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The Reaction of Vinylmercuric Iodide with Nonhalogen Acid¹

BY MAURICE M. KREEVOY AND RICHARD A. KRETCHMER

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The rate-determining step in the cleavage of vinylmercuric iodide to ethylene and HgI^+ is the transfer of a proton from a hydronium ion to carbon. The rate is first order in substrate and roughly proportional to the acid concentration up to $\sim 4 M$ perchloric or sulfuric acid. The solvent isotope effect, $k_{\text{H}}/k_{\text{D}}$, is 2.96 ± 0.10 at 25° in dilute perchloric acid. In $2.5 M$ sulfuric acid it is 2.2 ± 0.2 . The selectivity isotope effect, $\mathcal{R}_{\text{H}}/\mathcal{R}_{\text{D}}$, given by $(\text{RH/RD}) \times (x/1-x)$ where RH/RD is the ratio of normal to deuterated product and x , the atom fraction deuterium in an incompletely deuterated solvent, is 7.4 at 55° in $2.5 M$ sulfuric acid. The enthalpy and entropy of activation are $17.6 \pm 0.4 \text{ kcal. mole}^{-1}$ and $-16.5 \pm 1.3 \text{ cal. mole}^{-1} \text{ deg.}^{-1}$, respectively. These results require that proton transfer be rate determining and suggest a transition state somewhat more highly solvated than the starting state. It is further suggested that desolvation of the hydronium ion lags seriously behind the actual proton transfer. The HgI^+ , formed in the primary reaction, equilibrates rapidly with more substrate to give HgI_2 and $\text{C}_2\text{H}_3\text{Hg}^+$, which, in turn, decomposes to acetaldehyde and elemental mercury. The latter reacts slowly with HgI_2 to give Hg_2I_2 . Ethylene, acetaldehyde, and mercurous iodide have been demonstrated as final reaction products and HgI_2 has been shown to be an intermediate product.

In previous papers^{2,3} the rate and mechanism of cleavage of saturated alkylmercuric iodides by nonhalogen acids in aqueous solution have been examined. It would be expected that the vinyl compound would show quantitative and, perhaps, qualitative differences from the saturated compounds because of the availability of the π -electrons. These may permit the substrate to accept a proton without breaking the carbon-mercury bond. This expectation is strengthened by the observation⁴ that divinylmercury is cleaved about 100 times as rapidly as typical saturated dialkylmercurials by hydrochloric acid in a dimethylformamide-dimethyl sulfoxide mixture. The present paper describes the reaction of vinylmercuric iodide with aqueous perchloric and sulfuric acids. (The solvent also contained up to 3.4% methanol.) Products, dependence of rate on acid concentration, thermodynamic quantities of activation, and solvent isotope effect were studied. The reaction is much faster than that of typical saturated alkylmercuric iodides and shows other differences as well. A rather different mechanism is proposed.

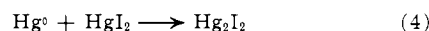
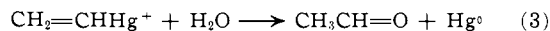
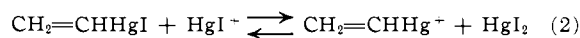
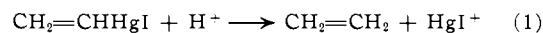
Results

Products.—In solutions containing $\sim 10^{-4} M$ vinylmercuric iodide, $\sim 5 M$ perchloric acid, and 2% methanol the ultraviolet spectrum of the starting material was progressively replaced with the familiar spectrum of mercuric iodide,^{2,3} as shown in Fig. 1. The presence of two clear isosbestic points indicates that no secondary reactions are important during the early stages of the cleavage. If the reaction was interrupted after 4 half-lives by the addition of somewhat more sodium acetate than required to react with the perchloric acid, then enough sodium iodide was added to make the final solution $0.13 M$ in iodide ion, the ultraviolet spectrum of HgI_4^{-2} was obtained. The intensity of that spectrum indicated the production of 0.43 mole of HgI_2 from each mole of vinylmercuric iodide at that time. The spectra of the product mixtures themselves suggested the eventual production of about 0.5 mole of HgI_2 from each mole of vinylmercuric iodide. However, these solutions did not reach a steady spectrum. Instead the optical density in the region of 2800 \AA .

reached a maximum sometime between five and ten half-lives and then began to fall at an appreciable rate. After ~ 200 half-lives a yellow-brown precipitate was observed in the reaction flask and the supernatant liquid contained no HgI_2 at all. The precipitate also gave HgI_4^{-2} on treatment with $0.13 M$ sodium iodide and was almost certainly mercurous iodide.⁵

It was not possible to determine the organic products of homogeneous reactions because of the low solubility of vinylmercuric iodide and the consequent small quantities of product available. When the reaction was carried out with vinylmercuric iodide present in excess of its solubility, each mole of vinylmercuric iodide produced 0.53 mole of ethylene. The amount of gas produced was determined manometrically and it was identified by its characteristic vapor phase infrared spectrum.⁶ In a similar experiment, part of the liquid product mixture was distilled directly into an alcoholic solution of 2,4-dinitrophenylhydrazine. The 2,4-dinitrophenylhydrazone of acetaldehyde was obtained, 0.24 mole from each mole of vinylmercuric iodide, m.p. and infrared spectrum identical with those of an authentic sample.

