ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Acid Cleavage of Methylmercuric Iodide

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The mechanism of the reaction of methylmercuric iodide with strong aqueous acid (non-halogen acid) to give methane and mercury salts has been studied. From zero to five molar $HClO_4$ and H_2SO_4 at 100° the pseudo first-order rate constant, k_1, displays a nearly linear dependence on the hydronium ion concentration. Change of solvent from H_2O to D_2O has no measurable effect on the reaction rate. The heat of activation, $\Delta H^{\ddagger}$, as determined by the method of least squares from six determinations of k_1 between 92 and 161° is 22.2 ± 0.3 kcal./mole and the entropy of activation, $\Delta S^{\ddagger}$, is -29 ± 1 e.u. at 161°. Reaction with molecular acetic acid has been demonstrated. These facts are all consistent with a mechanism in which the rate-determining step is a proton transfer from oxygen to carbon accompanied by a breaking of the carbon–mercury bond. The solvent isotope effect and the entropy of activation suggest, however, that the carbon–mercury bond is very stretched in the transition state while the proton transfer is just beginning.

Nucleophilic aliphatic substitution has been the subject of a large number of quantitative studies.[1] By contrast, the number of quantitative studies of electrophilic aliphatic substitution is small.[2,3] The present work is aimed at elucidating the mechanism of the reaction of methylmercuric iodide with acids other than hydrohalic acids in aqueous solution. This is formally one of the simplest of all electrophilic aliphatic substitutions.

The reaction proceeds at a convenient rate only at temperatures near or above the boiling point of water so it was carried out in sealed ampoules. These ampoules were broken from time to time and the contents analyzed spectrophotometrically for the product, mercuric iodide. In this way the rate was studied as a function of sulfuric and perchloric acid concentrations, the solvent isotope effect was determined, the dependence of rate on temperature was studied from 92 to 161° and molecular acetic acid was studied as a reagent.

Results

Products.—It has been known for a long time that the cleavage of alkyl mercuric halides with strong acids gives the hydrocarbon.[4] There are two courses the reaction may take.

$$H^+ + CH_3HgI \longrightarrow CH_4 + HgI^+ \qquad (1)$$

$$H^+ + 2CH_3HgI \longrightarrow CH_4 + CH_3Hg^+ + HgI_2 \qquad (2)$$

Ultraviolet spectra of HgI^+, HgI_2 and CH_3Hg^+ were obtained, the latter two in good agreement with previous results.[5] The spectrum of CH_3Hg^+ is weak compared with those of HgI_2 and HgI^+. Figure 1 compares the spectrum of the product with those of HgI_2 and HgI^+. The latter two are not very different, but it is clear that the quantitative agreement with HgI_2 is much better than that with HgI^+. Disproportionation according to eq. 3 has an equilibrium constant of 10^{-2} [6] so it cannot account for the formation of HgI_2.

$$2HgI^+ \rightleftarrows Hg^{++} + HgI_2 \qquad (3)$$

Equation 2 must, therefore, represent the course of the reaction.

Rate Law.—If it is assumed that eq. 4 represents the rate-determining step and that HgI_2 is formed in a subsequent, fast, step (eq. 5) then the

$$H^+ + CH_3HgI \longrightarrow CH_4 + HgI^+ \qquad (4)$$

$$HgI^+ + CH_3HgI \longrightarrow CH_3Hg^+ + HgI_2 \qquad (5)$$

pseudo first-order rate constant, k_1, will be given by eq. 6 if the rate-determining step is first order in methylmercuric iodide.[7] In eq. 6 D_t is the optical density at time t.

$$k_1 = \frac{2.303}{2(t - t_0)} \log \frac{(D_\infty - D_0)}{(D_\infty - D_t)} \qquad (6)$$

Figure 2 shows a typical plot of fraction unreacted, $(D_\infty - D_0)/(D_\infty - D_t)$, as a function of t on semi-log graph paper. It is plain that the precision is not great, but there is no observable trend. Repetition under similar conditions indicated that rate constants were reproducible within about 10%. The first-order rate constants calculated from eq. 6 were invariant, within the experimental uncertainty, under a fivefold change in the initial methylmercuric iodide concentration.

