| | CALCU: | LATED AND | MEASURED | VALUES OF dn/dc | AND (d/dt) | (dn/dc) AT | 30° | |
|---------------------|--------|---------------------------|------------|----------------------|--------------|---------------------------|--------|-----------------------|
| | | $\mathbf{C}_{\mathbf{C}}$ | yclohexane | | | Toluene | | |
| | | $\mathrm{d}n/\mathrm{d}c$ | | (d/dt)(dn/dc) | | $\mathrm{d}n/\mathrm{d}c$ | | (d/dt)(dn/dc) |
| Column no. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Wave length, $m\mu$ | 589 | 546 | 436 | 589 | 589 | 546 | 436 | 589 |
| Glassy | 0.159 | 0.162 | 0.174 | 4.2×10^{-4} | 0.0931 | 0.0935 | 0.0976 | 4.14×10^{-4} |
| Extrapd. | . 166 | .170 | . 183 | $2.8	imes10^{-4}$ | ,102 | . 1025 | . 1070 | $2.46	imes10^{-4}$ |
| Measured | | .1693 | .1800 | | | .1096 | .1134 | |

TABLE III . ..

curve above the glass temperature to lower temperatures. This makes the calculation more closely approximate the mixing of two liquids.

Unfortunately, the light-scattering measurements are conducted at 546 and 436 m μ rather than at the sodium-p line, so that the measurements of dn/dccannot be directly compared with the above calculations using Jenckel's data. The dispersion curve for glassy polystyrene has been given¹⁴ and fits a Cauchy relation. Similarly the dispersion of the solvents is known so that the dn/dc for glassy polystyrene can be calculated directly. The dispersion effects would be expected to be similar both above and below the glass temperature since it is directly a function of the internal molecular structure; therefore, the values for the dispersion dn/dc of the

(14) R. M. Boundy and R. F. Boyer, "Styrene, Its Polymers, Co-polymers, and Derivatives," Reinhold Publ. Corp., New York, N. Y., 1952.

extrapolated liquidus state of polystyrene may also be calculated. These values appear in columns 2, 3,6 and 7 of Table III. The temperature dependence of the refractive index of polystyrene and the solvents changes very little with wave length so the calculated value at 589 m μ can be directly compared with the measured values in Table II.

The excellent agreement of the calculated and experimental values for the dn/dc using the polystyrene constants extrapolated from the liquidus state is indeed encouraging, although the calculated temperature dependence of dn/dc in blue light does not seem to fit the measured values regardless of the choice of state. However, it is to be re-emphasized that there is a sizable temperature dependence of dn/dc and it must be taken into account in experimental measurements performed at different temperatures.

THERMODYNAMICS AND KINETICS OF THE REACTION OF MERCURIC SALTS WITH OLEFINS. PART I. THE REACTION WITH MERCURIC CHLORIDE

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The equilibrium constant of the reaction $HgCl_2 + C_2H_4 + H_2O \rightleftharpoons ClHgC_2H_4OH + HCl$ has been measured at 25° approaching the equilibrium position from both sides. The values are in agreement within the experimental error. The constant has also been determined at other temperatures between 15 and 40° commencing with mercuric chloride and ethylene and thus the heat content and entropy changes of the reaction have been calculated. The kinetics do not correspond to a first-order reaction opposed by one of the second order. Added sodium chloride had a marked retarding effect. The results are discussed and it is considered that they lend strong support to the hypothesis that the reaction proceeds by an ionic mechanism.

Introduction

The interaction of mercuric salts with olefins has been studied for many years. Many mercurials have been prepared and their reactions studied, but relatively little work has been reported on the thermodynamics and kinetics of these systems and the mechanism of the processes involved is still not clear.¹ Sand and Breest² investigated the equilibrium (1) and obtained values of the equilibrium

$$HgCl_2 + C_2H_4 + H_2O \xrightarrow{} ClHgC_2H_4OH + HCl \quad (1)$$

constant approaching the equilibrium position from both sides. Their work has been criticized,³ and certainly their method of calculating K is incorrect. However, this system is a relatively

(1) J. Chatt, Chem. Revs., 48, 7 (1951).