These observations can be rationalized on the basis of the reaction scheme shown.



The reactions shown in eq. 3 and 4 consume HgI_2 more slowly than it is produced in the reactions shown in eq. 1 and 2, but the factor is not large enough to permit a steady spectrum to be reached.

In further support of this scheme, vinylmercuric nitrate, produced by the action of silver nitrate on vinylmercuric iodide, has been shown to give acetaldehyde in the presence of water (isolated as its 2,4-dinitrophenylhydrazone). Also colloidal mercury, which can be produced by vigorously agitating the metal with water, has been shown to react with HgI_2 to give Hg_2I_2 at a rate compatible with the rate of decay of the HgI_2 spectrum in the kinetic experiments.

(1) Presented, in part, before the XIXth International Congress of Pure and Applied Chemistry, London, July, 1963.

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

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

(4) R. E. Dessy and Y. K. Lee, *ibid.*, **82**, 689 (1960).

(5) C. H. Rogers, T. O. Soine, and C. O. Wilson, "A Textbook of Inorganic Pharmaceutical Chemistry," 4th Ed., Leo and Febiger, Inc., Philadelphia, Pa., 1948, p. 418.

(6) American Petroleum Institute Project 44, infrared spectrum 18.

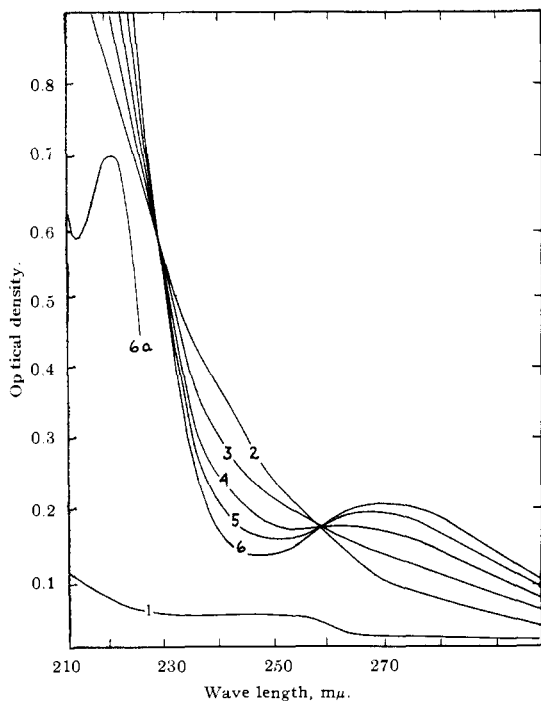


Fig. 1.—Spectra obtained during the cleavage of $8.2 \times 10^{-5} M$ vinylmercuric iodide by $5.9 M$ perchloric acid: 1 is the base line (solvent in both cells); 2 is the spectrum immediately after mixing; 3, after $\sim 30\%$ reaction; 4, after $\sim 60\%$ reaction; 5, about three half-lives; 6, highest concentration of mercuric iodide, reached after about seven half-lives. The short wave length end of spectrum 6 has been moved down 0.5 optical density unit and is shown as 6a.

Kinetics.—The progress of the reaction was followed by measuring the increase of optical density at 2800 \AA . corresponding to HgI_2 . The acid was always present in very large excess so that its concentration did not change significantly in the course of a single experiment. Attempts to use an integrated first-order rate law failed, presumably because consumption of HgI_2 by the reaction shown in eq. 4 becomes quantitatively significant during the latter part of the reaction. Pseudo-first-order rate constants, k_1 , could be obtained from the initial rate of change of optical density, dD/dt , by means of eq. 5 which is the differential rate law expressed in terms of optical densities.

$$k_1 = \frac{1}{l(S)_0(1/\epsilon_{\text{HgI}_2} - \epsilon_S)} \left(\frac{dD}{dt} \right)_0 \quad (5)$$

$S \equiv$ vinylmercuric iodide, $l \equiv$ cell optical path length, and $\epsilon \equiv$ molar extinction coefficient at $280 \text{ m}\mu$. (The light absorption by $\text{C}_2\text{H}_3\text{Hg}^+$ at $280 \text{ m}\mu$ has been ignored in eq. 5.) A typical evaluation of $(dD/dt)_0$ is shown in Fig. 2.

To improve the reliability of certain rate constants and to determine the precision with which rate constants could be evaluated by means of eq. 5, a number of separate experiments were carried out under each of three sets of conditions. Five determinations of k_1 by means of eq. 5 with $(S)_0$ $4 \times 10^{-5} M$ and $5.9 M$ perchloric acid at 25° gave an average value of $7.9 \times 10^{-4} \text{ sec.}^{-1}$ with an average deviation from the mean of $1.9 \times 10^{-4} \text{ sec.}^{-1}$. Six determinations of k_1 with $(S)_0$ $6.4 \times 10^{-5} M$ and $0.38 M$ perchloric acid gave an average value of $5.8 \times 10^{-5} \text{ sec.}^{-1}$ with an average deviation from the mean of $0.4 \times 10^{-5} \text{ sec.}^{-1}$. Six measurements of k_1 with $(S)_0$ $6.7 \times 10^{-5} M$ and $2.5 M$