Pseudo first-order kinetics always were observed because the acid always was kept in large excess and eq. 6 was used to obtain all the rate constants subsequently reported except those in acetic acid solution.

Dependence of Rate on Acid Concentration.—Tables I and II show the dependence of k_1 on acid concentration at 100° in sulfuric acid and perchloric acids, respectively. To a good approximation this dependence is linear in the region from one to five molar acid. Although somewhat different in value $k_1/(\mathrm{HA})$ is of the same order magnitude in perchloric and sulfuric acid. At concentrations of perchloric acid higher than five molar k_1 rises much more sharply than the acid concentration. With sulfuric acid the rates could not be followed to higher acid concentrations because of the increasing insolubility of the product, HgI_2.

It is clear from the third column in Tables I and II that the quantity k_1/h_0[8] is not constant.

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[1] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, Chapt. VII.

[2] S. Winstein and T. G. Traylor, THIS JOURNAL, **77**, 3747 (1955).

[3] F. Kaufman and A. H. Corwin, *ibid.*, **77**, 6280 (1955).

[4] F. C. Whitmore, "Organic Compounds of Mercury," The Chemical Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1921, p. 41.

[5] (a) H. Framherz and K. Lih, *Z. physik. Chem.*, **A167**, 103 (1933); (b) C. R. Crymble, *J. Chem. Soc.*, **105**, 658 (1914).

[6] L. G. Sillén and G. Infeldt, *Svensk. Kem. Tid.*, **58**, 61 (1946).

[7] The factor 1/2 enters because for each molecule of CH_3HgI that is consumed *via* eq. 3 another immediately disappears *via* eq. 4.

[8] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 275.

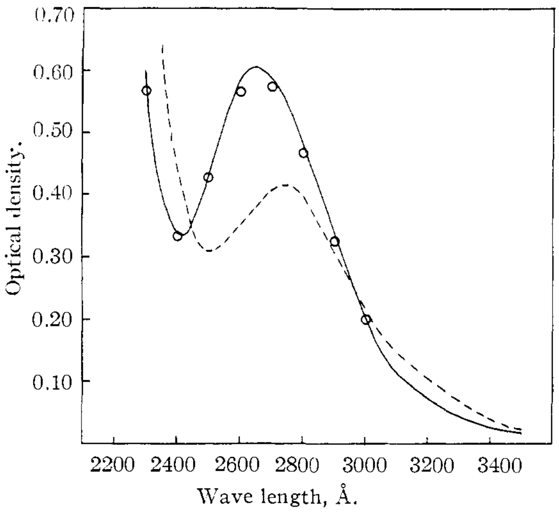

Fig. 1.—Product spectrum: ———, the calculated spectrum for 1.12×10^{-4} *M* HgI_2; ---------, the calculated spectrum for 2.24×10^{-4} *M* HgI^+; O, observed optical densities at 10 half-lives for a reaction mixture initially 2.24×10^{-4} *M* in CH_3H_2I.

Most of the data in Tables I and II were obtained from solutions which contained 4% by volume of methanol or dioxane. Comparison with experiments where these small volumes of organic solvent were not present (see Table III) indicates that they had no effect on the observed rate constants.

TABLE I

DEPENDENCE OF RATE ON SULFURIC ACID CONCENTRATION

(H_2SO_4),[a] moles/l.	$k_1/(H_2SO_4)$ l. mole^{-1} sec.$^{-1}$	k_1/h_0[b]
1.000	7.55×10^{-6}[c]	4.24×10^{-6}
1.077	7.57×10^{-6}[d]	4.08×10^{-6}
1.795	8.02×10^{-6}	2.68×10^{-6}
2.872	7.59×10^{-6}	1.47×10^{-6}
3.590	6.63×10^{-6}	6.73×10^{-7}
5.386	6.09×10^{-6}	1.14×10^{-7}

[a] Corrected for the change in density on heating; ref. 9. [b] h_0 is the anti-log of $-H_0$; values of H_0 obtained from M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1(1957). [c] Average of four determinations. Average deviation from the mean is 0.8×10^{-6}. [d] Average of two determinations.

