COORDINATION COMPLEXES OF THE MERCURIC ION WITH CYCLOHEXENE

Thesis by

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Coordination Complexes of the Mercuric Ion with Cyclohexene

Unsaturated compounds have the property of forming a class of compounds of relatively low stability. These are addition or coordination compounds and are distinctly different from the stable compounds formed by addition of halogens or hydrohalogens. Coordination complexes of silver ion with unsaturated compounds have been studied recently.(1) The reaction of olefins and silver salts was rapid and reversible so that it was possible to study it by the distribution method. Silver nitrate was shown to form three types of coordination complexes with ethylene compounds; viz: combinations of one silver ion with one unsaturated compound, two silver ions with one unsaturated compound and one silver ion with two unsaturated compounds.

The formation of compounds from mercury salts and olefins has been very extensively studied. Hofmann and Sand (2) showed that ethylene combined with mercuric salts in aqueous solutions to yield a compound which they designated by the formula CH_2OH-CH_2-HgX, or by a second formula, $C_2H_4 \cdot Hg(OH)X$, which represents an intermediate addition product of a molecule of ethylene and a molecule of a basic mercuric salt. Manchot (3) claimed that these were merely molecular addition compounds and do not correspond to any structural formula. Other investigators (4) have shown since that definite mercury-carbon bonds exist in these addition compounds, thus apparently disproving Manchot's theory of molecular compounds. The possibility that both complexes of the silver type and also stable addition compounds could exist, and that the equilibrium between these two types of compounds explains the mass of complicated data does not seem to have occurred to investigators before.

In this laboratory Lucas and Eberz (5) found that isobutene hydrated only partially in the presence of mercuric nitrate. That is, the complexed isobutene would not hydrate, but could still be determined by analysis. From this it seemed possible that mercury complexes analogous to silver complexes are formed. In this thesis is reported a research which has shown that mercuric ion and cyclohexene do form a complex analogous to that given by silver ion and the equilibrium constant for its formation has been determined.

In the research which forms the basis for this report there has been no attempt to isolate a compound and analyze it as done by other investigators of mercury complexes, but the nature of the compound was studied chiefly by the distribution method previously used by other investigators in this laboratory. (6)

For what follows it will be convenient to mention here the notations which are used in recording data and calculations. These notations conform with those used previously in the laboratory.

B = Cyclohexene

(Bt) = Total concentration of cyclohexene in aqueous phase in mols per liter.

(B) = Concentration of uncomplexed cyclohexene in aqueous phase in mols per liter.

$(B)_c$ = Concentration of cyclohexene in carbon tetrachloride in mols per liter.

(Hg^{++}) = Concentration of uncomplexed mercuric ion in aqueous phase in mols per liter.

(Hgt) = Total concentration of mercury in aqueous phase in mols per liter.

K_D = $(B)_c/(B)$ = Distribution ratio of cyclohexene between carbon tetrachloride and 1 N potassium nitrate.

$(B\cdot Hg^{++})$ = Concentration of the species $B\cdot Hg^{++}$ in the aqueous phase in mols per liter.

$(Hg\cdot OH\cdot B^{+})$ = Concentration of the species $Hg\cdot OH\cdot B^{+}$ in the aqueous phase in mols per liter.

(HNO_3) = Concentration of added acid in mols per liter.

(H^{+}) = Concentration of total acid in the aqueous phase in mols per liter.

$$\frac{K}{K_D} = \frac{(Bt)}{(B)_c\left[(Hgt)-(Bt)\right]} = \text{constant recorded}$$

$$= \frac{\left[(Bt)-(B)_c/K_D\right]}{(B)_c\left[(Hgt)-(Bt)+(B)c/K_D\right]} \text{ with negligible error.}$$

Experimental Section and Presentation of Data.

Materials.- In all cases the inorganic chemicals were of the C.P. or Reagent grade. The bromate-bromide solution was made up by weight and used as a standard. The sodium thiosulfate solution was prepared and standardized against the bromate-bromide solution. A stock solution of mercuric nitrate was made by dissolving a weighed amount of reagent grade crystals in water, adding a known amount of nitric acid just sufficient to redissolve the basic salts which had precipitated, and then making up to volume. This was titrated with standard potassium thiocyanate and then diluted until the ionic strength of the solution was 1μ.

Carbon tetrachloride was purified by passing in chlorine, allowing the solution to remain in sunlight for a time, removing the chlorine with sodium hydroxide solution, drying with calcium chloride and distilling. Blanks on the carbon tetrachloride showed that it neither used up nor liberated bromine or iodine.