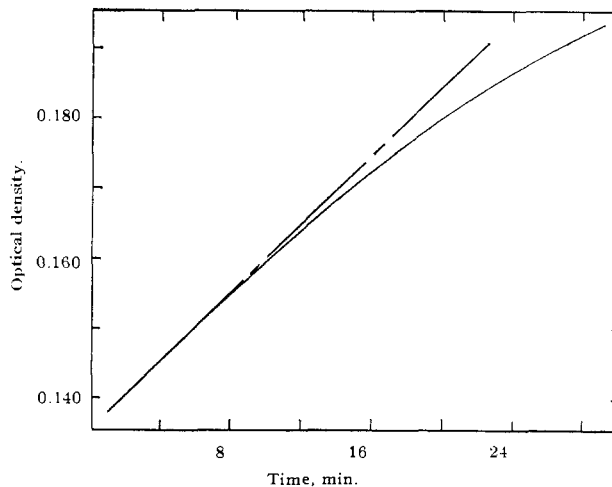


Fig. 2.—Typical plot from which $(dD/dt)_0$ was determined. The heavy line represents the trace produced by the spectrophotometer. The dashed line is the selected initial slope. The reaction was that of $6.7 \times 10^{-5} M$ vinylmercuric iodide with $0.17 M$ sulfuric acid at 25° in a 5.0-cm . cell.

sulfuric acid gave an average value of $8.5 \times 10^{-4} \text{ sec.}^{-1}$ and an average deviation from the mean of $0.8 \times 10^{-4} \text{ sec.}^{-1}$. These measurements suggest an uncertainty of about 10% in any individual determination of k_1 . This is, of course, reduced by taking the mean in each of the series of measurements cited above.⁷

To test the invariance of k_1 under changes in initial vinylmercuric iodide concentration it was determined in $5.9 M$ perchloric acid at 25° for six substrate concentrations covering a range of a factor of 14. The results, shown in Table I, provide satisfactory support for the hypothesis.

TABLE I
DEPENDENCE OF RATE ON SUBSTRATE CONCENTRATION IN
 $5.9 M \text{ HClO}_4$ AT 25°

$10^5(S)_0, M$	$10^4 k_1(\text{H}_3\text{O}^+), \text{sec.}^{-1}$
116	10.0
77.1	10.5
41.2	10.3
38.6	6.3
24.7	7.5
8.2	10.1

Acid Dependence.—Rates were measured in perchloric acid ranging from 0.4 to $7.1 M$ and in sulfuric acid ranging from 0.17 to $5.0 M$ at 25° . The rate rises with acid concentration in a roughly linear fashion up to $\sim 5 M$, as shown in Table II. In perchloric acid solutions more concentrated than $5 M$ there are systematic deviations toward still higher rates. Close examination of the perchloric acid data, particularly, reveals a shallow inflection at $\sim 2.5 M$ acid in a plot of k_1 vs. acid concentration. This could be eliminated by assuming a finite rate in the absence of acid.

In dilute perchloric acid a second-order rate constant, k_2 , can be defined by $k_1/(\text{H}^+)$, and the foregoing results show that k_2 is reasonably constant even up to $\sim 4 M$ perchloric acid. A value of $1.5 \times 10^{-4} \text{ l. mole}^{-1} \text{ sec.}^{-1}$ at 25° can be obtained from the first entry in Table II.

At comparable concentrations of acid k_1 in sulfuric acid is more than twice that in perchloric acid. Values of k_2 in sulfuric acid are not directly available because

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

TABLE II
DEPENDENCE OF RATE ON ACID CONCENTRATION

Acid	Concn., <i>M</i>	$10^4 k_1$, sec. ⁻¹	$10^{-4} k_2$ /(acid)
HClO ₄	0.376	0.58 ^a	1.54
HClO ₄	0.954	1.3	1.3
HClO ₄	2.36	2.9	1.2
HClO ₄	3.54	4.2	1.2
HClO ₄	4.72	6.1	1.3
HClO ₄	4.90	6.9	1.4
HClO ₄	5.90	9.0	1.5
HClO ₄	7.07	16	2.3
H ₂ SO ₄	0.172	0.70	4.1
H ₂ SO ₄	0.517	1.9	3.7
H ₂ SO ₄	1.034	4.2	4.1
H ₂ SO ₄	1.55	5.7	3.7
H ₂ SO ₄	2.07	6.7	3.2
H ₂ SO ₄	2.51	8.5 ^a	3.4
H ₂ SO ₄	2.61	7.5 ^b	2.9
H ₂ SO ₄	4.36	14	3.2
H ₂ SO ₄	5.04	18	3.5

^a Average of six determinations. ^b Average of five determinations.

of its partial dissociation as a dibasic acid in the dilute solutions and the presence of another acidic species, HSO₄⁻, which may also react with the substrate.

Temperature Dependence.—Rates were measured in perchloric acid solutions not exceeding 0.4 *M* at temperatures between 0 and 65°. A plot of log (k_2/T) vs. $1/T$ showed no systematic nonlinearity and the individual deviations from the line were consistent with a probable error of about 10% in each individual measurement. The enthalpy of activation was determined from eq. 6 by the method of least squares⁸ (*C* is a constant of integration; other symbols have conventional meanings). It has a value of 17.6 kcal. mole⁻¹ with 50% confidence limits⁸ of ±0.4 kcal. mole⁻¹, derived from a total of 19 rate constants. The entropy of activation, ΔS^\ddagger , derived from ΔH^\ddagger , the rate at 25°, and the usual thermodynamic equalities,⁹ is $-16.5 \pm$

$$R \ln (k_2/T) = -\Delta H^\ddagger/T + C \quad (6)$$

1.3 cal. mole⁻¹ deg.⁻¹.