TABLE II

DEPENDENCE OF RATE ON PERCHLORIC ACID CONCENTRATION

$(HClO_4)$,[a] moles/l.	$k_1/(HClO_4)$, l. mole^{-1} sec.$^{-1}$	k_1/h_0[b]
0.212	5.55×10^{-6}	5.55×10^{-6}
1.06	4.42×10^{-6}	2.63×10^{-6}
2.11	4.19×10^{-6}	1.19×10^{-6}
3.07	3.81×10^{-6}	4.66×10^{-7}
4.38	4.57×10^{-6}	2.00×10^{-7}
4.75	3.47×10^{-6}[c]	1.20×10^{-7}
6.57	9.67×10^{-6}	3.49×10^{-8}
7.66	27.4×10^{-6}	1.83×10^{-8}

[a] Corrected for the change in density on heating; ref. 9. [b] h_0 is the anti-log of $-H_0$; values of H_0 were obtained from M. A. Paul and F. A. Long, *Chem. Revs.*, **57**, 1 (1957). [c] Average of three determinations. Average deviation from the mean was $\pm 0.2 \times 10^{-6}$.

Effect of Temperature on Rate.—Table III shows the effect of temperature on k_1 for six temperatures in the range 92–161°. For these experiments the solutions were made up to constant acidity (1.122 *M*) with sulfuric acid. The final acidities, however, were slightly different, owing to thermal expansion. The final acid concentration was estimated by assuming that the specific gravity of a one molar sulfuric acid solution changes with temperature in the same way as pure water.[9] The second-order rate constant, $k_1/(H_2SO_4)$, was then used to calculate the heat of activation, $\Delta H^{\ddagger}$, and the entropy of activation, $\Delta S^{\ddagger}$.

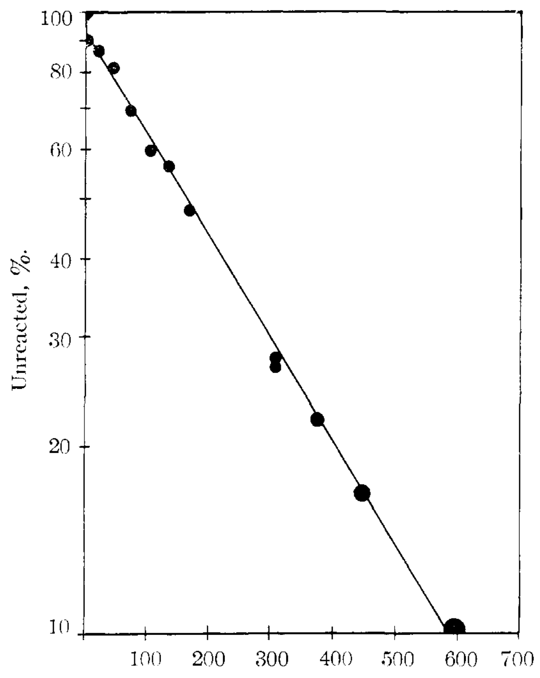

Fig. 2.—A typical plot of percentage unreacted *vs.* *t* on semi-log graph paper.

TABLE III

DEPENDENCE OF RATE ON TEMPERATURE

T,[a] °K.	k_1	Δ[b]
365.9	4.26×10^{-6}	−0.05
376.5	1.09×10^{-5}	.00
391.6	3.76×10^{-5}	+ .07
408.5	1.14×10^{-4}	− .03
420.9	2.99×10^{-4}	+ .11
433.7	5.34×10^{-6}	− .11
373.2	8.15×10^{-6}[c]	− .02

[a] Absolute temperature. [b] $\Delta = 2.303 \log \{k_1/(H_2SO_4) \times T\} + 11.184 \times 10^3/T - 12.27$. [c] Value obtained with 4% organic solvent—not used in the calculation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

The heat of activation was calculated from eq. 7[10] by the method of least squares.[11] The value

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[9] N. E. Dorsey, "Properties of Ordinary Water-Substance," Reinhold Publishing Corp., New York, N. Y., 1940, p. 591.

