Addition Compounds of Olefins with Metal Salts

I. The Reaction of Ethylene with Mercuric Ions in Aqueous Solution

PAUL BRANDT and OLUF PLUM

Chemistry Department A, Danish University of Technology, Copenhagen, Denmark

The first attempt to measure the equilibrium and rate constants for the reaction between a mercuric salt (mercuric chloride) and ethylene in aqueous solution was carried out by Sand and Breest¹ in 1907.

A very interesting result was obtained by the present authors when trying to repeat Sand and Breest's measurements; it was found impossible to detect any reaction at all between mercuric chloride and ethylene. Our experiments seem to show that no reaction takes place if the ethylene used is especially pure. Sand and Breest prepared their ethylene from ethanol and sulphuric acid, while ours was prepared from freshly distilled ethylene bromide and zinc at 40°C, whereby very pure ethylene was produced. When ethylene was prepared in a similar way to that of Sand and Breest, a reaction took place, but it was impossible to reproduce any of their results: every time a fresh quantity of ethylene was prepared, a new "equilibrium constant" which differed from the preceding one by a factor varying from 0.1 to 10 was obtained. Consequently, it seems that the results obtained by Sand and Breest are without value because of impurities in the ethylene used. With ethylene prepared in our way reproducible results using dissociated mercuric salts have been obtained.

Until 1935 most workers assumed that the reaction takes place as follows:

but more detailed views² on this point have also been advanced.

By measuring the partition coefficient of cyclohexene between mercuric nitrate solution and carbon tetrachloride Lucas, Hepner and Winstein ⁵ have determined both of the equilibrium constants*:

$$\frac{\left[\text{Hg}^{++} \text{C}_6\text{H}_{10} \right]}{[\text{Hg}^{++}] \cdot [\text{C}_6\text{H}_{10}]} = 2.2 \cdot 10^4 \text{ and } \frac{\left[\text{Hg}^+ \text{C}_6\text{H}_{10} \right]}{[\text{Hg}^{++}] \cdot [\text{C}_6\text{H}_{10}]} \cdot [\text{H}^+] = 5.0 \cdot 10^4$$

By dividing the second equilibrium constant by the first one we get for the apparent acidic dissociation exponent of the aquo cyclohexene mercuric ion: $\text{p}K = -0.36$. Professor J. Bjerrum has suggested to the present writers that the reason why the aquo ion I behaves as a strong acid must be that the assumed equilibrium between the two isomeric ions II and III is displaced strongly in favour of the converted hydroxo ion III.

Hietanen and Sillén ⁷ have recently found the following values for the acidic dissociation exponents of the diaquo mercuric ion: $\text{p}K_1 = 3.70$ and $\text{p}K_2 = 2.60$. If we can disregard the electronegative influence of the olefin substituent the isomerization constant of the hydroxo mercuric ion:

$$K_i = \frac{[\text{III}]}{[\text{II}]} \quad (6)$$

appears to be of the order of magnitude $\sim 10^4$.

Winstein and Lucas ⁸, Taufen, Murray and Cleveland ⁹, and Trueblood and Lucas ¹⁰ have investigated silver coordination complexes with olefins, and demonstrated that one silver ion combines with one molecule of olefin in analogy to the mercuric compounds, but in contrast hereto no measurable quantity of hydrogen ions are liberated. As, however, the aquo ethylene silver ion does not behave like an acid, it must be kept in mind that the diaquo silver ion is $\sim 10^8$ times weaker as an acid than is the corresponding aquo mercuric ion.

Winstein and Lucas ⁸ have determined the equilibrium constant:

$$\frac{\left[\text{Ag}^+ \text{C}_6\text{H}_{10} \right]}{[\text{Ag}^+] \cdot [\text{C}_6\text{H}_{10}]} = 81.2$$

and Trueblood and Lucas ¹⁰ have determined the equilibrium constant:

$$\frac{\left[\text{Ag}^+ \text{C}_2\text{H}_4 \right]}{[\text{Ag}^+] \cdot [\text{C}_2\text{H}_4]} = 85.3$$

* Lucas *et al.* do not distinguish between the ions II and III.

In a single experiment the present writers have also determined the latter constant and, in agreement with Trueblood and Lucas, have obtained the value: 87.2.

The present experiments have also shown that if one of the water molecules in the ions: $\text{Hg}(\text{H}_2\text{O})_2^{++}$ and $\text{Ag}(\text{H}_2\text{O})_2^+$ is replaced by another ligand, *e.g.* chlorine ion, bromine ion or ammonia (in the case of silver only by ammonia) a reaction occurs with ethylene, whereas no reaction whatsoever takes place with mercury when both of the water molecules are replaced by halide ions or ammonia.

