hydration of an aliphatic olefin. It is reasonable to suppose that the positive charge in the transition state is better dispersed in the styrene than in the aliphatic olefin case. This would imply that, in any particular medium, the former transition state is less strongly solvated (by water) than the latter. Consequently, as mineral acid molarity is increased (*i.e.*, a_{H_2O} decreased) the free energy of solvation of the former transition state should suffer less of a decrease. This then would lead to the steeper acidity dependence of the rate constants for hydration of styrene.[27,28] It is assumed that the medium effects on the differences in the free energy of solvation of the nonspecifically solvated olefins are of no great consequence.

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The Acid Cleavage of Allylmercuric Iodide

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Abstract: The rate-determining step in allylmercuric iodide cleavage by aqueous acid is proton transfer to carbon. The reaction shows a primary kinetic isotope effect, $\varkappa_H/\varkappa_D$, of 7.3 (measured competitively at 35°) and an over-all solvent isotope effect of 3.1 at the same temperature. From these values the rate constant at intermediate deuterium concentrations can be successfully calculated with no additional parameters. The temperature coefficient of $\varkappa_H/\varkappa_D$ leads to a $\Delta S°$ of -2.9 ± 0.3 cal. mole^{-1} deg.$^{-1}$, which suggests a certain amount of tunneling. The reaction shows general acid catalysis by molecular acetic acid and by methyldi(2-cyanoethyl)ammonium ion. For catalysis by the latter ΔH^* is 15.0 ± 0.4 kcal. mole^{-1} and ΔS^* is -27.7 ± 0.8 cal. mole^{-1} deg.$^{-1}$. For hydronium ion the comparable values are 16.21 ± 0.07 kcal. mole^{-1} and -12.6 ± 0.2 cal. mole^{-1} deg.$^{-1}$. In the absence of added iodide ion the original reaction is followed by complicating side reactions but these can be eliminated, without altering the rate constants, by adding small concentrations of sodium iodide.

In previous papers[2-4] the mechanism by which aqueous, nonhalogen acid cleaves the carbon–mercury bond has been examined. The present paper extends this study to allylmercuric iodide. The reaction products have been determined both for allyl- and crotylmercuric iodide. The form of the rate law has been studied both in the presence and in the absence of small amounts of iodide ion. General acid catalysis has been observed. Isotope effects, k_H/k_D, have been observed both by direct kinetic measurement and by competition experiments. The thermodynamic properties of activation, ΔH^* and ΔS^*, have been evaluated for both hydronium ion and methydi(2-cyanoethyl)-ammonium ion acting as acids. It is concluded from these that proton transfer is rate determining. Subsequent papers will explore the details of transition state structure more fully.

Results

Products. When allylmercuric iodide was treated with aqueous perchloric acid, 0.5 mole of propene, identified by its infrared spectrum, was produced per mole of allylmercuric iodide; the amount of product gas was determined manometrically. If the reacting solution contained sufficient sodium iodide to provide 1 mole of iodide ion per mole of allylmercuric iodide, 1 mole of propene per mole of starting material, identified both by its infrared and mass spectra, was produced. The quantity was determined manometrically. When the reaction was carried out in highly deuterated solvent, in the presence of 1 equiv. of iodide, the hydrocarbon product was mostly monodeuteriopropene with *no* dideuteriopropene. This was determined mass spectroscopically, and the precision is such that a few tenths of 1% of dideuteriopropene would have been detected.

In the presence of the iodide ion, 1 mole of mercuric iodide per mole of starting material is produced, identified by its ultraviolet spectrum and melting point. If no iodide is added, the ultraviolet spectrum of the reacting solution changes sequentially from that of the starting material to that of some unknown intermediate to a spectrum corresponding roughly to that of 0.5 mole of mercuric iodide per mole of starting material. Figure 1 shows a series of such spectra.

The reactions shown in eq. 1–4 are consistent with

$$\mathrm{CH_2{=}CH{-}CH_2HgI + H^+ \longrightarrow CH_3CH{=}CH_2 + HgI^+} \tag{1}$$

$$\mathrm{CH_2{=}CH{-}CH_2{-}HgI + HgI^+ \rightleftharpoons HgI_2 + A^+} \tag{2}$$

$$\mathrm{I^- + HgI^+ \rightleftharpoons HgI_2} \tag{3}$$

$$\mathrm{A^+ + H^+ \longrightarrow \text{other products}} \tag{4}$$

these observations and others that will be cited.

Attempts to determine the other products obtained in the absence of free iodide ion by means of vapor phase chromatography were unsuccessful. A number of low-intensity peaks were obtained, none of which could be positively identified. It was established that allyl alcohol was not among the products.

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(1) (a) Sloan Foundation Fellow, 1960–1964; (b) National Science Foundation Cooperative Graduate Fellow, 1963–1965; (c) National Science Foundation Undergraduate Research Participant, summer, 1964.

(2) M. M. Kreevoy, *J. Am. Chem. Soc.*, **79**, 5927 (1957).

(3) M. M. Kreevoy and R. L. Hansen, *ibid.*, **83**, 626 (1961).

(4) M. M. Kreevoy and R. A. Kretchmer, *ibid.*, **86**, 2435 (1964).

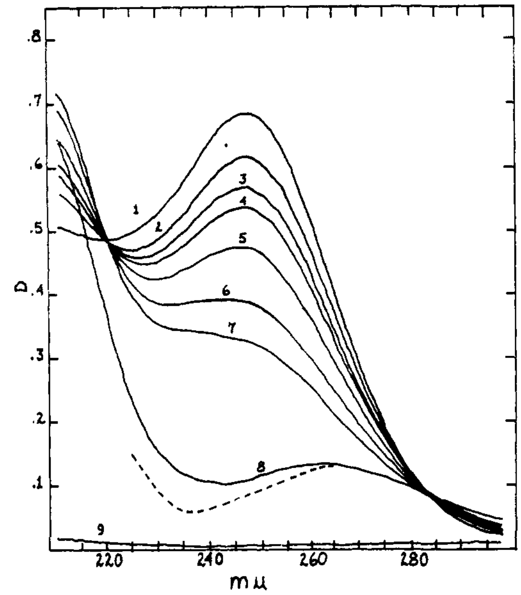

Figure 1. The ultraviolet spectrum of a reaction mixture initially containing 4.4×10^{-5} *M* allylmercuric iodide and 1.1×10^{-2} *M* perchloric acid: 1, is the initial spectrum (obtained without acid); 2, after 5 min.; 3, after 11 min.; 4, after 15 min.; 5, after 25 min.; 6, after 45 min.; 7, after 65 min.; 8, after 26 hr.; and 9, the base line. The dashed line is the spectrum of 2.2×10^{-5} *M* HgI_2.