- (2) J. Sand and F. Breest, Z. physik. Chem., 59, 424 (1907).
- (3) P. Brandt and O. Plum, Acta Chem. Scand., 7, 97 (1953).

simple one, and so the physical chemistry of the reaction of mercuric chloride and simple olefins has been reinvestigated by more direct methods.

Experimental

The uptake of ethylene or propylene by mercuric chloride solutions (volume 20 or 25 cc.) was followed at a constant pressure by conventional means. The 100-ml. reaction vessel was immersed in a thermostat, constant to $\pm 0.1^{\circ}$, and shaken about 350 times per minute. The rate of ab-sorption was independent of shaking rate. The air in the flask had previously been swept out by the olefin, and the volume absorbed was determined by means of a thermo-stated gas buret connected to the flask by wide capillary tubing and polythene tubing. Before an experiment the vessel was washed with concentrated nitric acid, distilled water and acetone, and dried over a flame. The solubility of the gas in water was determined in the same way. It was found in all the experiments that no uptake occurred until the solution was shaken.

The equilibrium was approached from the opposite direc-



Fig. 1.—Variation of the equilibrium constant K' of the reaction $C_2H_4 + HgCl_2 + H_2O \rightleftharpoons ClHgC_2H_4OH + HCl$, with temperature.

tion in the following manner. Solutions of hydroxyethylmercuric chloride were prepared as described later. In an experiment the reaction vessel containing a solution was immersed in the thermostat, air displaced by ethylene and the flask shaken. When the solution was saturated with gas, a known amount of hydrogen chloride in a small volume (<1 ml.) of aqueous solution was added. On shaking ethylene was evolved, and the total volume given off was measured.

When solvents other than water were used, they were stored and transferred to the reaction flask under dry conditions.

Hydroxyethylmercuric chloride was prepared by the method of Aranda and Pastor.⁴ The white solid melted at $153-154^\circ$ (cf. 155°), but contained a small amount of impurity insoluble in water at room temperature. On addition of a large excess of hydrochloric acid only 95% of the theoretical amount of ethylene was evolved and the insoluble impurity still remained. Solutions of the compound were prepared directly as follows. From the volume of ethylene absorbed by an aqueous solution of mercuric chloride the amounts of HCl formed and of HgCl₂ unreacted were calculated. A quantity of sodium hydroxide equal to that required to neutralize exactly the HCl and precipitate the unreacted mercury as HgO, was added. The precipitate was filtered and washed. The whole solution plus washings were made up with water to a definite volume which contained a known amount of hydroxyethylmercuric chloride. The accuracy of this procedure was checked by addition of a large excess of HCl to one such solution. The theoretical volume of ethylene was given off. An aqueous solution of mercuric chloride was shaken with

An aqueous solution of mercuric chloride was shaken with ethylene until no more gas was absorbed, and the conductivity of the equilibrium mixture was measured by means of a conventional Wheatstone bridge apparatus. From the amount of olefin taken up the concentration of mercuric chloride left in solution and of hydrogen chloride formed was calculated and a mixture prepared containing these concentrations of chloride and acid. The conductivity of this mixture was the same within experimental error as that of the equilibrium mixture, indicating that the conductivity of an aqueous solution of hydroxyethylmercuric chloride is negligible.

All water was purified by distillation from a trace of potassium permanganate in an all-glass apparatus. Mercuric chloride, sodium chloride, hydrochloric and perchloric acids, methanol, ethyl acetate, acetic and trichloroacetic acids were of Analar quality. Sodium perchlorate was prepared from Analar sodium carbonate and acid. Analar piperidine and nitrobenzene were distilled in a stream of nitrogen before use, and t-butyl hydroperoxide was distilled under reduced pressure. Benzoyl peroxide was recrystallized from Analar chloroform and a sample of boron trifluoride etherate used directly. Nitrogen was taken from a cylinder, freed from oxygen by washing with alkaline hydrosulfite solution and dried with magnesium perchlorate. Cylinder ethylene and propylene were shown to contain no appreciable impurity by gas chromatography. However, the former was passed through 85% H₂SO₄, a trap at -78° and a drying tube successively.