EXPERIMENTAL

Apparatus. All the experiments were carried out in a Brønsted shaking apparatus similar to that described by Hofman-Bang¹¹ with the following alterations: The cap with the little glass container was omitted, and through the bottom of the reaction flask a platinum wire was melted in for the sake of measuring the mercury-mercuric potential in the solution. As a rule, glass stoppers were used, but in the experiments where the mercury-mercuric potential had to be determined, a special glass stopper (a tube which nearly touched the bottom of the flask, ending in a glass filter plate and with a glass stopcock outside the flask) was placed in the reaction flask. The tube was filled with 1 *M* ammonium nitrate acting as bridge to the reference electrode, and sufficient mercury was placed in the reaction flask to cover the platinum wire completely.

The entire shaking apparatus, including the manometer which was filled with mercury, was lowered into a water thermostat, which usually was kept at $25.00^\circ \text{C} \pm 0.02^\circ \text{C}$.

The volume capacity of the apparatus was determined by measuring the pressure before and after addition, through a special funnel with a glass stopcock, of a known amount of mercury, and for the flask used in all the experiments for determination of the rate constant the average value: 74.51 ± 0.20 ml was found and for the special flask, only used for the determination of the equilibrium constant: 56.91 ± 0.20 ml was found.

Materials and solutions. The inorganic chemicals employed were all of analytical grade (Merck). The mercuric solutions were prepared by weighing mercuric oxide and dissolving it in 4 *M* perchloric or nitric acid in a volumetric flask and diluting with water and sufficient sodium perchlorate (or sodium nitrate) solution to obtain a total anion concentration of 1.000 mole per liter. The constants given here are therefore not the 'activity constants' but 'concentration constants' valid only under our specific conditions.

In this paper square brackets will be used for true concentrations and *C* for total concentrations, and all concentrations are given in mole per liter and all pressures in mm Hg.

Ethylene bromide and ethylene were prepared as described by Trueblood and Lucas¹⁰ with only a few unimportant alterations. The ethylene was kept in a water gasometer and purified just before it was transferred to the apparatus by passing through two Friedrichs washing bottles containing concentrated sulphuric acid and two bottles with basic pyrogallol solution.

PROCEDURE AND CALCULATIONS

A definite amount of mercuric salt solution is transferred with a Krogh syringe pipette into the reaction flask, as well as into the compensation flask. The glass stoppers are greased and as soon as the flasks are closed both chambers are evacuated by means of an oil pump until the solutions bubble briskly. The stopcock between the reaction chamber and the compensation chamber is now closed and the stopcock connected with the gasometer containing ethylene is opened until the desired pressure is attained. The experiment is started by switching on the motor which works the shaking mechanism, and the ethylene pressure is then read at definite intervals.

The concentration of the ethylene consumed is calculated by means of the equation:

$$C_x = \beta \cdot (P_0 - P_\infty) - \alpha \cdot P_\infty \quad (7)$$

where P_0 is the initial pressure, P_∞ the pressure of ethylene when the equilibrium is established (both expressed in mm Hg), α the molar solubility of ethylene in water at 1 mm Hg pressure and β an apparatus constant.

The values of α are those determined by Grollman¹², who found: at 20° C, $\alpha = 7.37 \cdot 10^{-6}$; at 30° C, $\alpha = 5.55 \cdot 10^{-6}$ and at 40° C, $\alpha = 4.52 \cdot 10^{-6}$. The values for temperatures within these intervals are determined by graphical interpolation, the value at 25° C is found in this way to be: $\alpha = 6.34 \cdot 10^{-6}$. These figures are only valid in pure water solutions, but they are used in this work as we have no knowledge of the exact value in 1 *M* salt solution. The true value can only be a few per cent less than the one employed, and it will be very easy to recalculate the results when an exact value is determined, as α is a factor in all the equations used in the present work.