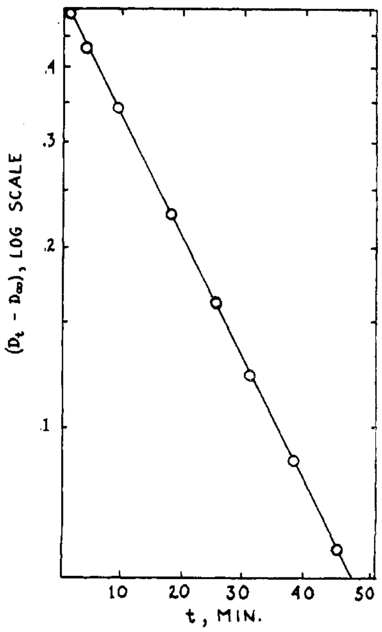

Figure 2. A test of the first-order rate law at 25°; the solution initially contained 4.4×10^{-5} *M* allylmercuric iodide, 5.08×10^{-2} *M* perchloric acid, and 4.4×10^{-5} *M* potassium iodide. The circles are the experimental points. The rate constant was obtained from the slope of the line which was fitted to the points visually. Every sixth experimental point is shown.

When *trans*-crotylmercuric iodide (stereochemistry determined by its infrared spectrum) was used in the place of allylmercuric iodide (with iodide ion) the gaseous product was 95% 1-butene and 5% *cis*-2-butene, identified by vapor phase chromatography. (It is possible that the latter came from a small amount of *cis*-crotylmercuric iodide, which could have escaped detection in the starting material.) No *trans*-2-butene could be detected. The rate with the crotyl compound is $^1/_8$ that with the allyl compound.

Rate Law. The progress of the reaction was followed spectrophotometrically, usually by following the disappearance of the broad, intense, allylmercuric iodide peak at 248 mμ. Except where otherwise indicated, all reaction mixtures contained 4% by volume of methanol (which was the solvent for the stock solution of allylmercuric iodide).

With initial substrate concentrations $\sim 4 \times 10^{-5}$ *M*, 1 mole of sodium iodide per mole of substrate, and perchloric acid concentrations between 5×10^{-3} and 2×10^{-1} *M*, the integrated, first-order rate law, shown in eq. 5,[5] was obeyed to >90% of completion within any one experiment (up to 97% in one case). In

$$k_1 = \frac{2.303}{t - t_0} \log \frac{D_0 - D_\infty}{D_t - D_\infty} \tag{5}$$

eq. 5 *t* is time, t_0 is some arbitrary initial time, *D* is an optical density, and the subscript on *D* indicates the time of the measurement. Figure 2 shows a typical test of the predicted linear relation between log $(D_t - D_\infty)$ and *t*. The pseudo-first-order rate constants, k_1, were evaluated in the usual way from the slopes of such lines. Repetitious determination of k_1 suggested an average deviation from the mean of about ±3%. Changes of initial substrate concentration in the range 4.4×10^{-5} to 1.1×10^{-5} *M* produced no measurable change in k_1.

Second-order rate constants, k_2, are given by $k_1/(H^+)$. Between 5×10^{-3} and 2×10^{-1} *M* these were invariant under changes in perchloric acid concentration apart from a small electrolyte effect which is discussed below. Values of k_2 at various temperatures, corrected for electrolyte effects, are given in Table II. The reaction is catalyzed by iodide ion but the effect of 10^{-4} *M* iodide on k_2 is <4%.[6] At the 4×10^{-5} *M* level which is typical of the present experiments the catalytic effect of iodide ion is less than the imprecision of the measurements.

As might be expected, eq. 5 is not obeyed in the absence of iodide ion. Figure 3 shows a typical plot of log $(D_t - D_\infty)$ *vs.* time under these conditions. The shape of such plots is not affected by changes in the initial substrate concentration from 8.8×10^{-6} to 4.4×10^{-5} *M*. An approximate evaluation of k_1 could be made as follows. The half-life of the first reaction was approximated from the first 50% of change in *D;* at 7 half-lives the reactions shown in eq. 1 and 2 should be 99% complete. A line was fitted to the curve extending from 7 to about 20 half-lives and this line was extrapolated back to t_0. The difference between the observed *D* and the extrapolated line, Δ, was taken as a measure of the progress of the reactions shown in eq. 1 and 2, and log Δ_t was plotted *vs.* time. These plots were reasonably linear and k_1 was obtained by means of eq. 6. The whole process is outlined in

$$k_1 = \frac{2.303}{2(t - t_0)} \log \left(\frac{\Delta_0}{\Delta_t}\right) \tag{6}$$

Figure 3. It is based on equations derivable by analogy

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(5) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," John Wiley and Sons, Inc., New York, N. Y., 1961, p. 29.

(6) M. M. Kreevoy, D. Goon, and R. A. Kayser, unpublished research.

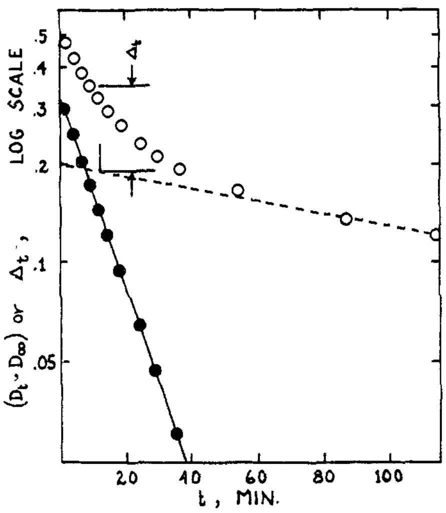

Figure 3. The change in optical density at 248 mμ as a function of time in the absence of iodide ion. Open circles are $(D_t - D_\infty)$ and closed circles are Δ_t. Every third experimental point is shown. The solution initially contained 4.4×10^{-5} M allylmercuric iodide and 3.3×10^{-2} M perchloric acid. The temperature was 25°.

with those for chains of radioactive decay,[7] and depends on the approximation that $k_1/(k_1' - 2k_1)$ is -0.5. (k_1' is the pseudo-first-order rate constant for the disappearance of the intermediate.) Actually the fraction is -0.53.