[10] Equation 7 was adapted from the differential equation of ref. 8, p. 97, relating the heat of activation to the rate constant k_1 and the absolute temperature *T*. k_0 is the pseudo first-order rate constant at some arbitrary absolute temperature T_0. The quantity in square brackets was treated as a parameter in the least squares determination of $-\Delta H^{\ddagger}/R$.

[11] T. B. Crumpler and J. H. Yoe, "Chemical Computations and Errors," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 217.

22.2 ± 0.3 kcal./mole was obtained. From the

$$2.303 \log \left\{\frac{k_1}{(H_2SO_4) \times T}\right\} = -\frac{\Delta H^{\ddagger}}{RT} + \left[\frac{\Delta H^{\ddagger}}{RT_0} - 2.303 \log \left\{\frac{T_0 \times (H_2SO_4)}{k_0}\right\}\right] \quad (7)$$

usual thermodynamic equalities[12] the value −29 ± 1 cal./mole deg. was obtained for $\Delta S^{\ddagger}$ at 161.7°.

If $\Delta H^{\ddagger}$ is temperature independent, then Δ, the difference between calculated and observed values of 2.303 log $\{k_1/(H_2SO_4) \times T\}$, should show no temperature dependence. The third column in Table III shows that Δ varies in a properly random fashion. The average absolute value of Δ is 0.06. A change of 10% in k_1 gives rise to a change of 0.09 in Δ, so the observed values of Δ are about what would be expected from the estimated uncertainty of k_1. The standard uncertainties in $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were calculated in the usual way and are listed with the quantities themselves.

The data in the last row of Table III were taken from the second row of Table I. The solutions used contained 4% of organic solvent (see Experimental) but were otherwise the same as those used to obtain the other data in Table III. The small value of Δ for these data indicates that the presence of the organic solvent had little effect on the rate constant, but they were not used in calculating $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ would have had the same values but slightly smaller probable uncertainties if these data had been so used.

Solvent Isotope Effect.—Substitution of deuterium for hydrogen in the solvent had no significant effect on the rate. For two reactions at about one molar D_2SO_4 in D_2O (the solutions contained 96 atom % D), k_1/D_2SO_4 was 7.65×10^{-6} l./mole sec. while $k_1/(H_2SO_4)$ in H_2O was 7.56×10^{-6} l./mole sec. at about the same acid concentration. Both of these values are, of course, subject to some uncertainty, but the solvent isotope effect cannot be large, in any event.

General Acid Catalysis.—At 161° acetic acid–acetate buffers would also bring about an increase in optical density at 2700 Å. The spectrum of the product resembled that of HgI^+ more than that of HgI_2, however, so $HgIOCOCH_3$ and CH_4 were assumed to be the final products. The pseudo first-order rate constants were evaluated by eq. 8.

$$k_1 = \frac{2.303}{t - t_0} \log \frac{D_\infty - D_0}{D_\infty - D_t} \quad (8)$$

Equation 8 was obeyed from 0 to 70% reaction.

At 1.40 *M* acetic acid and 0.183 *M* sodium acetate, k_1 had the value 1.21×10^{-5} sec.$^{-1}$, while at 0.280 *M* acetic acid and 0.0366 *M* sodium acetate k_1 had the value 2.9×10^{-6} sec.$^{-1}$. The value of k_1 thus seems to be approximately proportional to the acetic acid concentration at constant buffer ratio.

This is not, strictly speaking, general acid catalysis, as the acid actually is being consumed in this reaction. But the finding that molecular acetic acid will bring about this reaction in aqueous solution bears the same relation to this reaction that the finding of catalysis by acetic acid would bear to an *acid-catalyzed* reaction.

Discussion

All of the facts presented above are consistent with the picture of a single, rate-determining step in which the carbon–mercury bond is broken and the proton is transferred from oxygen to carbon. In the transition state the carbon–mercury bond is pictured as almost completely broken, to give a very large $C^{\ominus}$–$Hg^{\oplus}$ dipole while the hydrogen–oxygen bond is only slightly weakened and the carbon–hydrogen bond is just beginning to form. The facts are discussed in terms of this picture.