The apparatus constant β depends on the temperature and the volume of the gas in the reaction chamber, and is determined by the equation:

$$\beta = \frac{(V - v) \cdot 10^3}{v \cdot RT} \quad (8)$$

where V is the volume of the reaction chamber, v the volume of the solution, T the absolute temperature and R the gas constant which has the value: 62 359 when V and v are expressed in ml and pressure in mm Hg. The values of β in all the experiments for determination of rate constants are: at 20° C, $1.496 \cdot 10^{-4}$; at 25° C, $1.471 \cdot 10^{-4}$; at 30° C, $1.446 \cdot 10^{-4}$ and at 35° C, $1.423 \cdot 10^{-4}$ ($V = 74.51$ ml and $v = 20$ ml). The value of β at 25° C in the experiments for determination of the equilibrium constant is: $0.992 \cdot 10^{-4}$ ($V = 56.9$ ml and $v = 20$ ml).

The concentration of the hydrogen ion was measured with an ordinary glass electrode connected with a "Radiometer" valve potentiometer, model PHM 3i, and the true hydrogen ion concentration $[H^+]$ was determined in every case by standardizing against a solution containing the same concentration of mercuric nitrate and sodium nitrate and almost the same hydrogen ion concentration as the solution to be measured. When measuring the hydrogen ion concentration in a solution of the composition: $C_{Hg(NO_3)_2} = 0.0250$; $C_{HNO_3} = 0.0500$ and $C_{NaNO_3} = 0.9000$ the following average value of ten measurements was obtained; 0.0503 ± 0.0005 . As a rule, with one measurement alone there is an uncertainty of about 3 %.

The concentration of the mercuric ion in the solutions was determined by measuring the mercury-mercuric potential with the same valve potentiometer as mentioned above. The following cell was used:

As the diffusion potential may be considered constant for this cell, the mercuric ion concentration, when E° is known, may be calculated from the equation:

$$E = E^\circ + \frac{RT}{2F \cdot \log e} \cdot \log [Hg^{++}] \quad (9)$$

As the calomel electrode was only a simple working electrode, it was necessary to standardize it against a solution with a known mercuric ion concentration for determination of E° . The standard solution was made from a solution with the following concentrations: $C_{Hg(ClO_4)_2} = 0.0250$, $C_{HClO_4} = 0.0500$ and $C_{NaClO_4} = 0.9000$ mole per liter, by shaking with mercury for nine hours to establish the equilibrium between mercurous and mercuric ions. The mercuric ion concentration is calculated from the equation:

$$[Hg^{++}] = \frac{C_{Hg}}{1 + K_{Hg}} \quad (10)$$

where C_{Hg} stands for the total concentration of mercurous and mercuric ions, which in this case is the same as the initial concentration, and K_{Hg} is the equilibrium constant for the mercurous and mercuric ions. The value of K_{Hg} determined by Sillén¹³ is: 129.2, and the concentration of the mercuric ion in the standard solution, in equilibrium with the mercurous ions, is calculated from equation (10): $1.920 \cdot 10^{-4}$ and together with the measured value of E gives us the value of E° .

PRELIMINARY EXPERIMENTS

Some experiments were carried out in order to determine the number of molecules of ethylene that combine with one mercuric ion. The total concentration of the solution used was: $C_{\text{Hg}(\text{NO}_3)_2} = 0.0250$; $C_{\text{HNO}_3} = 0.0500$ and $C_{\text{NaNO}_3} = 0.9000$ mole per liter. The average number $\bar{n}$ of ethylene molecules bound to a mercuric ion is indicated by:

$$\bar{n} = \frac{C_x}{C_{\text{Hg}^{++}}} \quad (11)$$

where C_x stands for the consumed ethylene according to (7) and $C_{\text{Hg}^{++}}$ is the initial concentration of mercuric ions. The results are given in Table 1 from which it is seen that one molecule of ethylene combines with one mercuric ion.

Table 1. Results of experiments showing that nearly one molecule of ethylene combines with one mercuric ion.

The stoichiometric concentrations of the solution used were: $C_{\text{Hg}(\text{NO}_3)_2} = 0.0250$; $C_{\text{HNO}_3} = 0.0500$ and $C_{\text{NaNO}_3} = 0.9000$ mole per liter. P_0 is the initial pressure of ethylene and P_∞ the pressure when equilibrium is established at 25°C.

Expt. No.	P_0	P_∞	$P_0 - P_\infty$	C_x	$\bar{n}$
1	233.5	61.4	172.1	0.02493	0.995
2	221.1	49.1	172.0	0.02500	1.000
3	537.2	352.1	184.9	0.02497	0.998

Other experiments were carried out in order to determine the number of hydrogen ions that are liberated for every molecule of ethylene consumed. The solution used was the same as described above. The average number $\bar{\nu}$ of hydrogen ions liberated for every molecule of ethylene consumed is designated by:

$$\bar{\nu} = \frac{[\text{H}^+]_\infty - C_{\text{HNO}_3}}{C_x} \quad (12)$$

where $[\text{H}^+]_\infty$ is the measured hydrogen ion concentration when the equilibrium is established, and the difference, $[\text{H}^+]_\infty - C_{\text{HNO}_3}$, is an expression for the increase of hydrogen ion concentration.