Equation 6 differs from eq. 5 by a factor of 2 in the coefficient of the logarithm. This enters because of the stoichiometry.[2] As before, k_2 could be obtained by dividing k_1 by (H$^+$). These values are somewhat less reliable than those obtained in the presence of iodide, but likewise showed no systematic change under changes in the perchloric acid concentration except for the small electrolyte effect. After correction, seven determinations gave a best value of 1.61×10^{-2} l. mole^{-1} sec.$^{-1}$ for k_2 at 25°. This can be compared with the value, 1.41×10^{-2} l. mole^{-1} sec.$^{-1}$, obtained at the same temperature with iodide ion present.

The structure of the intermediate, A, is not known, nor is the nature of its decomposition reaction, but the rate of the decomposition reaction seems to be a linear function of the acid concentration. A solution having an ultraviolet spectrum similar to that of A can be produced by treating allylmercuric iodide with 1 equiv. of silver nitrate and carefully centrifuging out the resulting precipitate. That spectrum also disappears at a rate linearly dependent on the acid concentration. The latter rate, however, seems to be about half of that obtained by starting with allylmercuric iodide and acid, and letting the reactions shown in eq. 1 and 2 produce A.

The Electrolyte Effect. The reaction is accelerated by the addition of sodium perchlorate and k_2 is also somewhat larger in more concentrated perchloric acid. In the more dilute solutions this acceleration can be represented, within the uncertainty of the measurements, by eq. 7,[8] in which μ is the ionic strength and C is an

$$\log k_2 = \log k_2^\circ + C\mu \qquad (7)$$

arbitrary constant. Twelve measurements, with μ varying from 5×10^{-3} to 0.11 (μ contains contributions from both perchloric acid and sodium perchlorate) were used to graphically obtain a value of 0.56 for C at 25°. The plot of log k_2 *vs.* μ is shown in Figure 4. The infinite dilution value of k_2, 1.41×10^{-2} l. mole^{-1} sec.$^{-1}$, was obtained by extrapolation. It is k_2°. Equation 7 and the 25° value of C were assumed to be applicable at other temperatures, as well, and they were used to obtain k_2° values from k_2 values. The corrections are small, however; never more than 15%.

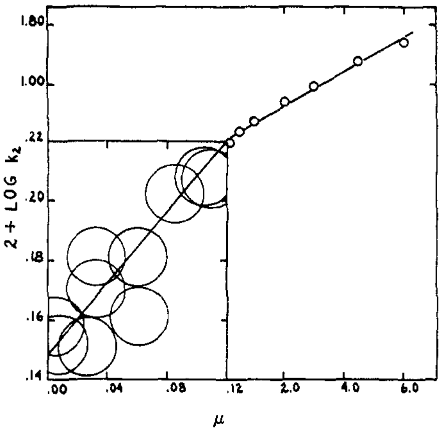

Figure 4. The effect of sodium perchlorate and perchloric acid on k_2. The two values of C were obtained from the two solid lines.

At higher sodium perchlorate concentrations, eq. 7 was still applicable, but a lower value of C was required, 0.23. An over-all view of the effect of sodium perchlorate and perchloric acid concentrations on k_2 is given in Figure 4.

General Acid Catalysis. Rates were measured in solutions containing methyldi(2-cyanoethyl)amine and its perchloric acid salt. A (constant) 1:1.1 ratio of amine to ammonium salt was maintained. Sodium perchlorate was used to maintain a constant ionic strength, 0.127 M. In the more concentrated buffer solutions there were noticeable deviations from a pseudo-first-order rate law at the lower fractional conversions, as shown in Figure 5. This could be eliminated by including mercuric iodide in the reaction mixture, in quantity approximately equivalent to the starting material. The pseudo-first-order rate constants so obtained tended to be higher by ~10% than those obtained from the straight portion of otherwise identical determinations in which the mercuric iodide was omitted. The origin of this difference is not clear, but it is not much larger than the random deviations. At the higher buffer concentrations, where the curvature was most marked, only k_1 values from solutions initially containing mercuric iodide were used. At lower concentrations k_1 values from both types of experiments were used.

At 35° a total of 10 values of k_1 were obtained, in solutions containing 1% of methanol, with weak acid concentrations between 0.02 and 0.11. An increase of a factor of 3.5 in k_1 was observed, from the lowest to the highest buffer concentration. The data are fitted satisfactorily by eq. 8[9] with a catalytic coefficient for the ammonium salt, k_{HA}, of $1.33 \pm 0.03 \times 10^{-4}$ l.

$$k_1 = k_2(\mathrm{H^+}) + k_{\mathrm{HA}}(\mathrm{HA}) \qquad (8)$$

mole^{-1} sec.$^{-1}$ and an intercept, k_2(H$^+$), of 2.4×10^{-6}

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[7] R. R. Williams, Jr., "Principles of Nuclear Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1950, pp. 127–129.

[8] Reference 5, p. 152.

[9] Reference 5, pp. 213–218.

sec.$^{-1}$.[9] The data were fitted to eq. 8 by the method of least squares.[10] The cited uncertainty in the slope is its 50% confidence limit. Confidence limits were not calculated at the other temperatures but the scatter seems comparable. Values of k_{HA} at various temperatures are shown in Table II.

