$$

$$(P) = K_a \frac{(O)(H_3O^+)\gamma_0\gamma_{H_3O^+}}{a_{H_2O}\gamma_P} = K'_a(O)a_{H^+}\frac{\gamma_0}{\gamma_P} \text{ so that}$$

$$\frac{\text{vel.}}{(O)} = k_c = kK'_a a_{H^+}\frac{\gamma_0}{\gamma_{\ddagger}} = k'_c a_{H^+}\frac{\gamma_0}{\gamma_{\ddagger}}$$

which is equation (4). Equation (1) follows from the relationship $a_0 = KP_0$ so that

$$\frac{\text{vel.}}{P_0} = k_P = kK'_a Ka_{H^+}\frac{1}{\gamma_{\ddagger}} = k'_P a_{H^+}\frac{1}{\gamma_{\ddagger}}$$

The proposed mechanism is further strongly confirmed on the basis that it is the only mechanism that is completely consistent with all of the following additional facts that are known concerning the hydration of olefins in aqueous acid: (1) the reaction involves specific acid catalysis by H_3O^+ (see reference 6 and Fig. 2); (2) no isomerization occurs during the course of the hydration of either 2-methylbutene-1 or 2-methylbutene-2 (which give the same (C), but different (P) carbonium ions) under conditions such that the rate of the reverse reaction is small compared to the forward rate[11]; (3) t-butyl nitrate is not an intermediate in the hydration of isobutene in aqueous nitric acid[12]; (4) the entropy of activation for the hydration of dissolved isobutene (at unit olefin and H_3O^+ concentrations) is $+2$ cal./deg.[13]; (5) the entropy of activation for the dehydration of t-butyl alcohol to isobutene is approximately $+25$ cal./deg. (at unit alcohol and H_3O^+ concentrations).[14] Points (1) and (3) argue strongly against any mechanisms involving participation by anions. Step (a) of the proposed mechanism fulfills the requirement for a reaction which shows specific acid catalysis. Point (2) supports the stereochemical requirements of the mechanism proposed. It is to be noted in this connection that no isomerization of *cis* and *trans* 2-butenes or 2-pentenes is obtained in the formation of Ag^+ com-

(8) (a) F. A. Long and M. Purchase, THIS JOURNAL, **72**, 3267 (1950); (b) F. A. Long, F. B. Dunkle and W. F. McDevit, *J. Phys. Colloid Chem.*, **55**, 829 (1951); (c) F. A. Long and L. Friedman, THIS JOURNAL, **72**, 3692 (1950).

(9) N. C. Deno and M. S. Newman, *ibid.*, **72**, 3852 (1950); **73**, 1920 (1951).

(10) (a) M. J. S. Dewar, *J. Chem. Soc.*, 406 (1946); (b) *Bull. soc. chim. France*, C71 (1951); (c) see ref. 22, p. 40.

(11) Unpublished results of J. B. Levy and L. P. Hammett.

(12) G. R. Lucas and L. P. Hammett, THIS JOURNAL, **64**, 1940 (1942).

(13) Calculated from the temperature coefficient work of Ciapetta and Kilpatrick[7] and of Lucas and Eberz.[18]

(14) (a) Calculated from the data of W. F. Eberz and H. J. Lucas, THIS JOURNAL, **56**, 1230 (1934); (b) a value of $\Delta\Delta S^{\ddagger} = +14.3$ cal./deg. (at unit alcohol and H_3O^+ concentration) was obtained by Taft, Levy, Aaron and Hammett (forthcoming publication in THIS JOURNAL) for the dehydration of 1-methylcyclopentanol-1 in 0.0909 M aqueous nitric acid

plexes with these olefins.[15] The π complex (P) is therefore analogous with the known Ag complexes in this respect, but the analogy is not complete for the formation of the Ag complex does not lead to hydration.[16,17]

It must be concluded that experimental evidence requires the existence of the free carbonium ion intermediate (C) first proposed by Whitmore[18] as well as a second kind of carbonium ion intermediate (P). Points (5) and (6) to be discussed in the next section add even further support. It is important to observe that the hydration mechanism requires that the rate-determining step in the reverse reaction (dehydration) is not the formation of carbonium ion (C) in step (c) but rather the isomerization of step (b). The basic ideas involved in this mechanism warrant serious consideration in allied carbonium ion reactions such as eliminations, rearrangements and polymerizations.