From Table 2 it will be seen that nearly one hydrogen ion is liberated for every molecule of ethylene consumed, in accordance with (2). In Expts. Nos. 2 and 3 there was an excess of ethylene, and Expt. 2 was interrupted before the equilibrium was established, thus causing the uncertainty in this experiment to be greater than that of the other.

DETERMINATION OF THE EQUILIBRIUM CONSTANT K

The expression for the equilibrium constant K is already given (5), and the experimental results are shown in Table 3. The average value is found to be: $3.5 \cdot 10^6 \pm 0.2 \cdot 10^6$.

Table 2. Results of experiments showing that nearly one hydrogen ion is liberated for every molecule of ethylene consumed.

The solution and temperature are the same as in Table 1.¹

Expt. No.	P_0	P_∞	C_x	$[H^+]_\infty$	ν
1	75.4	0.0	0.01109	0.06141	1.028
2	241.0	103.5	0.02231	0.07421	1.075
3	205.9	36.1	0.02498	0.07488	0.998

The concentration of the mercuric ion is calculated from equation (9).

As the equilibrium is strongly shifted in favour of the complex ion, the initial concentration of the mercuric ion has been used as the best approximation for the concentration of the complex ion instead of the calculated value of C_x from equation (7).

The concentration of the hydrogen ion is calculated as the sum of the initial concentration and the concentration of the complex ion.

As the solubility of ethylene is slight we may assume that Henry's law is undoubtedly fulfilled and the concentration of free ethylene may therefore be calculated from the equation:

$$[C_2H_4] = \alpha \cdot P$$

where the value of α is $6.34 \cdot 10^{-6}$ at $25^\circ C$, when P is expressed in mm Hg.

Expts. Nos. 1, 2, 3a and 4a were carried out as described above by shaking a solution of mercuric perchlorate with ethylene (the reaction proceeded from left to right according to equation (2)).

It was shown in two different ways that the reaction is reversible.

Table 3. Survey of experiments for the determination of the equilibrium constant K at $25^\circ C$.

The stoichiometric concentrations of the solution used were: $C_{Hg(ClO_4)_2} = 0.0250$; $C_{HClO_4} = 0.0500$ and $C_{NaClO_4} = 0.9000$ mole per liter.

Expt. No.	P_∞	$E - E^\circ$	C_x	$[H^+]_\infty$	$[Hg^{++}]_\infty$	$[C_2H_4]_\infty \cdot 10^4$	$K \cdot 10^{-6}$
1	39.8	- 0.1676	0.0250	0.0750	$2.12 \cdot 10^{-6}$	2.52	3.5
2	191.4	- 0.1873	0.0250	0.0750	$4.68 \cdot 10^{-7}$	12.1	3.3
3a	230.7	- 0.1919	0.0250	0.0750	$4.02 \cdot 10^{-7}$	14.6	3.2
3b	233.7	- 0.1548	0.0167	1.800	$5.78 \cdot 10^{-6}$	14.8	3.5
4a	297.7	- 0.2224	0.0250	0.0750	$2.95 \cdot 10^{-8}$	18.9	3.4
4b	40.2	- 0.1684	0.0250	0.0750	$1.99 \cdot 10^{-6}$	2.55	3.7
5	278.8	- 0.1923	0.0250	0.0750	$3.09 \cdot 10^{-7}$	17.7	3.4
6	113.9	- 0.1821	0.0250	0.0750	$6.85 \cdot 10^{-7}$	7.23	3.8

After equilibrium was established in Expt. No. 3a (which takes about nine hours) a definite amount of 4 *M* perchloric acid was added to the reaction mixture (this amount was calculated so that the salt concentration was still 1 *M*). The entire apparatus was now evacuated, then ethylene admitted to the reaction vessel until the pressure was as near as possible to the equilibrium pressure which had been established before the addition of acid. It was seen that the reaction now proceeded in the reverse direction, as the pressure of ethylene slowly increased (after nine hours the total rise was 1.7 mm Hg) and the concentration of the mercuric ion also increased (at zero it was $0.31 \cdot 10^{-6}$ after one hour it was $1.43 \cdot 10^{-6}$, after four hours $2.82 \cdot 10^{-6}$ and after nine hours it reached the highest value when the equilibrium was established again, *viz.* $5.78 \cdot 10^{-6}$) and the value of the equilibrium constant was satisfactory.