Solvent Isotope Effect.—The six previously mentioned experiments in 0.38 *M* perchloric acid at 25° were used to determine a mean value of 1.54×10^{-4} l. mole⁻¹ sec.⁻¹ for k_2 with an average deviation from the mean of 0.10×10^{-4} and a probable error⁷ of 0.04×10^{-4} . Three experiments carried out at the same temperature and acid concentration in D₂O gave a mean k_2 of 5.20×10^{-5} l. mole⁻¹ sec.⁻¹ with an average deviation from the mean of 0.22×10^{-5} and a probable error of 0.12×10^{-5} . Combining these two values the solvent isotope effect, k_H/k_D , is 2.96 with a probable error of 0.10 under these conditions. This would not be significantly altered by taking into account the fraction of 1% hydrogen present in the experiments in D₂O.

Similar experiments were also carried out in 2.5 *M* sulfuric acid, giving k_H/k_{obsd} of 2.10, with a probable error of 0.13. In this case, because the sulfuric acid used was not, itself, initially deuterated, 6.0% of hydrogen was present. Assuming a linear dependence of

k_H/k_{obsd} on the deuterium content of the solvent this gives an extrapolated value of 2.17 for k_H/k_D . Assuming a nonlinear behavior of the sort commonly associated with a fast proton transfer preceding the rate-determining step,¹⁰⁻¹² a value of 2.24 is obtained for k_H/k_D . (Purlee's eq. 14¹⁰ and parameters were used to obtain this value, but the various, rather different, formulations of the theory all give much the same result for highly deuterated solvents with k_H/k_D in this range.¹⁰⁻¹²) These values are identical within their experimental uncertainty, and their average, 2.2 ± 0.2 , can be adopted as k_H/k_D in 2.5 *M* sulfuric acid.

A kinetic isotope effect was also estimated by carrying out the reaction in 94.3% deuterated 2.5 *M* sulfuric acid at 55°, then collecting the ethylene produced and determining the ratio of ethylene to monodeuterio-ethylene mass spectroscopically.¹³ Like the product determinations, this experiment was necessarily heterogeneous because of the low solubility of vinylmercuric iodide. The ratio C₂H₄/C₂H₃D was 0.447, obtained from the intensity of the mass 29 and mass 28 peaks. This leads to a selectivity isotope effect, $\mathcal{K}_H/\mathcal{K}_D$, of 7.4 when divided by 0.0605, the H-D ratio. Assuming that $\mathcal{K}_H/\mathcal{K}_D$ reflects an enthalpy change, its 25° value, 9.0, is readily obtained from the usual equations.¹⁴ An uncertainty of 2-3% in these ratios was estimated from the accuracy with which the intensity of the mass 27, 26, 25, and 24 peaks could then be predicted.

The mass 30 peak observed was not in excess of that required by the natural abundance of C¹³ and the intensity of the mass 29 peak. Thus there is no C₂H₂D₂ in the product. About 2% of C₂H₂D₂ would have doubled the observed mass 30 peak and would have been unmistakably detected.

Oxygen Effect.—Some formally similar reactions have been shown to be profoundly influenced by the presence of oxygen.¹⁵ The rate of production of HgI₂ in the present case was shown to be identical in solutions deoxygenated with nitrogen and those saturated with oxygen.

Discussion

The reactions shown in eq. 1 and 2 are analogous to those previously suggested^{2,3} for the acid cleavage of other alkylmercuric iodides. The reaction shown in eq. 3 probably occurs *via* the enol, as reactions of this sort have been observed for alkylmercurials^{16,17} and vinylmercurials.¹⁸ Reactions of the type shown in eq. 3 and 4 were probably responsible for some of the imprecision in the measured cleavage rates of isopropyl- and *t*-butylmercuric iodides.³

The isotope effects are consistent with a rate-determining proton transfer, and suggest that the reaction coordinate has a large component of proton motion. The values of k_H/k_D are in accord with the general ex-

(10) E. L. Purlee, *J. Am. Chem. Soc.*, **81**, 263 (1959).

(11) V. Gold, *Trans. Faraday Soc.*, **56**, 255 (1960).

(12) E. A. Halevi, F. A. Long, and M. A. Paul, *J. Am. Chem. Soc.*, **83**, 305 (1961).

(13) We are indebted to Dr. L. Peterson, of General Mills, Inc., for the necessary mass spectra and to Dr. Peterson and Dr. Danby of the Physical Chemistry Laboratory, Oxford University, for consultation on their interpretation.

(14) L. Melander, "Isotope Effects on Reaction Rates," The Ronald Press Co., New York, N. Y., 1960, p. 45.

(15) M. M. Kreevoy and R. L. Hansen, *J. Phys. Chem.*, **65**, 1055 (1961).

(16) F. R. Jensen and R. J. Ouellette, *J. Am. Chem. Soc.*, **83**, 4477 (1961).

(17) F. R. Jensen and R. J. Ouellette, *ibid.*, **83**, 4478 (1961).

(18) D. J. Foster and E. Tobler, *ibid.*, **83**, 851 (1961).

(8) 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, p. 21.

(9) A. A. Frost and R. C. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 275.