The acid dissociation constant of methyldi(2-cyanoethyl)ammonium ion can be estimated from the intercept. The value, 4.0×10^{-2} l. mole^{-1} sec.$^{-1}$, was obtained for k_2 at 35° (with $\mu = 0.127$). This leads to 6.0×10^{-5} for (H$^+$). When this is combined with the buffer ratio an acid dissociation constant, K_{HA}, of 6.5×10^{-5} M is obtained. This acid dissociation constant can also be obtained in a more conventional way by pH titration with a glass electrode.[11] A value of 5.9×10^{-5} M was obtained for K_{HA} at 35°. This pertains to infinitely dilute aqueous solution. The Debye–Hückel first approximation (eq. 9) was used to obtain the re-

$$\log f_\pm = -0.51\sqrt{\mu}/(1 + \sqrt{\mu}) \qquad (9)$$

quired activity coefficient, $f_\pm$, in solutions of μ about 10^{-2}. The kinetically determined value pertains to solutions containing 1% methanol and having $\mu = 0.127$ M. In first approximation, however, this should not affect K_{HA}, as the dissociation involves no net change in charge type. The agreement is actually very satisfactory. Kinetically derived values of K_{HA} at a variety of temperatures are collected in Table I.

One value only for k_1 was obtained with an acetic acid–acetate buffer solution. This solution contained 0.174 M acid and 0.188 M acetate ion, at 59.6°, and gave $k_1 = 8.2 \times 10^{-5}$ sec.$^{-1}$. For such a solution (H$^+$) can be obtained from the known K_{HA}, 1.54×10^{-5},[12] and k_2 is available. Their product is 9.1×10^{-6} sec.$^{-1}$, smaller by a factor of 9 than the observed k_1. (Ionic strength effects on K_{HA} were estimated from the Debye–Hückel theory, those on k_2 from eq. 7.) When eq. 8 was applied to this datum a value of 4.2×10^{-4} l. mole^{-1} sec.$^{-1}$ was obtained for k_{HA}.

Isotope Effects. Fifteen determinations of $k_2°$ at 35° in the absence of methanol gave $3.90 \pm 0.21 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$.[13] Five similar determinations in D_2O gave $1.25 \pm 0.06 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$.[13] This leads to an isotope effect, $k_{\mathrm{H_2O}}/k_{\mathrm{D_2O}}$, of 3.12 with a probable error[14] of ±0.12.

Rates were also measured at 35° for intermediate isotopic compositions. These results are shown, along with a theoretical curve, in Figure 7.

A kinetic isotope effect was also determined by carrying out the reaction in partially deuterated solvents, collecting the propene produced, and determining the ratio of propene to monodeuteriopropene mass spectroscopically. Table I shows the invariance of the quantity $(\mathrm{RH/RD})_{\mathrm{product}} \times (\mathrm{D/H})_{\mathrm{solv}}$, dubbed $\varkappa_{\mathrm{H}}/\varkappa_{\mathrm{D}}$, under changes in solvent composition at 35°. The mean value of $\varkappa_{\mathrm{H}}/\varkappa_{\mathrm{D}}$ at 35° is 7.30 ± 0.08.[13] A series of measurements were also made at other temperatures, ranging from 25 to 80°. These are reported in Table II.

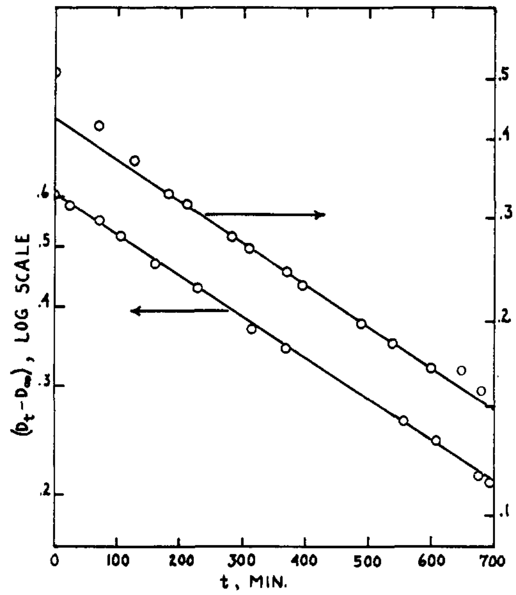

Figure 5. Cleavage of allylmercuric iodide by 0.126 M methyldi-(2-cyanoethyl)amine and 0.139 M of the corresponding ammonium perchlorate at 40°. The upper curve was obtained from a solution which initially contained no mercuric iodide; the lower from a solution initially containing 4.4×10^{-5} M substrate and 4.4×10^{-5} M mercuric iodide.

Table I. The Isotope Effect by Competition

$(\mathrm{D/H})_{\mathrm{solv}}$	$(\mathrm{RH/RD})_{\mathrm{prod}}$	$\varkappa_{\mathrm{H}}/\varkappa_{\mathrm{D}}$
0.677	10.57	7.16
1.09	6.072	7.34
1.57	4.633	7.27[a]
1.60	4.610	7.37
1.90	3.781	7.18
2.75	2.632	7.24
3.15	2.357	7.44
4.50	1.517	6.83[b]
10.47	0.703	7.36

[a] The allylmercuric iodide was predissolved so that the reaction mixture was homogeneous; details are given in the Experimental Section. [b] This was the first determination. $\varkappa_{\mathrm{H}}/\varkappa_{\mathrm{D}}$ differs from the mean of the other values by five times their average deviation from their mean. It was not included in the cited mean.

Rate and Equilibrium as a Function of Temperature. The parameters $k_2°$, k_{HA} (for methyldi(2-cyanoethyl)ammonium ion), K_{HA} (for methyldi(2-cyanoethyl)ammonium ion), and $\varkappa_{\mathrm{H}}/\varkappa_{\mathrm{D}}$ were all determined at various temperatures between 0 and 80°. The results are all collected in Table II.

Plots of log K_{HA} *vs.* $1/T$, log $(k_2°/T)$ *vs.* $1/T$, and log (k_{HA}/T) *vs.* $1/T$ were all without systematic curvature or scatter in excess of that suggested by their imprecision. The usual equations[15,16] were used to get the thermodynamic quantities of dissociation and activation by the method of least squares.[10] They are given in Table III.

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(10) C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and the Chemical Industry," John Wiley and Sons, Inc., New York, N. Y., 1954, pp. 36–40, 230, 231.