In Expt. No. 4b (which was started similarly to Expt. No. 3b) the pressure of ethylene had been decreased from 279.7 to 25.6 mm Hg after equilibrium was established. When equilibrium had been established again, the ethylene pressure had increased from 25.6 to 40.2 mm Hg and the mercuric ion concentration had also increased from $0.03 \cdot 10^{-6}$ to $1.99 \cdot 10^{-6}$. The value of the equilibrium constant was again satisfactory.

MEASUREMENT OF THE RATE OF REACTION

In Table 4 an example is given of an ordinary experiment, from which it will be seen that it takes about three minutes before an equilibrium is established between the solubility rate of ethylene and the velocity of the reaction with mercuric ions. In these first three minutes there is not enough ethylene in the solution (even though the solubility rate is very high) as the rate of reaction is extremely high as long as the mercuric ion concentration is of the same order as the initial concentration. As will be seen, nearly 50 % of the total amount of mercuric ions had already reacted with ethylene in these first three minutes.

Then, for about half an hour, the reaction takes place at such a rate that it is possible to measure the pressure exactly at the desired time, and the rate constant in this interval is almost a true constant. From this juncture until the equilibrium is established the reaction takes place very slowly.

The calculation of the rate constant, on the basis of the assumption that the reaction is bimolecular, is made by means of the equation:

$$-\frac{d[C_2H_4]}{dt} = k \cdot [Hg^{++}] \cdot [C_2H_4]$$

Table 4. Measurement and calculation of an ordinary experiment.

This experiment is the same as No. 1 in Table 7.

Time in minutes	P	$P_0 - P$	$\log \frac{P \cdot C_{\text{Hg}}^{++}}{P_0(C_{\text{Hg}}^{++} - \beta(P_0 - P))}$	$k = \frac{\beta \cdot \log e}{\alpha(P_0\beta - C_{\text{Hg}}^{++})} \cdot \log \frac{P \cdot C_{\text{Hg}}^{++}}{P_0(C_{\text{Hg}}^{++} - \beta(P_0 - P))}$
0	91.9	0		
2.5	52.1	39.8	0.128	276
3	46.9	45.0	0.156	270
3.5	42.3	49.6	0.184	264
4	37.9	54.0	0.215	263
4.5	34.2	57.7	0.246	263
5	30.9	61.0	0.274	260
5.5	27.9	64.0	0.308	262
6	25.1	66.8	0.342	263
6.5	22.9	69.0	0.372	263
7	20.9	71.0	0.403	262
7.5	18.9	73.0	0.437	263
8	17.0	74.9	0.475	266
8.5	15.7	76.2	0.503	265
9	14.1	77.8	0.542	268
9.5	12.9	79.0	0.574	268
10	11.9	80.0	0.604	267
10.5	10.9	81.0	0.637	267
11	10.0	81.9	0.671	268
12	8.5	83.4	0.733	267
13	7.1	84.8	0.807	270
14	6.2	85.7	0.859	266
16	4.9	87.0	0.954	258
18	3.9	88.0	1.047	250
20	3.3	88.6	1.117	250
40	0.9			
60	0.5			
540	0.0			

The integrated form of this equation is:

$$\log \frac{(\beta(P_0 - P_\infty) - \alpha P_\infty) \cdot \log e}{\alpha P_0(\beta(P_0 - P_\infty) - \alpha P_\infty) - \alpha C_{\text{Hg}}^{++}(P_0 - P_\infty)} \cdot \frac{(P_0 - P_\infty) \cdot P \cdot C_{\text{Hg}}^{++}}{P_0(C_{\text{Hg}}^{++}(P_0 - P_\infty) - (P_0 - P)(\beta(P_0 - P_\infty) - \alpha P_\infty))} = k \cdot t \quad (13)$$

For pressures less than about 175 mm Hg there is a deficit of ethylene, so that pressure P_∞ when equilibrium is established is so small (less than 0.1 mm Hg) that it can be neglected and the integrated form can be simplified to:

$$\frac{\beta \cdot \log e}{\alpha(\beta \cdot P_0 - C_{\text{Hg}}^{++})} \cdot \log \frac{P \cdot C_{\text{Hg}}^{++}}{P_0 (C_{\text{Hg}}^{++} - (P_0 - P))} = k \cdot t \quad (14)$$

As a rule the rate constant was determined from the slope of the straight line plot of the logarithmic expression against t . In all the tables in this paper the rate constants are given in mole per liter per minute.