Results

Thermodynamic.—The equilibrium constant for reaction 1 is easily calculated from the volume of

(4) V. G. Aranda and O. S. Pastor, Combustibles, 10, 183 (1950); C. A., 46, 423 (1952). gas at a known temperature and pressure taken up (allowing for the physical solubility in water) and the initial concentration of mercuric chloride, approaching the equilibrium position from the L.H.S., and from the initial concentrations of hydroxyethylmercuric chloride and HCl added and the volume of ethylene given off, approaching the equilibrium position from the R.H.S. Since water was the solvent Table I shows values of

$$K' = \frac{[ClHgC_2H_4OH]_{e} [HCl]_{e}}{[HgCl_2]_{e} [C_2H_4]_{e}}$$

under various conditions.

Irreproducible results were obtained when the pressure of ethylene was much below or above atmospheric due to difficulty in measuring the volume change, and it was not possible to investigate the variation of water concentration since suitable "inert" solvents, e.g., acetone, to replace part of the water had high vapor pressures, causing expansion when shaking was started.

The individual values of K' are not very accurate since the volume of ethylene taken up or evolved was less than 20 ml., owing to the limited solubility of mercuric chloride and hydroxyethylmercuric chloride. Any error in this volume involves at least double the percentage error in K'. The accuracy of the experiments was less for the reaction of the addition compound and hydrochloric acid, owing to the number of operations necessary to prepare the aqueous solution of hydroxyethylmercuric chloride. Nevertheless the various values of K' at 25° agree quite well approaching the equilibrium position from both sides and at other temperatures for the $HgCl_2-C_2H_4$ reaction. The equilibrium may be displaced completely to one side or the other by the addition of excess base to the aqueous mercuric chloride solution or excess HCl to the solution of addition compound. Addition of sodium chloride to the mercuric chloride solution appeared to reduce K' somewhat, but the presence of sodium perchlorate had little or no effect. Addition to 0.066 M HClO₄ to 0.111 M HgCl₂ at 25° decreased the amount of ethylene taken up, but calculation of K' on the assumption that the acid concentration at equilibrium was given by $[HClO_4] + [HOC_2H_4HgCl]_e$ gave a value of 6.5. It was found that the addition of excess acetic acid to the aqueous solution of hydroxyethylmercuric chloride led to the evolution of only about 12% of the theoretical volume of ethylene, whereas all the olefin was given off when excess trichloroacetic acid was added.

The variation of K' with temperature is shown in Fig. 1. The results between 15 and 20° were rather erratic owing to the very long time necessary to attain equilibrium and the reduced solubility of the hydroxyethylmercuric chloride. However, above 25° at any rate the Van't Hoff isochore was a straight line from the slope of which the heat content change in the reaction was calculated to be +3790 cal. mole⁻¹. Taking into account the concentration of water the true value of the equilibrium constant K at 25° is 0.055 l. mole⁻¹.