Cyclohexene was prepared by the dehydration of cyclohexanol with sulfuric acid. It was purified by distilling, drying over sodium at least over night, and redistilling over sodium in an atmosphere of nitrogen. Solutions of cyclohexene in carbon tetrachloride were made by weighing cyclohexene into a volumetric flask and filling the flask with carbon tetrachloride to volume. To test for freedom from peroxides, the cyclohexene or its solution was shaken with acid-potassium iodide-starch solution.

Analysis for Cyclohexene.- The analysis of the cyclohexene was carried out by bromination with standard bromate-bromide solution. The technique previously described (7) for cyclohexene was slightly modified. Bromate-bromide solution was put in a titration flask and the flask evacuated. 5 ml. of 6 N sulfuric acid were added and the flask was allowed to stand five minutes or more for the liberation of bromine. The flask was wrapped in black cloth to lower the amount of bromine substitution catalyzed by light. In the analysis of the carbon tetrachloride phase 5 ml. of mercuric nitrate solution were added to the flask. None was added to the water phase, so that conditions would be comparable for the analysis of each phase. The sample was run in and the flask shaken for one minute. 10 ml. of 2 N sodium chloride solution were added to break a mercury-bromine complex. Shaking was continued for five minutes, after which time 10 ml. of 2 N potassium iodide solution were added and shaking was continued for one or two minutes. The vacuum was broken and the contents of the flask were titrated with sodium thiosulfate solution to the starch-iodine end point. Five minutes or more were found necessary for the liberation of bromine. It is thought that mercury inhibited the liberation of bromine, thus giving rise to this time requirement. Shaking was necessary after adding the sodium chloride and before adding potassium iodide because bromination was not completed with the mercury-bromine complex unbroken. The excess of bromate-bromide could be varied from fifteen to sixty five per cent without introducing an error greater than ±0.5 per cent in the analysis of cyclohexene. Varying the time of shaking after adding sodium chloride solution from five to eleven minutes made only +0.1 per cent error (twenty per cent excess bromate-bromide was used). The amount of sodium chloride had to be sufficient to form a chloride with all the mercury present.

The Distribution Method.- "The procedure consists in distributing the organic compound [cyclohexene] between carbon tetrachloride and 1 N potassium nitrate, and then combining the resulting distribution ratio with the other data obtained by distributing the same unsaturated compound [cyclohexene] between carbon tetrachloride..."(1) and a solution, whose total ionic strength is 1μ, of mercuric nitrate, nitric acid and potassium nitrate. The data needed are the concentrations of cyclohexene in the two phases, the concentration of the mercuric salt, and of the nitric acid in the aqueous phase.

The procedure followed for the distributions of cyclohexene between carbon tetrachloride and the mercuric nitrate solution was essentially the same as that used in the silver work.(1) It was found that shaking the mixture with air caused the cyclohexene to absorb oxygen, which resulted in errors in the analysis. The returning of the blue starch-iodine color in the titration solution was considered as an indication that peroxide was present. In several cases the color would return almost as fast as sodium thiosulfate could be added in a titration. This difficulty was overcome by replacing the atmosphere of air above the solutions by an atmosphere of nitrogen. Shaking the flasks in the thermostat proved irregular and inconvenient, so mercury sealed stirrers were used for the mixing of the two phases, thus giving more uniform and thorough agitation. The mechanical stirring made duplication of results possible for the same stirring times. A two neck flask was used for distributions. Through one was placed the mechanical stirrer and in the other was inserted a two hole rubber stopper. Through one hole in the stopper was a tube with a two way stopcock, and through the second hole was a piece of glass tubing of ten mm. inside diameter over the outside end of which was a piece of rubber tube fitted with a screw clamp. See Figure 1.

Carbon tetrachloride and mercuric nitrate solution were put in the flask and the whole ring stand with the flask, stirrer, and motor was put into the water thermostat which was kept at 25° ±0.03°. The air above the liquids in the flask was displaced by nitrogen. After allowing the contents of the flask to come to the tem-