In most of the experiments a deficit of ethylene was used because it was easier to calculate the rate constant from the more simple expression (14) and it also provided a check of the purity of the ethylene used since the pressure P_∞ must be very near zero. Where this was not the case, the value of the pressure when equilibrium had been established was used to calculate how much atmospheric nitrogen was mixed with the ethylene, and then this value was used for correction of the pressure. Small amounts of atmospheric air are always present in the ethylene when it is kept in a gasometer, as the water that enters when the gas is let out is saturated with air.

In all the experiments, except one, the composition of the solution when working in nitrate medium was the same as described under preliminary experiments, and in perchlorate medium it was: $C_{\text{Hg}(\text{ClO}_4)_2} = 0.0250$; $C_{\text{HClO}_4} = 0.0500$ and $C_{\text{NaClO}_4} = 0.9000$ mole per liter. As the hydrogen ion concentration in all the experiments in this paper is greater than 0.0250, the hydrolysis of the aquo mercuric ion is less than 1 % in all the solutions⁷.

In Expt. No. 12 (Table 7) another initial concentration was employed because mercurous nitrate was used instead of mercuric nitrate. Almost the same rate constant was obtained in this case as in all the other experiments in nitrate solution. It is only possible to make small alterations in the mercuric ion concentration in pure mercuric solutions, as the capacity of the apparatus is limited, and a certain fall in pressure of ethylene is necessary in order to obtain the least possible deviation.

The initial pressure of ethylene was varied from 66 to 712 mm Hg without any influence on the rate constant being observed. The results of these tests are shown in Table 5.

Table 5. Variation of ethylene pressure at 25° C.

The solution used was the same as in Table 1.

Expt. No.	P_0	k
1	66	317
2	90	307
3	167	282
4	213	287
5	283	308
6	537	287
7	712	282

Table 6. Variation of initial hydrogen ion concentration at 25° C.

The initial concentrations were: $C_{\text{Hg}(\text{NO}_3)_2} = 0.0250$ and $C_{\text{NaNO}_3} = 0.9000$ mole per liter.

Expt. No.	C_{HNO_3}	k
1	0.0250	326
2	0.0500	332
3	0.200	332

Table 6 gives the results of a few experiments made with different initial concentrations of the hydrogen ion. These concentrations lie between 0.0250 to 0.200 mole per liter. As there is nothing to indicate any influence on the rate constant, this shows that the reaction takes place between an ethylene molecule and the diaquo mercuric ion and not with the hydroxo mercuric ion as suggested by some of the earlier authors.

In the experiments with 1 M nitrate medium, several difficulties were encountered. The rate constant showed some inexplicable dependence on the purity and age of the ethylene. Thus, freshly prepared ethylene gives about 5–10 % higher values than older ethylene, and a minimum value is obtained after about four days and remains constant. We may assume that the dependence on the purity of ethylene in this case is of the same type as already mentioned with the experiments analogous to those of Sand and Breest, employing mercuric chloride. In 1 M perchlorate solutions there was no significant dependence on the purity and age of ethylene.

A summary of experiments made at different temperatures is given in Tables 7 and 8. Employing Arrhenius' equation in 1 M perchlorate and 1 M nitrate medium respectively, all the results may be expressed as follows:

$$\log_{10} k = \log_{10} A - \frac{E_A}{RT \cdot \log e} = 5.15 - \frac{5.810}{4571 \cdot T} \quad (15)$$

$$\log_{10} k = 4.94 - \frac{5.855}{4571 \cdot T} \quad (16)$$

From the above it will be seen that the value of energy of activation (expressed in kcals.) and the value of the frequency exponent are exceedingly small, and less than usually found in rapid complex reactions¹⁴. The value of the rate constant given in the last column is calculated from these equations, and there is a very good agreement with the experimental average value.

The difference between the rate constants with nitrate or perchlorate as medium may be due to the tendency of mercuric ion to associate with the nitrate ion. According to Sillén¹³, it is about 50 % associated in 1 M nitrate

Table 7. Results of experiments at various temperatures for determination of the rate constant in 1 M sodium nitrate solution.