 $\Delta G^{0}_{298} = -2.303 RT \log K = +1720 \text{ cal. mole}^{-1}$

| Temp. °C. | Solubility of C_2H_4 , mole/1, ^a $\times 10^3$ | Initial concn. HgCl ₂ , mole/l. X 10 ² | Concn. additive mole/1. | Vol. C2H4 reacted per l. HgCl2 soln. (ml. at S.T.P.) | <i>K'</i> | Average K' |
|---|--|--|---|---|---|--------------|
| 15.2 | 4.7 | $\begin{cases} 6.2 \\ 11.3 \\ 18.0 \end{cases}$ | · · · · · · · · · · · · · · · · · · · | 542 750 989 | $\left. \begin{array}{c} 3.3 \\ 3.0 \\ 3.0(5) \end{array} \right\}$ | 3.1 |
| $\begin{array}{c} 16.4 \\ 17.5 \end{array}$ | $\begin{array}{c} 4.6 \\ 4.5 \end{array}$ | 11.8 5.9 | | 735 497 | 2.7(5) 2.9 | |
| 20.8 | 3.8 | $\left\{ egin{array}{c} 7.3\\ 11.6\\ 13.3 \end{array} ight.$ | | 526 679 751 | $\left. \begin{array}{c} 2.9 \\ 2.8 \\ 3.0 \end{array} \right\}$ | 2.9 |
| 25.0 | 3.1 | $\left\{\begin{array}{c}5.6\\11.4\\11.8\\16.8\\17.6\\5.7\\5.8\\4.2\\4.2\end{array}\right.$ | 0.0643 (HCl) 0.0101 (piperidine) Excess piperidine 0.034 (NaCl) 0.12 (NaCl) | 400 628 684 820 414 542 1200 (5.4×10^{-2} mole) 314 373 | 2.8 3.0 3.3 3.3 3.0 3.3 2.3 3.3 | 3.0(5) |
| 30.0 | 2.7 | $ \left\{\begin{array}{c} 4.7\\ 11.2\\ 11.8\\ 17.0 \end{array}\right. $ | | 368 630 645 802 | $ \begin{array}{c} 3.3 \\ 3.5 \\ 3.4(5) \\ 3.5 \end{array} $ | 3.4 |
| 35.5 | 2.3 | $\begin{cases} 5.7 \\ 8.8 \\ 11.9 \\ 16.9 \end{cases}$ | · · · · · · · · · · · · · · · · · · · | 425 528 616 785 | $ \begin{array}{c} 4.1 \\ 3.7(5) \\ 3.6 \\ 4.0 \end{array} $ | 3.8(5) |
| 39.7 | 1.9 | $\left\{ \begin{array}{c} 5.8(5) \\ 11.8 \end{array} \right.$ | | 402 589 | $\left.\begin{array}{c} 4.2 \\ 4.0 \end{array}\right\}$ | 4.1 |

 TABLE I

 Section (a) Values of the Equilibrium Constant K' of the Reaction of Mercuric Chloride and Ethylene in Aqueous Solution

Section (b) Values of the Equilibrium Constant K' of the Reaction of Hydroxyethylmercuric Chloride and Hydrogen Chloride in Aqueous Solution

| Temp., °C. | Solubility of C_2H_4 , mole/1. $\times 10^3$ | Initial conen. ClHgC ₂ H ₄ OH, mole/l. × 10 ² | Initial conen. HCl, mole/l. | Vol. C ₂ H ₄ given off per l. soln. (ml. at S.T.P.) | K' | Av. K' |
|---------------|---|--|--------------------------------|---|-------|--------|
| 25.0 | | (1.27^{b}) | 1.60 | 150 | 2.7) | |
| | | 1.42^{b} | 1.91 | 165 | 3.5 | |
| | 9 1 | 1.83 | 1.92 | 228 | 2.3 { | 2.0 |
| | ð, 1 | 1.88^{b} | 1.70 | 201 | 2.8 { | 5.0 |
| | | 3.06 | 3.92 | 444 | 3.4 | |
| | | 4.92^{c} | 4.80 | 681 | 3.5) | |

 $^{\circ}$ Mean of several determinations. $^{\circ}$ ClHgC₂H₄OH prepared in solution. $^{\circ}$ Using solution of solid "complex"—concn. corrected for purity.

$$\Delta G^{0}_{298} = \Delta H^{0} - T \Delta S^{0}$$

$\Delta S^0 = +7.0$ cal. degree⁻¹ mole⁻¹

...

The absorption of propylene by an aqueous solution of mercuric chloride also ceased before one mole per mole $HgCl_2$ was taken up. Values of the equilibrium constant

$$K^{\prime\prime} = \frac{[\mathrm{HOC}_{3}\mathrm{H}_{6}\mathrm{H}\mathrm{gCl}]_{\mathrm{e}} \ [\mathrm{HCl}]_{\mathrm{e}}}{[\mathrm{H}\mathrm{gCl}_{2}]_{\mathrm{e}} \ [\mathrm{C}_{3}\mathrm{H}_{6}]_{\mathrm{e}}}$$

were somewhat inconsistent [Table II] owing to the fact that, even at 40°, the addition compound tended to precipitate, the solubility being less than that of hydroxyethylmercuric chloride. It was thus difficult to obtain an "infinity" reading, owing to a slow drift, even by plotting values of the uptake at intervals during an experiment and extrapolating. However, the values of K'' do show that the equilibrium constant is not altered appreciably by changing from ethylene to propylene.