Proportionality between rate and mineral acid concentration in the 1–5 molar acid region indicates that the activity coefficient ratio, $f_{\ddagger}/f_s f_{H_3O^+}$, is not a function of the acid concentration and suggests that a water molecule is covalently bound to the substrate in the transition state.[13,14] In the suggested transition state the water is bound through the proton. The striking failure of the rate to be proportional to h_0[8] indicates that the reaction *cannot* be represented by a rapid equilibrium in which the proton is reversibly transferred to the carbon atom followed by a simple, rate-determining, carbon–mercury bond cleavage. The h_0 values were obtained at 25° and are being applied at 100°. It seems very highly unlikely, however, that h_0 should become proportional to the acid concentration at 100°.

The rapid increase of $k_1/(HClO_4)$ at acid concentrations above 5 molar is thought to be caused by changes in the activity coefficient ratio, although at least part of this increase may be due to reaction with molecular perchloric acid. Sulfuric acid may be a slightly more effective reagent than perchloric in this reaction because of reaction with the fairly strong acid HSO_4^- in sulfuric acid solutions, but it seems more likely that the activity coefficient ratio is simply somewhat lower in sulfuric than in perchloric acid.

The finding, by Winstein and Traylor,[15] that the acetolysis of dialkylmercurials in acetic acid as a solvent is not inhibited by acetate ion suggested that molecular acetic acid would bring about the present reaction. This has now been directly confirmed in fairly dilute aqueous solution. In addition it has been pointed out that some of the data on mineral acids suggest reaction with molecular acids.

Finding of a reaction with molecular acid requires that the conjugate base of the acid as well as the proton be present in the transition state,[14,16] which is consistent with the proposed mechanism.

The absence of a measurable solvent isotope effect means that the proton is as tightly bound in the transition state as in the starting state.[17] The postulated mechanism explains this by having the hydrogen–oxygen bond in the transition state very slightly disturbed and the hydrogen–carbon bond just beginning to form.

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[12] Reference 8, p. 96.

[13] L. Zucker and L. P. Hammett, THIS JOURNAL, **61**, 2791 (1939).

[14] Reference 8, p. 280.

[15] S. Winstein and T. G. Traylor, THIS JOURNAL, **77**, 3747 (1955).

[16] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 275.

[17] R. P. Bell, "Acid-Base Catalysis," Oxford at the Clarendon Press, London, 1941, p. 144.

Negligibly small isotope effects have previously been noted for the formally similar reaction of Grignard reagents with water[18] and with methanol.[19]

The present mechanism attributes the large negative entropy of activation to three sources. These are: the loss of freedom on going from two particles in solution (the hydronium ion and methylmercuric iodide) to a single transition state; "freezing" of water molecules by the new partial charges on the methyl group and on the mercury atom; possible loss of rotational freedom by the methyl group in the transition state. Unfortunately it is only possible to estimate these three quantities very crudely. The entropy of freezing of water at 0° is -5.5 cal./mole deg.[20] The hydronium ion is of about the same size, shape and mass as a water molecule, so the entropy loss due to the first cause listed above may be about 5 cal./mole deg. Negative entropies of ionization in aqueous solution range up to 30 cal./mole deg.,[20] and the postulated transition state contains a very substantial charge separation. The rotation of the methyl group in aqueous methylmercuric iodide must be very nearly free. If this free rotation is lost in the transition state due to the strong interactions of the positively charged mercury with solvent, a loss of as much as 2 cal./mole deg. might take place.[21] There will be no important gain of entropy since the hydronium ion is still essentially intact in the transition state. Taken together these considerations show that the proposed mechanism is consistent with the measured entropy of activation, although it cannot be rigorously tested because of the difficulty of making quantitative estimates.

The present work gives no insight into the stereochemistry of the reaction. This, and also the relation between structure and reactivity, are currently under study in this Laboratory.