A comparison of the present results with the data of Winstein and Lucas on the hydration of *trans*-crotonaldehyde[19] and of Lucas, Stewart and Pressman on the hydration of β,β-dimethylacrolein[20] is most interesting and instructive. In the former case the reversible hydration to aldol was investigated in aqueous HNO_3 and $HClO_4$ solutions from 0.5 to 1.9 M. The rate of hydration was found to be closely proportional to the stoichiometric acid concentration and showed very little specificity to the anion present. Although the range of acidities is not as great as covered by the present investigation, the slight trend in the specific rate, $k/(H_3O^+)$, downward with increasing acid concentration indicates that rate could not parallel h_0 at higher acidities. The reversible hydration of β,β-dimethylacrolein to β-hydroxyisovaleraldehyde was studied in 0.5 and 1 M HNO_3 solutions and the rate of hydration is also strictly proportional to the acid concentration.

The different type of rate dependence on acidity than for isobutene, therefore, indicates by the Hammett theory that crotonaldehyde and β,β-dimethylacrolein hydrate by a different mechanism than ordinary aliphatic olefins. The reaction may be regarded as resulting from the nucleophilic attack by a water molecule on one of the unsaturated carbons, so that water is bonded in the transition state. The process is undoubtedly facilitated by a preliminary fast reversible addition of a proton to the conjugated carbonyl group.[19,21] This

picture is consistent with the general theory that ordinary olefins are normally nucleophilic but are rendered electrophilic by the presence of conjugated electron-seeking groups.[22] Additional evidence strongly supporting this view is discussed below.

Entropies of Activation and Reaction Mechanism. —The entropies of activation calculated by the absolute rate theory[23] for the reactions considered above provide striking confirmation of the Hammett theory that reactions whose rates parallel h_0 do not have water bonded[24] in the transition state whereas those whose rates parallel acid concentration do.

A consideration of the nature of steps (a) and (b) leads to the prediction that there should be *no large change in entropy* in the formation of the transition state for a hydration proceeding by this mechanism since there is no loss of translational motion accompanying these steps. On the other hand, any of the mechanisms in which one or more water molecules are bonded in the transition state should result in a large negative entropy of activation because of the loss in translational motion accompanying such an activation process. Further, it is apparent that since the reverse of step (c) involves the freeing of translational motion, the dehydration reaction should have a *large positive entropy* of activation. Any mechanism in which water is bonded in the transition state should not, however, be expected to have such a favorable entropy change accompanying the reverse reaction.

These expectations are clearly confirmed by entropies of activation which have been calculated from the available rate data,[25] and summarized below:

Olefin–alcohol	Hydration $\Delta S_f^{\ddagger}$, cal./deg.[26]	De-hydration $\Delta S_r^{\ddagger}$, cal./deg.[26]
Isobutene $\underset{r}{\overset{f}{\rightleftarrows}}$ *t*-butyl alcohol	+ 2	+25
1-Methylcyclopentene-1 $\underset{r}{\overset{f}{\rightleftarrows}}$ 1-Methylcyclopentanol-1	– 5	+14
Crotonaldehyde $\underset{r}{\overset{f}{\rightleftarrows}}$ aldol	–23	– 2
β,β-Dimethylacrolein $\underset{r}{\overset{f}{\rightleftarrows}}$ β-Hydroxyisovaleraldehyde	–23	– 9

(15) (a) H. J. Lucas, R. J. Moore and D Pressman, THIS JORRNAL, **65**, 227 (1943); (b) S. Winstein and H. J. Lucas. *ibid.*, **59**, 45 (1943).