(11) V. Gold, "pH Measurements," John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter VI.

(12) G. Kortum, W. Vogel, and K. Andrussow, "Dissociation Constants of Organic Acids in Aqueous Solution," Butterworth and Co. (Publishers) Ltd., London, 1961, p. 241.

(13) The uncertainty is the average deviation from the mean.

(14) R. Livingston, "Physico Chemical Experiments," The Macmillan Co., New York, N. Y., 1948, pp. 29, 30.

(15) G. N. Lewis and M. Randall, "Thermodynamics," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1961, p. 173.

(16) M. M. Kreevoy in "Investigation of Rates and Mechanisms of Reactions," S. L. Friess, E. S. Lewis, and H. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, p. 1392.

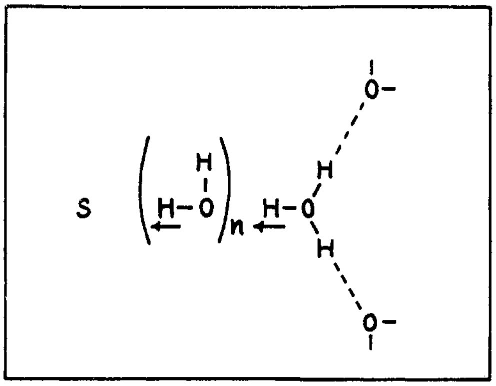

Figure 6. A reasonable picture of the transition state. *n* may be either 0 or some small integer. It is thought that only the innermost three hydrogens of the aqueous hydronium ion have isotopic compositions different from that of the solvent.[21–23] This figure points out the possibility that the transition state may have more.

The exact physical significance of $\varkappa_H/\varkappa_D$ is not entirely settled, and it is discussed below. It is clear, however, that it can be regarded formally as an equilibrium constant, and the associated thermodynamic quantities can be evaluated in the usual way.[15] They are also given in Table III. The plot of log $(\varkappa_H/\varkappa_D)$ *vs.* $1/T$ also shows no systematic curvature. Unfortunately it does show more scatter than might be expected from the 1% average deviation from the mean obtained at 35°. At other temperatures this scatter would seem to reflect an average of about ±5% uncertainty in the individual values. The origin of this difficulty is not known.

Table II. Rate and Equilibrium as a Function of Temperature

T, °C.	10^3 $k_2°$, l. mole^{-1} sec.$^{-1}$	10^5 k_{HA},[a] l. mole^{-1} sec.$^{-1}$	10^5 K_{HA},[a] M	$\varkappa_H/\varkappa_D$
0.0	0.95			
15.1	5.0			
25.0	14.1	4.4	4.6	7.7
35.0	34	13.3[b]	6.5[b]	7.30
39.2	54	21[c]	6.1[c]	
46.1	102			
48.1				6.05
54.9				6.15
59.8	250	81	12.7	5.43
64.1	380			
67.7				5.42
69.8				4.38
74.7	840	220	17.1	5.10
79.8				4.68

[a] For methyldi(2-cyanoethyl)ammonium ion at ionic strength 0.127. [b] These were measured in solutions containing 1% instead of 4% methanol. [c] The temperature was 40° instead of 39.2°.

Table III. Thermodynamic Parameters

Parameter	$\Delta H°$ or ΔH^*,[a] kcal. mole^{-1}	$\Delta S°$ or ΔS^*,[a] cal. mole^{-1} deg.$^{-1}$
$k_2°$	16.42 ± 0.05[b]	−11.9 ± 0.2[b]
	16.21 ± 0.07[c]	−12.6 ± 0.2[c]
k_{HA}	15.0 ± 0.4	−27.7 ± 0.8
K_{HA}	5.8 ± 0.3	−0.6 ± 0.9
$\varkappa_H/\varkappa_D$	−2.1 ± 0.1	−2.9 ± 0.3

[a] The tabulated uncertainties are 50% confidence limits. [b] Evaluated from all the data. [c] Evaluated from data pertaining to temperatures between 25 and 75°, so that the temperature range covered would coincide with that for k_{HA}.

Discussion

The stoichiometry shown in eq. 1–4 is in general accord with expectations for an allylmercury compound. In most respects it is similar to the pattern observed by Sleezer, Winstein, and Young.[17,18] when crotylmercuric bromide was cleaved with various acid solutions. The result with crotylmercuric iodide establishes that the position of attack is predominantly the γ-carbon, and the fact that this is slower than allylmercuric iodide cleavage makes it very likely that the latter compound is also attacked at the γ-carbon.

The *cis*-2-butene may arise from *cis*-crotylmercuric iodide present in the starting material. There is little question, from its infrared spectrum, that the bulk of the crotylmercuric bromide, which is the precursor of the crotylmercuric iodide, has the *trans* structure. The strong band, at 965 cm.$^{-1}$, characteristic of *trans* olefin, is present and the bands for *cis* olefins at 700 and 1600 cm.$^{-1}$ [19] are absent. However, this would not preclude the presence of the *cis* compound as an impurity. These compounds melt with decomposition, so that the melting point is not an assurance of purity. On the other hand, both *cis*- and *trans*-crotyltrimethyltin gave 98% 1-butene, 1–2% *cis*-2-butene, and little or no *trans*-2-butene, when cleaved with methanolic HCl.[20]

The absence of dideuteriopropene in the product of reactions in D_2O precludes the *reversible* formation of any intermediate in which the added proton becomes equivalent with any of the allylmercuric iodide protons. It is quite consistant with a rate-determining proton transfer.