Experimental

Materials.—Methylmercuric iodide was prepared by the method of Frankland[22] and had m.p. 140–142° (cor.). Water used was deionized and redistilled "conductivity water." Sulfuric acid was du Pont, C.P. reagent, fumed for 4 days before use. If this fuming was omitted, deviations from first-order kinetics were observed, as noted. Perchloric acid was Baker and Adamson, reagent grade. Acetic acid was du Pont, C.P. reagent grade, and was redistilled (b.p. 114.6–114.9°) to give a material transparent down to a wave length of 2600 Å. Sodium hydroxide solutions were prepared from saturated sodium hydroxide (Merck, reagent grade) concentrations determined by titration against J. T. Baker analyzed, "primary standard" potassium acid phthalate. The concentration of the various acids was determined by titration against standard sodium hydroxide. Methanol and dioxane were commercial solvents. The methanol was transparent down to 2200 Å. The dioxane was purified by the method of Vogel[23] and residual benzene was removed by azeotropic distillation with methanol. The final product had a b.p. 99.6–100.4° and was transparent down to 2200 Å. Mercuric iodide and mercuric nitrate were Mallinckrodt, "Analytical reagent" grade.

Kinetic Methods.—Most of the runs in which the dependence of rate on acid concentration was determined were made up as follows. Standard solutions of methylmercuric iodide (about 5×10^{-3} M) were made up in methanol or dioxane. Two ml. of such a solution was added to a 50-ml. volumetric flask, the acid was added and the solution was made up to volume with water; 16 3-ml. portions were then transferred to individual ampoules, sealed and thermostated. Ampoules were withdrawn at intervals and the optical density at 2700 Å. was determined on a Beckman DU spectrophotometer. Experiments in which the solvent isotope effect was determined were conducted in essentially the same way except that D_2O (Stuart Oxygen Co., 99 atom % D) was used in the place of ordinary water.

For experiments on the temperature dependence of the rate constant the procedure was the same except that 25 ml. of a standard solution of methylmercuric iodide (4.64×10^{-4} M) in water was used in the place of the methanol or dioxane solutions. The data in Table III above indicate that the organic solvents cannot have an important effect on the rate. Experiments on the acetic acid reaction were also carried out using the aqueous standard solution of methylmercuric iodide.

For some of the perchloric acid experiments the temperature was maintained at 99.5 ± 0.2° by a steam thermostat. For the remainder of the perchloric acid experiments and for the sulfuric acid experiments, the temperature was maintained at 100.2 ± 0.2° by an electrically controlled, heated and stirred oil thermostat of conventional design. For the experiments on the dependence of rate on temperature the temperature was controlled ±0.1°. The acetic acid experiments were conducted at 161.0 ± 0.2° in a thermostat as described.

In the sulfuric acid experiments it was found, in the slow reactions, that the graphically determined rate constant began to fall off at about 60% reaction unless the sulfuric acid was fumed not more than a week before use. The product spectrum seemed unchanged. The rate constant determined from the early points was the same as that obtained with freshly fumed acid. For the most part rate constants reported here were obtained from experiments in which good first-order kinetics were observed. The origin of the phenomenon is not known and it was never observed in reactions with half-lives of 4 hr. or less.

Rate constants were determined graphically from plots of $\log (D_\infty - D_t)$ *vs.* time where D_∞ is the measured optical density at 8–20 half-lives and D_t is the optical density at time t. Optical densities at zero time were in good agreement with those predicted from the measured molar extinction coefficient of methylmercuric iodide at 2700 Å. Infinite time optical densities did not generally vary by more than 5% from those predicted from the measured molar extinction coefficient of HgI_2 at 2700 Å.

Beer's law was independently shown to hold for HgI_2 at 2700 Å. by measuring the optical density of solutions of known concentration.

Ultraviolet Spectra.—The ultraviolet spectra of methylmercuric iodide, mercuric iodide and mercuric nitrate were determined in the usual way with a Beckman DU spectrophotometer. The ultraviolet spectrum of HgI^+ was obtained by adding a small excess of mercuric nitrate to a standard solution of mercuric iodide, while the spectrum of CH_3Hg^+ was obtained by adding a small excess of mercuric nitrate to methylmercuric iodide.

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[18] K. B. Wiberg, THIS JOURNAL, **77**, 5987 (1955).

[19] M. Orchin, I. Wender and R. A. Friedel, *Anal. Chem.*, **21**, 1072 (1949).

[20] Reference 8, p. 123.

[21] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 524.

[22] Frankland, *Ann.*, **85**, 361 (1853).

[23] A. I. Vogel, "Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1948, p. 175.