(16) W. F. Eberz, H. J. Welge, D. M. Yost and H. J. Lucas. *ibid.*, **59**, 45 (1937).

(17) Attention is called in this connection to the considerations of Dewar leading to the conclusion that the bonding in the Ag + complex is of a different type than that in the π-complex with H +, and as a result the former is much more stable; ref. 10b, during discussions.

(18) F. C. Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

(19) S. Winstein and H. J. Lucas, THIS JOURNAL, **59**, 1461 (1937).

(20) H. J. Lucas, W. T. Stewart and D. P. Pressman, *ibid.*, **66**, 1818 (1944).

(21) The reversible addition of the proton to form a π complex with the C–C double bond in the preliminary step is not inconsistent with the rate data. However, the facts that the energy of activation is considerably less for the hydration of dissolved crotonaldehyde than isobutene (approximately 17.6 compared to 22.9 kcal.), and that crotyl alcohol and *trans*-crotonic acid do not hydrate at an appreciable rate (reference 16), as well as consideration from the standpoint of general theory, favor the view expressed above.

(22) C. C. Price, "Mechanisms of Reactions at the Carbon–Carbon Double Bond," Interscience Publishers, Inc., New York, N. Y., 1946, p. 46.

(23) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw–Hill Book Co., Inc., New York, N. Y., 1941.

(24) The phrase "water molecules bonded in the transition state" is used throughout this paper in the sense that there is a strong interaction of covalent character between these water molecules and the substrate molecule. Any positive ion in aqueous solution is of course hydrated by dipolar interaction, but this is not the type of interaction being considered.

(25) Data of references 13, 14, 19 and 20. See equations (8) and (9) of reference 2. Where required the ideal dilution law has been used to obtain entropies of activation at unit H_1O^+ concentration.

(26) Although some of the entropies of activation given probably have rather large uncertainties (as large perhaps as ±5 cal./deg.), the effects involved are of such magnitude as to he clearly outside of experimental error.

In essence, these data show that in each of these reactions the conversion of olefin to alcohol is accompanied by a decrease in entropy on the order of 20 cal. deg.$^{-1}$ mole^{-1}, but, according to expectations the ordinary aliphatic olefins have transition states whose formation from olefin results in little change in entropy. The α,β-unsaturated aldehydes, on the other hand, have transition states which are formed with a decrease in entropy even slightly greater than that for the olefin to alcohol conversion.

The complete accord between the entropies of activation from the absolute rate theory and the Hammett theory regarding the hydration mechanisms indicates that both are powerful tools for the investigation of reaction mechanisms.

Acknowledgment.—The author appreciates the helpful comments of Drs. F. A. Long, Victor Gold, N. C. Deno and L. P. Hammett.

Experimental

The experimental method was the same as previously reported (procedure B).[2] In every case plots of log $(P - P^e)$ vs. time gave straight lines over the entire region of the reaction studied (60 to 91% completion) and of the same high precision previously obtained. The rate constants, k_p, for 0.0909 and 0.973 m HNO₃ were obtained from the previous data.[2] In the other cases values of k_p are average values obtained by equation (5) of reference 2 from at least two experiments conducted at the indicated acidity. A value of h of 6 × 10^{-3} mole 1.$^{-1}$ atm.$^{-1}$ was used in each case to calculate k_p. The pair of experiments (at given acidity)

were carried out at appreciably different r values (r/RT = 0.08 to 0.125) but of such a magnitude that an error of 50% in h would introduce an error of no more than 3% in k_p. Shaking rates of 333 to 400 r.p.m. were used (the latter at the higher acidities). The temperature was controlled to 25.00 ± 0.01°.