The kinetic evidence strongly suggests that proton transfer from acid to carbon is rate determining. The primary hydrogen isotope effect, $(k_H/k_D)_I$, is the ratio of rate constants for the reactions shown in eq. 10 and 11, carried out in a common solvent. The M's can be either protium or deuterium, but must be the same in eq. 10 and 11. A reasonable picture of the transition state, which defines *n* and is useful in further discussion, is shown in Figure 6. Since the processes represented in eq. 10 and 11 determine the products, the product ratio in a mixed solvent is given by eq. 12, in which H or D is the hydrogen to be transferred to the substrate.

$$S + H\cdot(M_2O)_{n+1}^+ \longrightarrow SH^+ + (n+1)M_2O \qquad (10)$$

$$S + D\cdot(M_2O)_{n+1}^+ \longrightarrow SD^+ + (n+1)M_2O \qquad (11)$$

$$\frac{RH}{RD} = \frac{(S)\{H\cdot(M_2O)_{n+1}^+\}}{(S)\{D\cdot(M_2O)_{n+1}^+\}}\left(\frac{k_H}{k_D}\right)_I \qquad (12)$$

Since all the mobile protons in an aqueous acid solution are in rapid equilibrium, the ratio $\{H\cdot(M_2O)_{n+1}^+\}/\{D\cdot(M_2O)_{n+1}^+\}$ can be related to the isotopic content of the solvent by eq. 13, the equilibrium constant for which is λ. Combining eq. 12 and 13 it is readily

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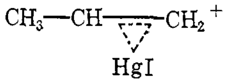
$$H\cdot(M_2O)_{n+1}^{+} + D_{solv} \overset{\lambda}{\rightleftharpoons} D\cdot(M_2O)_{n+1}^{+} + H_{solv} \qquad (13)$$

shown that $(k_H/k_D)_I$ is given by $\lambda(\kappa_H/\kappa_D)$. If $n \neq 0$ the hydrogen being transferred comes from an environment very similar to that in the bulk of the solvent, and it is likely that λ is close to unity. In that case $(k_H/k_D)_I$ is 7.3 at 35°. If $n = 0$, then λ is l, the isotopic fractionation constant for protons between the bulk of the solvent and the H_3O^+ unit of aqueous acids. This is thought to be around 0.7 at 25°[21,22] and only slightly temperature dependent,[23] leading to a value of 5.1 for $(k_H/k_D)_I$ at 35°.

In the "one frequency approximation"[24] the isotope effect expected for the transfer of a proton from a water-like environment at 35° is 10.4 (taking 3400 cm.$^{-1}$ as the O–H stretching frequency and 2400 cm.$^{-1}$ as the O–D stretching frequency). The frequencies appropriate to the H_3O^+ and D_3O^+ units of the $H\cdot(M_2O)_{n+1}^+$ molecules are not reliably known but they are certainly less than those for a water-like environment, so the predicted isotope effect would also be less. Examination of the two likely values of $(k_H/k_D)_I$ leaves little doubt that proton transfer is the chief component of the reaction coordinate. It is not required that the protonated substrate be a metastable intermediate,[25] but an attractive structure is available. This is the



same sort of intermediate which has been established for deoxymercuration[26] and suggested for vinylmercuric iodide cleavage.[4] Its formation in the rate-determining step would go a long way toward explaining the extreme facility of the present reaction.

The observation of general acid catalysis is also quite consistent with a rate-determining proton transfer. It is possible, of course, that the kinetically equivalent catalysis by general bases and the hydronium ion is being observed. In that case the proton transfer would be from the hydronium ion in each case and the base would, presumably, catalyze by complexing to the mercury. Iodide ion does function as a catalyst in this sense,[6] but it is very unlikely that acetate ion, which has a very feeble affinity for mercury,[27] would do so. The formation constant for $Hg(C_2H_3O_2)_2$ from Hg^+ and $C_2H_3O^-$ is some 16 powers of 10 smaller than that for HgI_2.[27] Deoxymercuration, which shows more pronounced iodide catalysis than the present reaction,[6,28] shows no catalysis by acetate ion.[26,29]

The isotope effect, k_{H_2O}/k_{D_2O}, 3.12, is obtained by exchanging *all* the exchangeable protons for deuterons. Since k_{H_2O}/k_{D_2O} is less than $(k_H/k_D)_I$, $(k_H/k_D)_{II}$, defined by eq. 14, must be less than unity. The existence of

$$(k_H/k_D)_I\,(k_H/k_D)_{II} = k_{H_2O}/k_{D_2O} \qquad (14)$$

such an effect in proton-transfer reactions was first suggested by Bunton and Shiner.[30] They used the model in which $n = 0$, and if that model is used in the present case, $(k_H/k_D)_{II}$ is 0.61, very close to the value suggested by Bunton and Shiner.[30] It is also very similar to the value, 0.54, which can be inferred from the data of Gold and Kessick[31] for acid-catalyzed hydration of isobutene, and the value, 0.60, obtained by Kresge and Onwood[32] for acid-catalyzed aromatic hydrogen exchange in 1,3-dimethoxybenzene. Earlier the effect had been semiquantitatively demonstrated for the acid cleavage of vinylmercuric iodide.[4] In the model with $n = 0$ that work would seem to lead to $(k_H/k_D)_{II} = 0.35$. The value of n is the object of current studies. If it should develop that $n \neq 0$, all of these values should be multiplied by 0.7.

There is no reason why $(k_H/k_D)_{II}$ should be the same for all reactions, and its value can be used to evaluate a quantity, α, related to α of the Brønsted catalysis law. Kresge[33] has recently defined α by means of eq. 15

$$l^{1-\alpha} = \frac{(D_2O\cdots M\cdots S^+)^{1/2}(H_2O)^{1/2}}{(H_2O\cdots M\cdots S^+)^{1/2}(D_2O)^{1/2}} \qquad (15)$$

for the model in which $n = 0$. Thus α will be near unity when the nontransfering protons are very much like the protons of water and near zero when they are very similar to those of the hydronium ion, varying, qualitatively at least, just as the Brønsted α would vary with the degree of proton transfer in such a transition state. From eq. 15 it is readily shown that α is given by eq. 16. In the present case α is 0.65, in qualitative accord with the large value of $(k_H/k_D)_I$. Both suggest that the transfering proton is in "mid-flight" in the transition state.

$$\alpha = \frac{\log (k_H/k_D)_{II}}{2 \log l} \qquad (16)$$

If the vinylmercuric iodide value of $(k_H/k_D)_{II}$ could be taken seriously, it would be in conflict with this theory, as it is $< l^2$. However, a rather large uncertainty is associated with that value, and some uncertainty is also associated with l, so that the inconsistency may be only apparent. All the other values of $(k_H/k_D)_{II}$ are greater than l^2, as required.