The stoichiometric concentrations of the solution used in all the experiments except Nos. 12 and 13 were: $C_{\text{Hg}(\text{NO}_3)_2} = 0.0250$; $C_{\text{HNO}_3} = 0.0500$ and $C_{\text{NaNO}_3} = 0.9000$ mole per liter. In Expt. No. 12 mercurous nitrate was used and the initial concentration of the mercuric ion was only: 0.0001935. In Expt. No. 13 three per cent of the nitrate ions were exchanged with perchlorate ions. In Expts. Nos. 22, 23 and 24 freshly prepared ethylene was used. The value of k in the last column is calculated from equation (4).

Expt. No.	Temperature in °C	k	k average	k calculated
1	20°	265	266	266
2	20°	267		
3	25°	317		
4	25°	318		
5	25°	315	316	314
6	25°	315		
7	25°	315		
8	25°	317		
9	25°	313	335	335
10	25°	320		
11	25°	319		
12	25°	306		
13	25°	313	366	366
14	27°	335		
15	30°	369		
16	30°	367		
17	30°	365	429	427
18	30°	364		
19	30°	364		
20	35°	419		
21	35°	440	338	338
22	25°	338		
23	27°	361		
24	35°	461		

solution, whereas the perchlorate ion is supposed to have a very little tendency to associate with mercuric ion. If an ordinary experiment is calculated on the basis of an initial concentration of only 60—65 % of the total, a rate constant is obtained which agrees with the corresponding value in perchlorate medium. Thus it seems that ion association explains most of the effect of the medium ¹⁵. One experiment (No. 13, Table 7) in which 3 % of the nitrate ions were exchanged with perchlorate ions was carried out, in order to ascertain whether the perchlorate ion might have a catalytic effect, but the rate constant was exactly the same as in pure nitrate solutions.

Table 8. Results of experiments at various temperatures for determination of the rate constant in 1 *M* sodium perchlorate solution.

The stoichiometric concentrations of the solution used in all the experiments were: $C_{\text{Hg}(\text{ClO}_4)_2} = 0.0250$; $C_{\text{HClO}_4} = 0.0500$ and $C_{\text{NaClO}_4} = 0.9000$ mole per liter. The value of k in the last column is calculated from equation (3).

Expt. No.	Temperature in °C	k	k average	k calculated
1	20°	371		
2	20°	361		
3	20°	372	366	369
4	20°	364		
5	20°	363		
6	25°	430		
7	25°	437		
8	25°	441	436	434
9	25°	430		
10	25°	436		
11	25°	454		
12	30°	510		
13	30°	523	510	510
14	30°	508		
15	30°	499		

The value of the rate constant in dilute aqueous solution must be of the same order of magnitude as the one found in 1 *M* salt solution, because the reaction occurs between an ion and a neutral molecule¹⁶.

MEASUREMENT OF THE RATE CONSTANT WITH OTHER IONS

In the literature, only one example has been mentioned in which a reaction takes place between mercurous ion and an unsaturated compound, *viz.* by Biilmann¹⁷ who investigated the reaction between mercurous nitrate and allyl alcohol.

One experiment was made using mercurous nitrate and ethylene (Expt. No. 12, Table 7). As there was an uptake of ethylene and the velocity appeared to be about 10–20 times less than in the experiments with mercuric nitrate (after 3 minutes only about 10 % had reacted, after 30 minutes only 30 % and after two hours 60 %), it was assumed at first that the mercurous ion had reacted with ethylene, but when calculating the rate constant from equation (13) it was obvious that this could not be the case, as no straight line was formed when plotting the logarithmic expression against t . When we calculate the rate constant assuming that only the mercuric ion in the mercurous nitrate

solution reacts with ethylene, the value obtained is nearly the same as found in the experiments with pure mercuric solutions. In making the calculation we assumed that the mercuric ion is formed instantaneously from mercurous ions.

As previously demonstrated by Biilmann, the reaction occurs with precipitation of mercury which is readily seen, since the solution becomes grey and muddy after about half an hour. The initial concentration of mercurous ion is: 0.0250 and the initial concentration of mercuric ion calculated according to equation (10) is: 0.0001935.

It has also been shown that no reaction takes place when two or more ligands are bound to the mercuric ion, *e.g.*, HgCl_2 ; HgCl_3^- ; HgCl_4^{2-} ; HgBr_2 ; $\text{Hg}(\text{NH}_3)_2^{++}$; $\text{Hg}(\text{NH}_3)_3^{++}$.