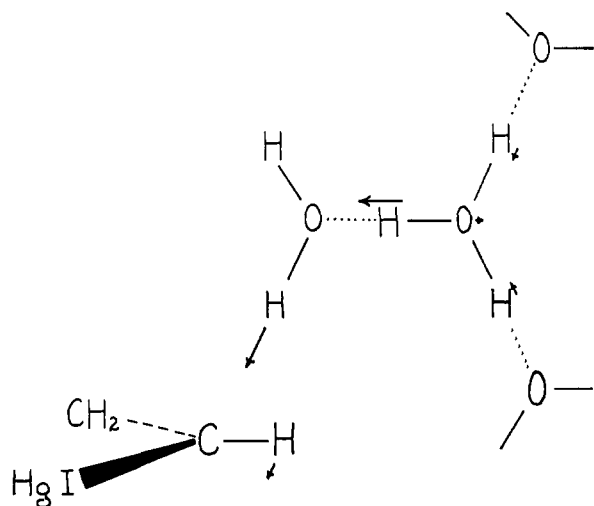


Fig. 3.—A plausible reaction coordinate. The arrows indicate the direction and approximate magnitude of the atomic motions. The dashed bond is behind the plane of the paper and the wedge bond is in front of it.

pectations arrived at by a consideration of zero-point vibrational energy^{19a} but in direct conflict with the idea of Long^{19b} that proton transfers from hydronium ion should not be subject to large isotope effects. At least two previous instances of $k_H/k_D \sim 3$ in proton transfer from hydronium ion have been reported.²⁰ The difference between k_H/k_D in dilute perchloric acid (2.96 ± 0.1) and k_H/k_D in 2.5 *M* sulfuric acid (2.2 ± 0.2) is probably real, as it is nearly three times the combined probable error. Differences of this sort have been observed previously,²¹ and suggest changes in the details of hydronium ion and transition state solvation.

If the zero-point vibrational energy point of view^{19a} is accepted $\mathcal{K}_H/\mathcal{K}_D$ is given, to a good approximation, by

$$\mathcal{K}_H/\mathcal{K}_D = \exp \frac{hc}{2kT} \left(\sum_3 \nu_H^{\text{aq}} - \sum_3 \nu_H^\ddagger - \sum_3 \nu_D^{\text{aq}} + \sum_3 \nu_D^\ddagger \right) \quad (7)$$

in which each of the summations is taken over the three vibrational frequencies of the proton or deuteron to be transferred. The observed value of $\mathcal{K}_H/\mathcal{K}_D$ leads to a value of 910 cm^{-1} for the quantity in parentheses. This is almost exactly the value that would result from the loss of a single stretching frequency in water.²² The difference between k_H/k_D and $\mathcal{K}_H/\mathcal{K}_D$ is probably due to the "secondary solvent isotope effect," suggested by Bunton and Shiner,²³ although the detailed interpretation of the relation between these two quantities depends on the models chosen for the transition state and the proton.

The absence of any $\text{C}_2\text{H}_2\text{D}_2$ from the reaction product in deuterated solvent precludes any appreciable reversibility in the proton transfer.

(19) (a) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, Chapter XI; (b) T. Riley and F. A. Long, *J. Am. Chem. Soc.*, **84**, 522 (1962).

(20) (a) R. P. Bell, J. Preston, and R. B. Whitney, *J. Chem. Soc.*, 1166 (1962); (b) A. J. Kresge and Y. Chiang, *J. Am. Chem. Soc.*, **84**, 3976 (1962).

(21) H. G. Kuivila and K. V. Nahabedian, *ibid.*, **83**, 2164 (1961).

(22) C. I. P. van Eck, H. Mendel, and J. Fahrenfort, *Proc. Roy. Soc. (London)*, **A247**, 472 (1958).

(23) C. A. Bunton and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **83**, 3214 (1961).

The most straightforward intermediate which could be formed by proton transfer to vinylmercuric iodide

is the primary carbonium ion $\overset{+}{\text{C}}\text{H}_2\text{CH}_2\text{HgI}$. However, the facility of the present reaction militates against this. It is many powers of ten faster than the hydration of ethylene under similar conditions.²⁴ The ethylene-mercuric iodide π -complex, $\text{CH}_2=\text{CH}_2^+ \cdot \text{HgI}$, which has the



same composition as the primary carbonium ion, is an intermediate in the facile deoxymercuration of $\text{CH}_3\text{-OCH}_2\text{CH}_2\text{HgI}$,²⁵ and may be the first metastable intermediate in the present reaction. However, it would be hard to form the π -complex in a well coordinated proton transfer and skeletal rearrangement because of the disparity in mass between the proton and the carbon atoms (and even more so between the proton and the mercury atom). This is supported by the relatively large values of k_H/k_D and $\mathcal{K}_H/\mathcal{K}_D$. Thus, if the π -complex is the first metastable intermediate, it is likely that extensive skeletal deformation takes place prior to the actual proton transfer.