Kresge[33] has developed eq. 17 relating k_x, the rate

$$\frac{k_x}{k_H} = \frac{(1 - x + xl^{1-\alpha})^2(1 - x + xl^{1+2\alpha}k_{H_2O}/k_{D_2O})}{(1 - x + xl)^3} \qquad (17)$$

constant in a D_2O–H_2O mixture containing x atom fraction of deuterium, to k_{H_2O}/k_{D_2O}, α, x, and l. Figure 7 compares the curve calculated from eq. 17 with the experimental data for the present reaction. The agreement is satisfactory. It supports the value of $(k_H/k_D)_{II}$ and the evaluation of α by means of eq. 16. Equation 17 pertains to the model in which $n = 0$. A model with $n \neq 0$ involves the introduction of arbitrary parameters, but a reasonable assignment of these parameters gives an entirely equivalent curve, so that

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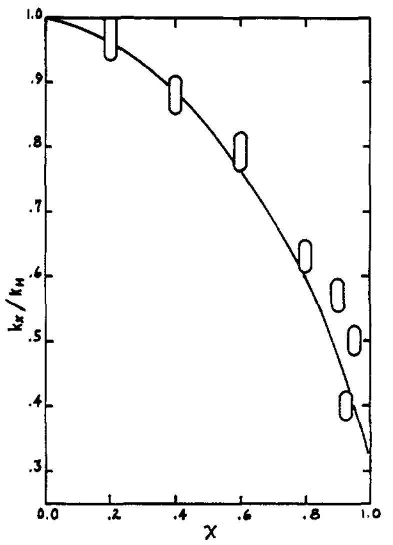

Figure 7. Comparison of observed k_x/k_H and that calculated using eq. 16 and 17. The calculated curve (solid line) is obtained without reference to any of the experimental points shown. The error outlines reflect an uncertainty of 5% in k_x/k_H and 2% in x.

although the agreement is consistent with $n = 0$, it does not uniquely prove it.

Gold[31] has recently shown that RH/RD for olefin hydration is given by eq. 18, thus avoiding the factoring

$$\mathrm{RH/RD} = (\mathrm{H/D})_{\mathrm{solv}} l^{(1+2\alpha)}(k_{\mathrm{H_2O}}/k_{\mathrm{D_2O}}) \tag{18}$$

of $k_{\mathrm{H_2O}}/k_{\mathrm{D_2O}}$ into primary and secondary effects. For the model in which $n = 0$, eq. 12 and 13 readily give the result shown in eq. 19. Equation 20 is obtained from

$$\mathrm{RH/RD} = (\mathrm{H/D})_{\mathrm{solv}} l^{-1}(k_{\mathrm{H}}/k_{\mathrm{D}})_{\mathrm{I}} \tag{19}$$

eq. 14 and the exponential form of eq. 16. From these

$$(k_{\mathrm{H}}/k_{\mathrm{D}})_{\mathrm{I}} = (k_{\mathrm{H_2O}}/k_{\mathrm{D_2O}}) l^{-2\alpha} \tag{20}$$

two, eq. 18 is obtained easily. Contrary to the previous supposition[31] this result has no bearing whatsoever on the comparative importance of the secondary solvent isotope effect, and differs from the present results only in formalism.

If the model with $n \neq 0$ is adopted, $(k_{\mathrm{H}}/k_{\mathrm{D}})_{\mathrm{II}}$ becomes more complicated because, now, *three* protons are becoming water like, and one of them is not the same as the other two. If the approximation is made that they *are* identical, α can be defined by eq. 21. Since the

$$\alpha = \frac{\log (k_{\mathrm{H}}/k_{\mathrm{D}})_{\mathrm{II}}}{3 \log l} \tag{21}$$

calculated value of $(k_{\mathrm{H}}/k_{\mathrm{D}})_{\mathrm{II}}$ goes down, in every case, by a factor of l, the qualitative position in comparing these values of $(k_{\mathrm{H}}/k_{\mathrm{D}})_{\mathrm{II}}$ with l^3 is exactly the same as when the previous values were compared with l^2. Quantitatively, all the values of α are a little higher.

The value of ΔS^* for hydronium ion is qualitatively similar to those previously observed for acid cleavage of organomercurials,[2-4] substantially negative. It is, however, numerically smaller than most of those previously reported. Qualitatively it is in accord with the generalization that proton transfer from hydronium ion to carbon involves a substantial, negative, activation entropy.

The comparison of ΔS^* for the hydronium ion and the amine salt is interesting. The former is very heavily hydrated in the starting state and presumably loses some of this hydration on its way to the transition state. This makes a positive contribution to ΔS^*. The latter has less to lose, and so, contributes less. The general origin of substantial negative activation entropies for proton transfer to carbon is still not understood, however.

The substantial electrolyte effect may contribute to the problem of interpreting rates in more concentrated acid for this type of reaction.[4]

Experimental Section[34]

Materials. Allylmercuric iodide was prepared by the method of Zinnin,[35] from allyl iodide and elemental mercury. It had m.p. 130–131° dec. (lit.[35] 135° dec.). In our hands the melting point was reduced on attempted purification by recrystallization.

Allyl iodide was prepared by a method described by Vogel[36] from allyl alcohol and hydriodic acid, and used immediately without further purification.

Crotylmercuric iodide was prepared from crotymercuric bromide, by equilibrating a solution of 1 g. of the latter, in 50 ml. of chloroform with four 50-ml. portions of 10% aqueous sodium iodide. It had m.p. 103–104° dec., taken in a sealed tube, after recrystallization from methanol. *Anal.* Calcd. for C_4H_7HgI: C, 12.57; H, 1.84. Found: C, 12.72; H, 1.64.

Crotylmercuric bromide was prepared by the method of Sleezer[17] from crotyl bromide (kindly furnished by Professor W. M. Lauer; $n^{20}\mathrm{D}$ 1.4783) *via* the Grignard reagent. It had m.p. 88–90° dec. (lit.[17] 90.8–91.2° dec.). Its infrared spectrum (mull) was as described,[17] and both infrared and n.m.r. spectra were appropriate to *trans*-crotylmercuric bromide, but 5–10% of *cis* material might have gone undetected.