Kinetic.—Under the conditions of the experiments it might be supposed that the kinetics would correspond to those of a first-order reaction opposed by one of the second order. It can be shown quite simply⁵ that for the equilibrium, $A \rightleftharpoons B+C$, the velocity constant of the forward reaction is given by

$$k = \frac{2.303x_{\text{e}}}{t(2a - x_{\text{e}})} \log\left(\frac{ax_{\text{e}} + x(a - x_{\text{e}})}{a(x_{\text{e}} - x)}\right)$$

where a is the initial concentration of A and x and x_e the amounts of A reacted at time t and equilibrium. For the ethylene-mercuric chloride reaction, substituting for a, x_e and x

(5) S. Glasstone, "Textbook of Physical Chemistry," The Macmillan Co., New York, N. Y., 1940, p. 1051.



Fig. 2.—Kinetic plots of the rates of oxymercuration of ethylene with aqueous mercuric chloride on the assumption that a first-order reaction is opposed by one of the second order. a, b, and c, temp. 25.0° ; concn. HgCl₂, 0.056, 0.114 and 0.168 *M*, respectively. d and e, temp. 39.7° ; concn. HgCl₂, 0.0585 and 0.118 *M*, respectively.

 $T_{ABLE} II$

Values of the Equilibrium Constant K'' of the Reaction of Mercuric Chloride and Propene in Aqueous Solution

| DOLUTION | | | | | | |
|---------------|--|---|--|--|----------------------------|--|
| Temp., °C. | Solubility of C3H6, mole/l. × 103 | Initial concn. HgCl ₂ , mole/l. \times 10 ² | Vol. C ₃ H ₆ reacted per l. HgCl ₂ soln. (ml. at S.T.P.) | <i>K''</i> | $\overset{\mathrm{Av}}{K}$ | |
| 25.0 | 3.7 | $\left\{\begin{array}{c}3.34\\5.36\\7.34\end{array}\right.$ | $340 \\ 439 \\ 560$ | $\left. \begin{array}{c} 3.4 \\ 3.0[5] \\ 3.5 \end{array} \right\}$ | 3.3 | |
| 35.0 | 2.5 | $\left\{\begin{array}{c}1.85\\3.45\\3.84\\4.72\\5.36\\5.72\\6.85\end{array}\right.$ | $170 \\ 314 \\ 358 \\ 412 \\ 394 \\ 470 \\ 394$ | $\begin{array}{c c} 2.1 \\ 3.8 \\ 4.6 \\ 4.7 \\ 3.4 \\ 4.9 \\ 2.4 \end{array}$ | 3.7 | |
| 40.0 | 2.16 | $ \left\{\begin{array}{c} 1.83\\ 1.85\\ 3.25 \end{array}\right. $ | $215 \\ 224 \\ 313$ | $ \begin{array}{c} 4.9 \\ 5.4 \\ 4.9 \end{array} $ | 5.1 | |

$$k = \frac{2.303\Delta V_{\rm e}}{t(2\Delta V_{\infty} - \Delta V_{\rm e})} \log \left(\frac{\Delta V_{\infty} \Delta V_{\rm e} + \Delta V(\Delta V_{\infty} - \Delta V_{\rm e})}{\Delta V_{\infty}(\Delta V_{\rm e} - \Delta V)}\right)$$