A satisfactory picture of the reaction coordinate is shown in Fig. 3. If this picture were correct, and if desolvation went on, apace, as the proton was transferred, a small, probably positive, value of ΔS^\ddagger would be expected.²⁶ However, it is quite likely that proton transfers among properly oriented and activated molecules take place with half times of the order of 10^{-12} to 10^{-13} sec.^{27,28} On the other hand, the reorientation time for water seems to be of the order of 10^{-11} sec. at 25°, so it is unlikely that disorientation can keep pace with the actual transfer of the proton. Extensive prior disorientation, as part of the activation process, is also unlikely because of the very high heat of hydration of the hydronium ion (~ 100 kcal. mole⁻¹).³⁰ A substantial, negative entropy is quite reasonable if the proton transfer must occur from a still-oriented H_3O_4^+ unit, as the proton must be localized near the substrate and presumably some orientation of water around the substrate must take place as part of the activation process.

Other rate-determining proton transfers in aqueous solution also seem to give rise to substantial, negative entropies of activation. Alkylmercuric iodide cleavage by acid gives ~ -24 cal. mole⁻¹ deg.⁻¹ (a discussion of cyclopropylmercuric iodide will be postponed); acid-catalyzed enolizations give ~ -21 cal. mole⁻¹ deg.⁻¹³¹; the acid-catalyzed isomerization of *cis*-cinnamic acid gives -26 cal. mole⁻¹ deg.⁻¹.³² Nahabedian and Kuivila³³ give -5 cal. mole⁻¹ deg.⁻¹ as ΔS^\ddagger for protodeboronation of *p*-methoxybenzenboronic acid in 30% perchloric acid, but this appears to refer

(24) R. W. Taft, Jr., private communication.

(25) M. M. Kreevoy and F. R. Kowitz, *J. Am. Chem. Soc.*, **82**, 739 (1960).

(26) Following on the general lines of reasoning of L. L. Schaleger and F. A. Long in "Advances in Physical Organic Chemistry," V. Gold, Ed., Academic Press, Inc., New York, N. Y., 1963, pp. 14-17.

(27) T. Ackermann, *Z. physik. Chem.*, **27**, 34 (1961).

(28) M. M. Kreevoy and C. A. Mead, *J. Am. Chem. Soc.*, **84**, 4596 (1962).

(29) J. A. Saxton, *Proc. Roy. Soc. (London)*, **213**, 473 (1952).

(30) Reference 19a, p. 24.

(31) D. S. Noyce and W. L. Reed, *J. Am. Chem. Soc.*, **80**, 5539 (1958).

(32) D. S. Noyce, P. A. King, F. B. Kirby, and W. L. Reed, *ibid.*, **84**, 1632 (1962).

(33) K. V. Nahabedian and H. G. Kuivila, *ibid.*, **83**, 2167 (1961).

to the 30% acid as the standard state for the hydronium ion. Assuming that the rate parallels the Hammett acidity function,³⁴ the more conventional ΔS^\ddagger is -12 cal. mole⁻¹ deg.⁻¹. The acid-catalyzed hydration of ethynyl ethers³⁵ and thioethers³⁶ sometimes show ΔS^\ddagger close to zero, but the values become more negative with decreasing complexity of structure (-10 cal. mole⁻¹ deg.⁻¹ for methoxyethyne³⁵) so the solvent contribution to ΔS^\ddagger in these reactions may also be substantially negative. If negative entropies of activation are the rule they support the principal that, in proton transfers to water, the orientation of the solvent shell must occur prior to the actual act of transfer, while in proton transfers from hydronium ion desolvation cannot take place till after the actual proton transfer.

The behavior of k_1 as a function of acid concentration is almost identical with that of the methylmercuric iodide cleavage rate constant.² If $(\log k_1 + H_0)$ is plotted against the logarithm of the activity of water,³⁷ a_{H_2O} , strong curvature is observed. The best straight line drawn through the four points of lowest acidity has a slope of ~ 10 while the best straight line drawn through the four points of highest acidity has a slope of ~ 4 . The plot of $\log \{k_1/(H^+)\}$ against a_{H_2O} ³⁴ is more nearly linear and gives a best slope of ~ -0.4 (w^*), but close examination of this curve also reveals a slight, systematic nonlinearity. The curves are shown in Fig. 4. This sort of nonlinearity has led Kreevoy and Hansen³ to give $w \sim 12$ for the acid cleavage of alkylmercuric iodides, while Bunnett³⁴ cites values ~ 5 obtained from essentially the same data. In addition, some reactions, known to have proton transfer as their rate-determining step, give quite different behavior in moderately concentrated acid.^{20,32,37b} Thus the role of this criterion in determining the mechanism of such reactions still remains in doubt.

Rates in moderately concentrated sulfuric acid about twice those in perchloric acid of similar concentration have been observed in several proton transfer reactions^{2,20a,34} and have been variously attributed to a special mechanism³⁴ and to general acid catalysis by the bisulfate ion,^{20a} but the origin of this phenomenon, also, is not clear.

If the thermodynamic quantities of activation are used to extrapolate the present rate to 110° it is larger by a factor of 10³ than that of methylmercuric iodide and by an even larger factor than that of other alkylmercuric iodides³ (with the exception of cyclopropylmercuric iodide, which will be discussed separately). This is consistent with the hypothesis that the presence of the π -electrons opens up a new mechanism not available for the cleavage of ordinary alkylmercuric iodides. It is likely that this is also true in the hydrochloric acid cleavages,⁴ where a similar pattern of relative reactivities prevails.