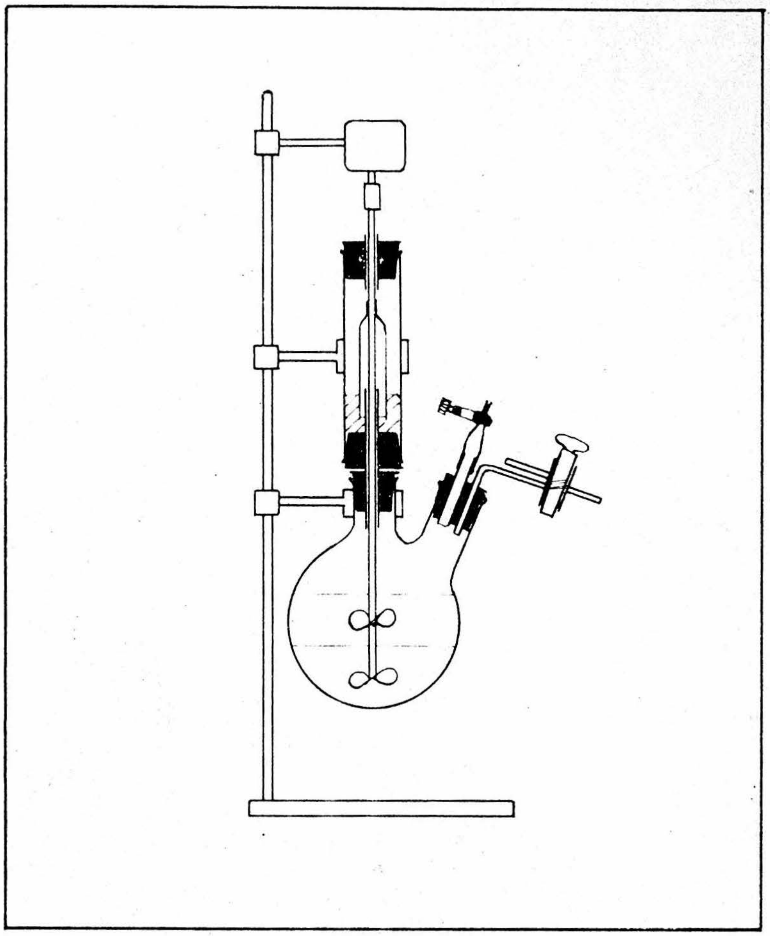


Figure 1.

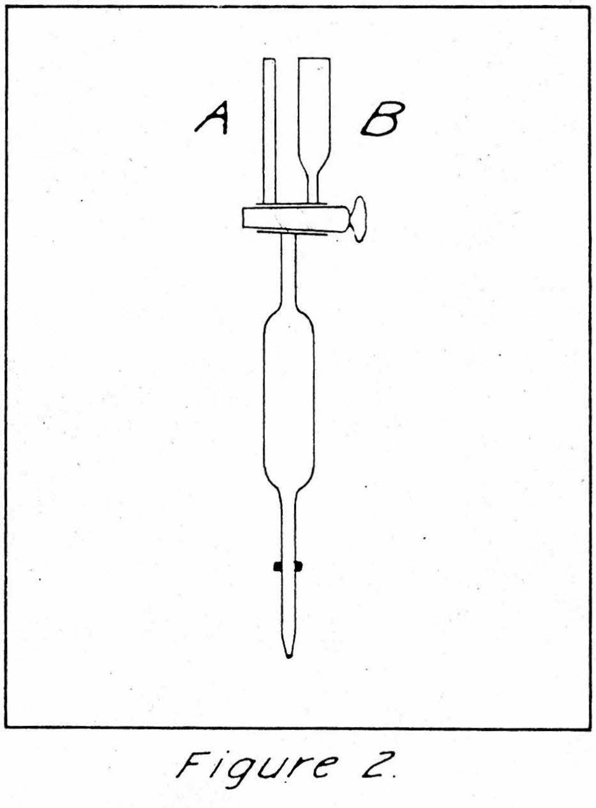


Figure 2.

peratures of the thermostat the cyclohexene was added in the form of a certain volume of concentrated solution in carbon tetrachloride. It was added through the large tube in the rubber stopper while nitrogen was flowing through to prevent the possibility of any air entering. The contents of the flask were stirred for a certain time and then allowed to stand until the phases separated quite clearly.

Sampling was done in the following manner: A small amount of nitrogen was allowed to flow through the stopcock out the open tube. As the screw clamp was opened the stopcock was turned so that nitrogen was flowing into the flask. A sampling pipet (Figure 2) was inserted through the large tube and into the phase to be sampled. A ring of rubber tubing on the pipet was pushed against the tubing on the stopper to prevent the escape of nitrogen. This forced the liquid up into the pipet. When it was filled the stopcock on the pipet was turned and the pipet removed. The tip of the pipet was attached to the evacuated titration flask and the contents washed into the flask with carbon tetrachloride or water, depending upon the phase of the sample taken. The sample was forced up into tube A and the wash liquid put in funnel B. The pipet was calibrated to contain, up to the stopcock.