where ΔV_{∞} is the volume of ethylene corresponding to complete reaction, and ΔV and ΔV_e are the volumes taken up at time t and equilibrium. Thus a plot of the log term versus the time should be a straight line. The results at 25 and 39.7°, plotted in this way, are shown in Fig. 2. It can be seen that the lines are by no means straight, except possibly over the last 30% or so of the reaction before equilibrium was attained, the apparent value of k decreasing as the reaction proceeded. Even the value of k calculated from the slopes of the "straight" portions of the graphs varied as the initial concentration of mercuric chloride was increased at a constant temperature (at 25° , k/2.303 = 4.85, 5.11 and 5.36×10^{-2} min.⁻¹ with [HgCl₂]_i = 5.6, 11.4 and 16.8 $\times 10^{-2}$ M, respectively; at $39.7^{\circ} k/2.303 = 9.9$ and 13.5×10^{-3} min.⁻¹ with [HgCl₂]_i = 5.85 and 11.8 $\times 10^{-2} M$, respectively). The temperature coefficient of k is low. It increases about 2.3 times between 25 and 39.7°, implying an apparent energy of activation of about 10 kcal, mole⁻¹. It was found that plots of $\log (\Delta V_{\infty} - \Delta V)$ and $\log (\Delta V_{e} - \Delta V)$ versus time were also curved.

Addition of sodium perchlorate or perchloric acid had little effect on the rate of reaction, but addition of sodium chloride reduced it greatly. At 25° with 0.042 M HgCl₂ $t_{1/2}$ was 9.3 min. without and 40 min. with 0.034 M NaCl present. In the presence of 0.71 M NaCl the reaction was too slow to measure.

When dissolved in ethyl acetate or nitrobenzene mercuric chloride did not react with ethylene. With methanol as solvent a very slow reaction occurred. Addition of water increased the rate and it is probable that, if the alcohol has been anhydrous--it actually contained 0.12 mole % H_2O_2 ,—no reaction would in fact have taken place. It has been reported that a solution of mercuric chloride in piperidine absorbs ethylene over a period of 48 hr. to give C₅H₁₀NCH₂CH₂-HgCl.⁶ It was hoped to investigate the kinetics of this reaction, but with purified reagents no uptake of gas took place over 60 hr., even in the presence of 10 vol. % methanol. On addition of benzoyl peroxide, *t*-butyl hydroperoxide or boron trifluoride etherate (catalysts for mercuration), or when impure piperidine was used, a very slow reaction occurred, and a precipitate, probably piperidine hydrochloride as reported by the Russian workers, was formed. Addition of water, however, led to a rapid absorption of ethylene.

Discussion

The reaction of cyclohexane with mercuric chloride in "anhydrous" methanol is also very slow.⁷ Brandt and Plum³ have claimed that "very pure ethylene" prepared by the reaction of freshly distilled ethylene dibromide and zinc did not react with aqueous mercuric chloride, and they suggested that the results of Sand and Breest² were due to impurities in the ethylene as prepared by their method (from ethanol and concentrated sulfuric acid). The ethylene used in this work certainly contained no detectable impurities and consistent results were obtained. It can only be assumed that the apparatus used by Brandt and Plum was not capable of detecting the uptake of gas under their conditions.

The method for the calculation of equilibrium constants makes no assumption as to the mechanism of the forward or back reactions, the mercuric being considered as in two states either combined with the olefin or not. Thus the results in Table I confirm that the reaction of aqueous mercuric chloride with ethylene is indeed (1) and show that K' and K'' (or K) are true thermodynamic equilibrium constants. The values of the heat content and entropy changes are therefore meaningful.

Sand and Breest² measured the increase in conductivity of an aqueous solution of mercuric chloride, due to the formation of HCl as the reaction with ethylene proceeded. Unfortunately it is difficult to connect this conductivity change with

(6) R. KR. Freidlina and N. S. Kochetkova, Bull. Acad. Sci. U.S.S.R. Classe Sci. chim., 128 (1945).