In every case but for 5.04 m HNO₃, the calculated values of k_p for the two experiments agreed to within 2%, and the internal consistency with equation (5) was as good as the accuracy warrants. In the exceptional case, four experiments were performed and the maximum deviation from the average value of k_p was 7%. No systematic deviation of the k_p values with r was obtained, indicating (in view of the excellent nature of plots of log $(P - P^e)$ vs. time) that the reaction rate is so fast in this case ($t_{1/2}$ 6 to 10 minutes) as to approach the limit of accuracy of the experimental method. In view of these results, the value of k_p given for 5.04 m HNO₃ should be accurate to 10%, whereas the other values should not be in error by more than 5% (probably less in most cases).

Experiments were also performed in the 1.242, 3.111 and 6.22 m sulfuric acid solutions. In the former case, the values of k_p calculated as above from two experiments agreed within 5%. The average value is reported in Table I. In the latter two cases, the values of k_p calculated from experiments carried out at appreciably different r values differed by as much as 30%. Four experiments were performed in 3.111 m sulfuric acid, and the calculated values of k_p showed a regular decrease with increasing r. A more marked trend in the same direction was shown by k_p values calculated from two experiments in 6.22 m acid. The results in 3.111 and 6.22 m acid are not listed in Table I since the data indicate that equation (5) does not hold under these conditions. No reason can be given for these results, and the system was not further investigated. The crude values of k_p obtained in these two cases are markedly less than the corresponding values in nitric acid solution at equivalent h_0.

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The Copper-catalyzed Decomposition of Diazoketones[1]

By Peter Yates[2]

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The reaction of α-diazoketones with alcohols in the presence of copper has been shown to occur without rearrangement to give α-alkoxyketones. The reaction of α-diazoacetophenone with phenol, thiophenol, aniline and piperidine has also been shown to yield the analogous unrearranged products: in the reaction with phenol, 2-phenylbenzofuran was obtained as a second product. It is suggested that these reactions proceed with the intermediate formation, by the interaction of the diazoketone and copper, of the moiety, RCOCH, which then reacts with the active hydrogen compound.

Arndt and Eistert[3] state that silver, copper or platinum may be used as catalysts for the decomposition with rearrangement of diazoketones, i.e., for the Wolff rearrangement. Subsequent general discussions[4,5] of the Arndt–Eistert reaction have reiterated that copper may be used in place of the conventional silver oxide. The original literature, however, reveals very few instances of the use of copper. Arndt and Eistert[3] treated diazomethyl α-naphthyl ketone with aqueous ammonia in the presence of copper at 100° and obtained α-naphthylacetamide in 20% yield, whereas by the use of ammoniacal silver nitrate at 100° the amide was

obtained in 85% yield. The only other reference by these authors to the use of copper is to its action on 2-diazoacetyl-1-nitroanthracene in acetic acid solution, when the evolution of nitrogen and the formation of a red color was observed but no product was isolated. Reichstein and Morsman[6] observed that the action of copper on methyl α-diazothienonylacetate in methanol at 140–150° gave the methyl ester of thienylmalonic acid together with another unidentified product; the yield was unspecified. *Thus it may be seen that in the few cases where copper has been used in the Wolff rearrangement, either the yields have been abnormally low or the conditions have been abnormally forced.*

In a search for a catalyst more efficacious than silver oxide the decomposition of 1-diazo-2-nonadecanone[7] in ethanolic solution at 65–70° in the

(1) From a dissertation presented to the Faculty of the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1951.

(2) Socony-Vacuum Company Fellow, Yale University, 1949–1950.

(3) F. Arndt and B. Eistert, *Ber.*, **68**, 203 (1935).

(4) W. E. Bachmann and W. S. Struve, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 38.

(5) B. Eistert, "Newer Methods of Preparative Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1948, p. 513.

(6) T. Reichstein and H. J. Morsman, *Helv. Chim. Acta*, **17**, 1119 (1934).

(7) Cf. F. A. Vandenheuvel and P. Yates, *Can. J. Research*, **B28**, 556 (1950).