In solutions with maximum concentration of monocomplex, *i.e.*, about 30 % of the ion: HgCl^+ ; HgBr^+ or $\text{Hg}(\text{NH}_3)^{++}$, a reaction takes place with almost the same velocity as for the mercuric ion. For this reason the reaction with these ions is assumed to occur mainly according to:

Since some mercuric ions are present in the solution, a reaction according to (2) runs parallel to (17) and therefore an equilibrium between the ions II and IV may be assumed. After a few hours a white precipitate is formed, thus making it difficult to carry out further investigations with these ions. Only in a few cases was it possible to calculate the rate constant for these complex

Table 9. Results of experiments for determination of the rate constant at 25° C with different complex ions and salts.

Expt. No.	Complex ion	<i>k</i>
1	Hg_2^{++}	0
2	HgCl^+	263
3	HgBr^+	258
4	$\text{Hg}(\text{NH}_3)^{++}$	(300)
5	HgCl_2	0
6	HgBr_2	0
7	$\text{Hg}(\text{NH}_3)_2^{++}$	0
8	HgCl_3^-	0
9	HgCl_4^{2-}	0
10	$\text{Hg}(\text{NH}_3)_3^{++}$	0
11	$\text{Hg}(\text{NH}_3)_4^{++}$	0

ions. In the calculation, correction is to be made for the reaction with the mercuric ions as well as for the displacement of the equilibrium:

which has been thoroughly investigated by Sillén¹³.

A list of these experiments is given in Table 9. The values for the mono-halide ions were only determined from one experiment and the value may therefore only be considered as preliminary. This is particularly the case in the experiment with the monoammine mercuric ion, where a precipitate was formed after a few minutes.

SUMMARY

Kinetic investigations have been carried out on the reaction between mercuric salts and ethylene. It has been shown that the reaction is bimolecular with regard to the aquo mercuric ion and ethylene and that the uptake of ethylene is instantaneously followed by dissociation of a hydrogen ion. The following equilibria are suggested:

The equilibrium between the ions II and III must be well to the side of the organic form. This explains why the coordination compound I behaves as a strong acid.

It has been shown that the reaction is reversible and the value of the equilibrium constant is found to be:

$$K = \frac{([\text{II}] + [\text{III}]) \cdot [\text{H}^+]}{[\text{Hg}^{++}] \cdot [\text{C}_2\text{H}_4]} = 3.5 \cdot 10^6$$

The relation between the rate constant (time in seconds) and the absolute temperature in 1 *M* perchlorate medium has been found to be:

$$\log_{10} k = 5.15 - \frac{1280}{T}$$

The rate constant at 25°C is found to be: 7.23 mole per liter per second.

Some experiments have been made to investigate the reaction with other mercuric salts and with mercurous nitrate.

The authors take the opportunity to thank Professor J. A. Christiansen for suggesting this investigation, and Professor J. Bjerrum and Dr. N. Hofman-Bang for discussions during the course of this work.

REFERENCES

1. Sand, J., and Breest, F. *Z. physik. Chem.* **59** (1907) 424.
2. Chatt, J. *Chem. Revs.* **48** (1951) 7.
3. Brooke, A. G., and Wright, G. F. *Can. J. Research B.* **28** (1950) 623.
4. Brooke, A. G., and Wright, G. F. *Can. J. Chem.* **29** (1951) 308.
5. Lucas, H. J., Hepner, F. R., and Winstein, S. *J. Am. Chem. Soc.* **61** (1939) 3102.
6. Bjerrum, J. *Chem. Revs.* **46** (1950) 396.
7. Hietanen, S., and Sillén, L. G. *Acta Chem. Scand.* **6** (1952) 747.
8. Winstein, S., and Lucas, H. J. *J. Am. Chem. Soc.* **60** (1938) 836.
9. Taufen, H. J., Murray, M. J., and Cleveland, F. F. *J. Am. Chem. Soc.* **63** (1941) 3500.
10. Trueblood, K. N., and Lucas, H. J. *J. Am. Chem. Soc.* **74** (1952) 1338.
11. Hofman-Bang, N. *Acta Chem. Scand.* **3** (1949) 874.
12. Grollman, A. *J. Biol. Chem.* **82** (1929) 317.
13. Sillén, L. G. *Svensk kem. Tid.* **58** (1946) 52.
14. Bjerrum, J., and Poulsen, K. G. *Nature* **169** (1952) 463.
15. Bell, R. P., and Prue, J. E. *J. Chem. Soc.* 1949, 362.
16. Brønsted, J. N. *Z. physik. Chem. A.* **102** (1922) 169.
17. Büllmann, E. *Ber.* **33** (1900) 1641.

Received November 22, 1952.