(7) A. Rodgman, D. A. Shearer and G. F. Wright, Can. J. Chem., 35, 1377 (1957).

the equilibrium concentrations of reactants and products and thus their values of K' are not really significant. However, in order to approach the equilibrium position from the opposite direction they reacted an aqueous solution of hydroxyethylmercuric chloride with hydrochloric acid and measured the pressure of ethylene evolved. They incorrectly attempted to allow for the formation of $HgCl_3$ ions but it is easy to recalculate K' from their results, the values being 4.4 and 3.5 at 25° , assuming the solubility of ethylene given in Table I. In order, presumably, to simplify matters they used a saturated solution of complex containing excess solid and nearly all the HCl added ($\sim 85\%$) had reacted at equilibrium. Thus their values of K' cannot be very accurate. However, that of 3.5 is probably the better, since the concentration of acid added was double that in the first experiment, and it agrees quite well with the value of K' at 25° in Table I.

Rowland and Kluchesky⁸ investigated the reaction of mercuric chloride with allylacetic acid and o-allylphenol in aqueous solution. They also took into account the concentrations of $HgCl_3^$ and $HgCl_4^=$ ions, but recalculation of their few results showed that the value of K''', corresponding to K' and K'', agreed quite well approaching the equilibria from opposite directions, the average constants being 18.6 and 540, respectively, at room temperature. Thus both the mercurials are more stable toward decomposition by hydrochloric acid than those from olefins, the phenol compound being most stable, probably because of its ring structure.

Sand and Breest² also found that, as the reaction between ethylene, mercuric chloride and water proceeded to equilibrium, the apparent velocity constant decreased. The reaction is therefore not taking place in the simple way suggested by the stoichiometry. Chatt¹ has given an excellent discussion of the probable mechanisms of the formation and decomposition by acids of addition compounds of mercuric salts and unsaturated compounds. There seems to be a choice between two—one essentially molecular, favored by Wright⁹ on the basis of his studies of methoxymercuration in non-aqueous solvents, and the other involving ions, supported by Chatt himself. Applied to mercuric chloride these are



(8) R. L. Rowland and E. F. Kluchesky, J. Am. Chem. Soc., 73, 5490 (1951).

(9) E.g., A. G. Brook and G. F. Wright, Can. J. Research, B28, 623 (1950).



In a solution of mercuric chloride the relative proportion of positive ions is very small and decreases rapidly to virtually zero as excess chloride is added, $HgCl_3^-$ and $HgCl_4^-$ becoming the main species present.¹⁰ The salt is also hydrolyzed to a slight extent according to equation 1.¹⁰ Thus assuming the velocity constants of reactions 2 or 4 were high, the over-all rate of oxymercuration would be measurable as found experimentally. Also the autoretardation and retardation by added chloride is easily explained on either mechanism as having been due to the effect on the equilibria 1 or 3.

Nevertheless there are several strong objections to the molecular mechanism. For instance mercuric chloride did not react in solution unless water was present, though methoxymercuration by mercuric acetate in dry methanol takes place readily.⁹ Despite reduced hydrolysis on the addition of perchloric acid, the rate of reaction with ethylene was not greatly altered. However, the main support for mechanism B is the fact that the system is thermodynamically reversible, which mechanism A is not. Even if it could be modified to correct for this the fact that the back reaction involved hydrogen and chloride ions, since the HCl must have been completely dissociated at such low concentrations, means that the oxymercuration must also have involved ions. The fact that there was a positive entropy change of formation of hydroxyethylmercuric chloride, despite the concurrent formation of hydrated hydrogen ions, suggests that the entropy of hydration of a HgCl+ [or Hg⁺⁺] ion was being lost during the reaction.

The fact that the strength of the acid was important in the deoxymercuration further supports the ionic mechanism, the first stage being a proton transfer from an H_3O^+ ion to the basic oxygen atom of the non-ionic hydroxyethylmercuric chloride, *i.e.*, the reverse of stage 6. However, the efficiency of the trichloro-acetic acid might be partly accounted for if mercuric trichloroacetate was only weakly dissociated in aqueous solution. Thus perchloric acid although a strong acid was by no means as effective as HCl in decomposing the addition compound, probably because equilibrium 3 was not affected by ClO_4^- ions.

(10) M. C. Sneed and R. C. Brasted, "Comprehensive Inorganic Chemistry," Vol. IV, D. Van Nostrand Co., New York, N. Y., 1955.