Experimental³⁸

Materials.—Vinylmercuric iodide was prepared from vinylmercuric chloride by shaking a chloroform solution of the latter (17.0 g., 0.065 mole, in 500 ml. of chloroform) with three suc-

(34) H. G. Kuivila and K. V. Nahabedian, *J. Am. Chem. Soc.*, **83**, 2159 (1961).

(35) E. J. Stamhuis and W. Drenth, *Rec. trav. chim.*, **80**, 797 (1961).

(36) W. Drenth and H. Hogeveen, *ibid.*, **79**, 1002 (1960).

(37) (a) J. F. Bunnett, *J. Am. Chem. Soc.*, **83**, 4956 (1961); (b) *ibid.*, **83**, 4978 (1961).

(38) All melting points are corrected. Those for mercurials were obtained in sealed, evacuated capillaries.

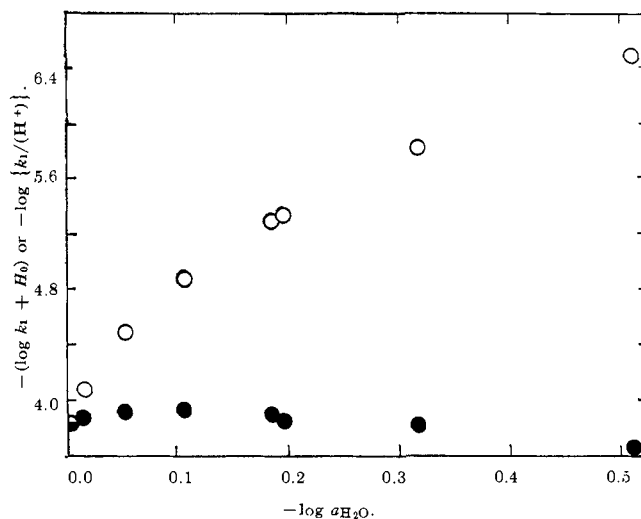


Fig. 4.—Plot of $(\log k_1 + H_0)$, open circles, and $\log \{k_1/(H^+)\}$, closed circles, against a_{H_2O} . The farthest point on the left is common to both curves.

cessive portions of 10% aqueous sodium iodide. After drying, removing the chloroform, and recrystallizing once from chloroform, vinylmercuric iodide, m.p. 152.5–153.5° (reported³⁹ 150–151.5°), crystallizing in large white plates, was obtained. The apparent yield was 51% (11.7 g., 0.033 mole), but the true yield was undoubtedly larger because the vinylmercuric chloride was contaminated with mercuric chloride.

Vinylmercuric chloride, m.p. 177–177.5° (reported³⁹ 185–186°), was prepared by dropping vinylmagnesium chloride in tetrahydrofuran solution⁴⁰ through a glass wool plug into a solution of 81.5 g. (0.30 mole) of mercuric chloride in 150 ml. of tetrahydrofuran, then allowing the mixture to stand overnight. The reaction mixture was diluted with 200 ml. of ether, then washed once with water and once with saturated sodium chloride. After drying, the volume was reduced to ~ 50 ml. under vacuum and 29 g. of crude product obtained by adding low boiling petroleum ether. This gave 17 g. of purified product after two sublimations under vacuum. The apparent yield was 31%, based on magnesium (the limiting reagent). The mercuric chloride content of this material was determined by dissolving 0.071 g. of it in 50 ml. of methanol, then diluting 1.0 ml. of this solution to 50 ml. with 0.1 M potassium iodide and examining the spectrum in the region of 320 m μ , where HgI_4^{-2} has $\epsilon 1.96 \times 10^4$. (Vinylmercuric compounds do not absorb in this region in the presence of 0.1 M iodide ion.) An optical density of 0.643 was observed, corresponding to 31% mercuric chloride in the vinylmercuric chloride.

Solvents, standard acid, and standard base were prepared and analyzed in the usual way.²

Product Isolation.—Vinylmercuric iodide (1.02 g., 2.86 mmoles) was mixed with (but did not dissolve in) 50 ml. of 6.1 M sulfuric acid in a flask with a standard taper joint. This was attached to a vacuum line, cooled with a Dry Ice–acetone mixture, and evacuated. The reaction mixture was then allowed to warm up to room temperature and outgas, whereupon it was recooled and re-evacuated. This was repeated twice more. Then the reaction mixture was magnetically stirred at 25° until no more gas was evolved (57 hr.). The final pressure over the reaction mixture was 126.1 mm., of which 10.1 mm. is the vapor pressure of water over 6.1 M sulfuric acid⁴¹ (verified by direct measurement). From the known volume of the available space, 116 mm. of gas was found to be 1.53 mmoles; 107% based on the stoichiometry of eq. 1 and 2. The gas was then allowed to expand, through a trap cooled with Dry Ice–acetone, into an evacuated infrared gas cell (10 cm.) in which its spectrum was obtained. It was unmistakably ethylene.

In a similar experiment starting with 1.16 g. (3.26 mmoles) of vinylmercuric iodide, part of the aqueous product mixture was distilled directly into 70 ml. of alcoholic 2,4-dinitrophenyl-

(39) D. Seyferth, *J. Org. Chem.*, **22**, 478 (1957).

(40) S. D. Rosenberg, A. J. Gibbons, and H. E. Ramsden, *J. Am. Chem. Soc.*, **79**, 2137 (1957).