Allylmercuric chloride was prepared in 39% yield from allyl chloride by adding Grignard reagent[37] to a tetrahydrofuran solution of an equivalent quantity of mercuric chloride. It had m.p. 105° dec. (lit. 102–103°,[38] 111–112°[39]), a suitable infrared spectrum, and, in the presence of excess iodide ion, gave cleavage rates identical with those of allylmercuric iodide. Attempts to purify it by crystallization lowered its melting point, but it could be stored for considerable lengths of time at room temperature without decomposition.

Methyldi(2-cyanoethyl)amine was prepared by twice cyanoethylating methylamine, as described by Preobrazhenski, *et al.*[40] The yield was 78% after vacuum distillation, $n^{20}\mathrm{D}$ 1.4610 (lit.[40] $n^{20}\mathrm{D}$ 1.4618).

Methanol used as a solvent for substrate stock solutions was redistilled commercial solvent. Acetic acid was Du Pont reagent grade material. Water used was deionized. Inorganic reagents were the best grades commercially available, and were used without further purification. Acid and base concentrations were determined by conventional titrations.

Rate Measurements. Rate measurements were carried out as previously described[26,29] except that the disappearance of the substrate peak at 2480 Å. was followed instead of the buildup of the mercuric iodide peak. Reactions in which the half-life was 24 hr. or less and the temperature no more than ~15° removed from room temperature were generally allowed to proceed in the spectrophotometer cell compartment. Those with longer half-lives or at temperatures further removed from room temperature were carried out in volumetric flasks in thermostats, with samples periodically removed for spectroscopic analysis.

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Product Collection. Most of these experiments were carried out in the general manner previously described,[4] except that cooling with ordinary ice was found to be sufficient during the outgassing procedure. As before, most of these reaction mixtures were physically heterogeneous. In most of these experiments, also, allylmercuric chloride was the starting material, and a twofold excess of iodide ion was used. It was assumed that the reaction actually takes place in solution and that allylmercuric chloride is rapidly converted to the iodide in a solution containing excess iodide ion. In a kinetic experiment identical cleavage rates were observed with allylmercuric iodide and chloride as starting materials and an excess of iodide ion. In addition one of the product collection experiments in which RH/RD was determined was carried out with predissolved allylmercuric iodide. The result is indistinguishable from the others.

The Effect of Charge-Transfer Complexation on the Hydrolysis of Some Carboxylic Acid Derivatives[1]

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Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois. *Received September 13, 1965*

Abstract: 3,5-Dinitrobenzoate ion has been shown to form a complex in aqueous solution with N-(indole-3-acryloyl)imidazole, *p*-nitrophenyl 3-indoleacrylate, and *p*-nitrophenyl 3-indoleacetate. The association constant for the first complex was determined both spectrophotometrically and kinetically, while the association constants of the other two complexes were only determined kinetically. Kinetic analysis indicates that, when complexed with 3,5-dinitrobenzoate ion, all three substrates are unreactive to hydroxide ion, or more specifically react with hydroxide ion less than 3% as fast as the uncomplexed substrate. The lack of reactivity of the complex between N-(indole-3-acryloyl)imidazole and 3,5-dinitrobenzoate ion is probably not due to electrostatic repulsion of the hydroxide ion by the carboxylate ion of the complexing agent, because the complex is also inert to reaction with the neutral nucleophile, *n*-butylamine. The inhibition of the hydrolysis of N-(indole-3-acryloyl)imidazole can not be attributed to steric effects due to complexation with the imidazole portion of the substrate since *p*-nitrophenyl 3-indoleacrylate is likewise inhibited and possesses a similar association constant. The results are rationalized in terms of the relative stabilization of the ground and transition states due to complexation.

The reactivities of labile compounds in solution have often been found to change in the presence of reagents that complex with them. For example, Higuchi and Lachman[3] found that caffeine will complex with ethyl *p*-aminobenzoate and inhibit its hydrolysis. Later Lach and Chin[4] discovered an even larger retardation of the hydrolysis of ethyl *p*-aminobenzoate, using β-cyclodextrin as the complexing agent. Recently Connors and Mollica[5] demonstrated a small inhibition of the hydrolysis of methyl cinnamate by imidazole. Ross and Kuntz[6] showed that the decrease in the bimolecular rate constants for the reaction between aniline and 2,4-dinitrochlorobenzene with increasing aniline concentration was due to molecular compound formation. While most of the examples in the literature involve rate inhibitions, rate increases due to complexation are also possible. One of the most notable of these is the work of Colter and coworkers[7] who studied the catalysis of the acetolysis of 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfonate by the donor molecule, phenanthrene. Also Cramer and Kampe[8] have shown that the association of cyclodextrins with β-keto acids will facilitate decarboxylation of these compounds. In most of the studies mentioned above the determination of association constants by kinetic methods was possible. In some instances information about the complexes was obtained that would be difficult to get otherwise. Thus these reactions serve as an important probe into the chemistry of complex formation. Furthermore, since all enzymatic processes involve reactions of substrates in the complexed state, the study of reactions of simple complexes may be very useful in the elucidation of enzymatic mechanism.

This research is concerned with the chemical behavior of carboxylic acid derivatives when subjected to charge-transfer complexation. It is well known that electronegative substituents on the acyl portion of benzoate esters greatly enhance their susceptibility to hydrolysis. If a bound complexing agent is regarded as a substituent of unknown location,[9] then it might be expected that a strong electron acceptor, which is able to bind with an aromatic acid derivative, would also increase its reactivity. Of course, other factors such as steric hindrance by the complexing agent may be important. It was hoped here to effect catalysis of the hydrolysis of a carboxylic acid derivative by proper complex formation between a donor substrate and an acceptor complexing agent.

The present study primarily involves an investigation of the hydrolysis of N-(indole-3-acryloyl)imidazole (I) in the presence of the complexing agent, 3,5-dinitrobenzoate ion (II) in aqueous solutions. The latter compound was chosen because it is known that poly-

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(1) This research was supported by a grant from the National Science Foundation.

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