(41) E. W. Washburn, "International Critical Tables," Vol. III, McGraw-Hill Book Co., Inc., New York, N. Y., 1928, p. 303.

hydrazine solution.⁴² The 2,4-dinitrophenylhydrazone obtained (0.18 g., 0.79 mmole, 48% based on the stoichiometry of eq. 1-4) had m.p. 165.5-166.5°; m.p. of authentic material, 165.5-167.5°. The derivative of the reaction product and the authentic sample had superimposable infrared spectra.

The experiment in which the partially deuterated ethylene was obtained for mass-spectrographic analysis was carried out in much the same way as that in which the sample was obtained for infrared analysis, except that an ordinary small container with a standard taper joint and a stopcock was used to collect the final product.

Comparison Experiments.—Silver nitrate (0.90 g., 5.3 mmoles) was added to 50 ml. of vinylmercuric iodide (1.18 g., 3.3 mmoles) solution in ethyl acetate. After the silver nitrate had metathesized to silver iodide, giving a solution of vinylmercuric nitrate in ethyl acetate, 50 ml. of water was added and the mixture was stirred for 18 hr. Then 10 ml. of the reaction mixture was distilled directly into 40 ml. of alcoholic 2,4-dinitrophenylhydrazine.⁴² Yellow-orange crystals separated, m.p., mixture m.p., and infrared spectrum identical with that of the 2,4-dinitrophenylhydrazone of acetaldehyde. The yield was 0.32 g., 43% based on vinylmercuric iodide.

It has been found that colloidal suspensions of mercury in water (and in other solvents) can readily be prepared by vigorously agitating the solvent with the liquid metal. The resulting liquids have spectra typical of suspensions—optical density rising continuously with decreasing wave length—but they are clear to the eye. The mercury content can be determined by adding an excess of sodium triiodide in 0.2 *M* sodium iodide and determining, spectrophotometrically, the amount of triiodide converted to HgI_4^{-2} . Such a suspension was made up containing $\sim 10^{-4}$ g.-atom l^{-1} of mercury. To this was added, as a stock solution in methanol, enough mercuric iodide so that the final solution contained 3.5×10^{-5} *M* of that substance. (The solution also contained 2% methanol.) Immediately after mixing, the ultraviolet spectrum was identical with that predicted by adding the spectra of the two starting materials, showing the HgI_2 peak at 260 $\text{m}\mu$ (λ_{max} slightly depressed because it rests on the continuously rising spectrum of the dispersion). On standing, the mercuric iodide peak decreases steadily in intensity, becoming a shoulder at ~ 60 hr., and no longer discernible at all after 140 hr. This behavior is consistent with the slow disappearance of the HgI_2 spectrum from the product solutions in kinetic experiments. The mercury would presumably come from the decomposition of $\text{C}_2\text{H}_5\text{Hg}^+$.

Kinetic Experiments.—Most kinetic experiments were carried out in the cell of a spectrophotometer. For experiments at 25° the temperature of the cell compartment was controlled by pumping water from a conventional thermostat through its housing. Both Beckman DU and DK-2 spectrophotometers were used, the former with a 1-cm. path length, the latter with a 5-cm. path length. All experiments at temperatures other than 25°

(42) R. L. Shiner, R. C. Fuson, and D. Y. Curlin, "The Systematic Identification of Organic Compounds," 4th Ed., John Wiley and Sons, Inc., New York, N. Y., 1959, p. 219.

(except those at 0°, which are described below) were carried out in the Beckman DK-2 spectrophotometer, using the electrically heated and controlled cell block to maintain the temperature (and cooling, when necessary, by pumping cold water through the housing). The temperature in the reaction cell was determined from the resistance of a calibrated thermistor immersed in the reference cell immediately before the reaction was carried out. Experiments at 0° were carried out in a volumetric flask immersed in a dewar of cracked-ice slush. Samples were withdrawn periodically for the measurement of optical density. If the measurement was made in the DK spectrophotometer the instrument was set to record optical density as a function of time at 280 $\text{m}\mu$ and the initial slope was evaluated directly from the resulting chart.

Spectra.—Infrared spectra were made on a Perkin-Elmer Model 21 spectrophotometer. Ultraviolet spectra were made on a Beckman DK-2 spectrophotometer.

Mass spectra were made on a Consolidated 21-103C mass spectrometer with an ionizing voltage of 70 v., a pressure of 41.6 μ , and wide slits. A small correction was made for air by assuming that the mass 32 peak was entirely due to atmospheric oxygen. The usual correction for the natural abundance of C^{13} reduced the mass 29 peak to 0.1% of the mass 28 peak in the undeuterated ethylene. After these corrections, the mass spectrum of undeuterated ethylene differed from that reported⁴³ by an average of 0.1% in the mass 28-26 peaks and by about 1% in the much less intense mass 25 and 24 peaks. The reported cracking pattern of monodeuterioethylene was used, along with the height of the mass 29 peak, to evaluate the contribution of the deuterated species to the mass 28 peak in the mixture. The residue was attributed to undeuterated ethylene and the ratio of the two species was calculated, using the reported⁴³ relative sensitivities. The heights of the mass 27-24 peaks could then be estimated by adding the contributions of the deuterated and the undeuterated species. These differed from the corrected experimental heights by $\sim 0.2\%$ in the case of the mass 27 and 26 peaks and $\sim 3\%$ in the case of the mass 25 and 24 peaks.

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(43) American Petroleum Institute Research project 44, mass spectrum 1164.