Before distributions were made a small amount of cyclohexene was dissolved in mercuric nitrate solution and samples of this solution were analysed over a period of several hours. The concentration of cyclohexene remained constant, which showed that there was no hydration in the presence of mercuric ion. It was possible however that hydration of cyclohexene was taking place, but the cyclohexanol formed might use up the same amount of bromine as cyclohexene. Cyclohexanol was purified by washing with sodium hydroxide solution to remove phenol, washing with water, washing with dilute hydrochloric acid, drying with potassium carbonate and distilling. The purified cyclohexanol was taken as the constant boiling fraction at 159° (161.5° corrected) M.P. 22°C. This purified cyclohexanol was dissolved in carbon tetrachloride and it used no bromine. A water solution of cyclohexanol also used no bromine.

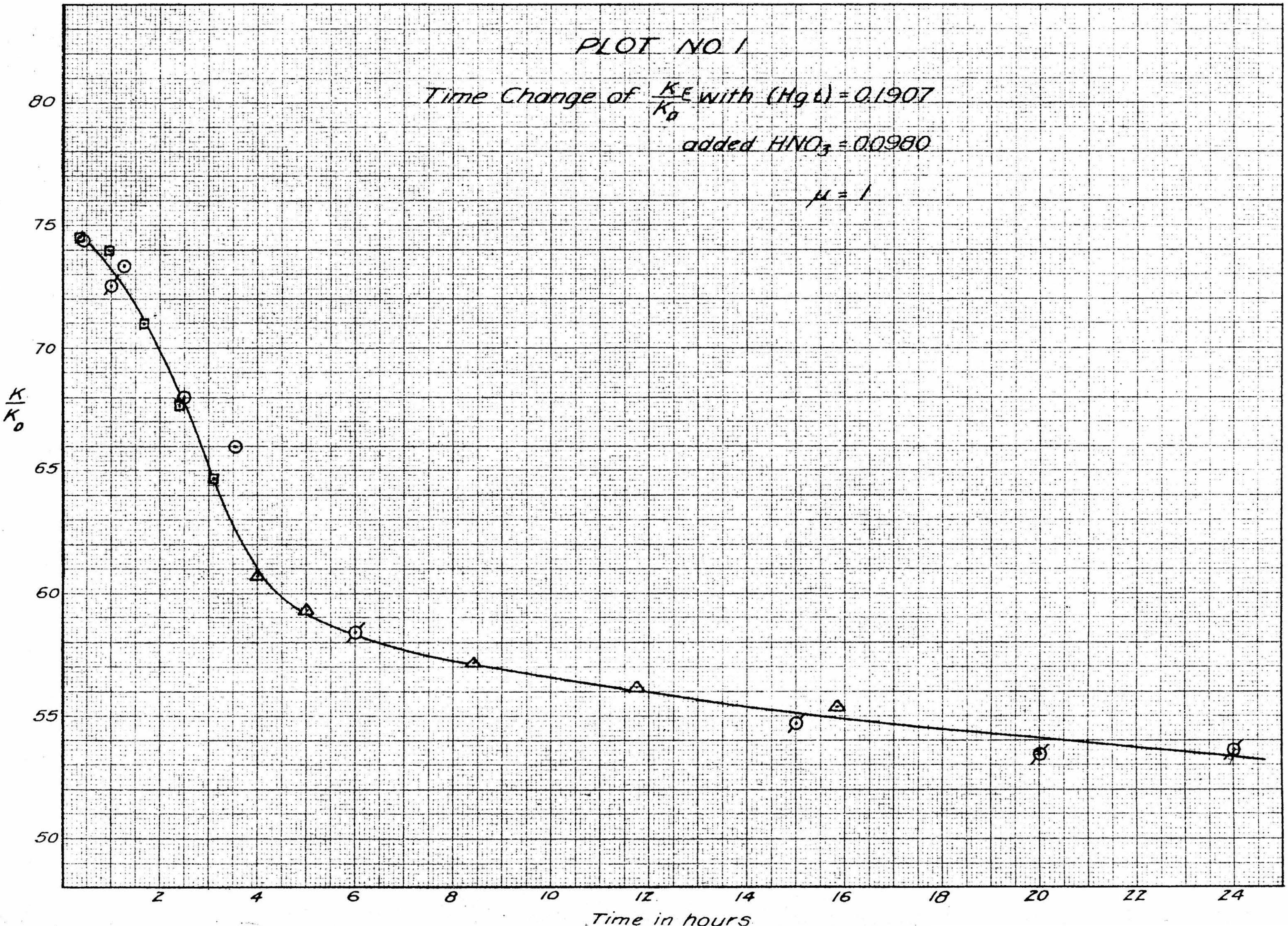
In order for the distribution method to be valid it was necessary that none of the mercury appeared in the carbon tetrachloride phase. To test this 50 ml. of carbon tetrachloride phase were evaporated just to dryness in a small evaporating dish over a very low flame. One ml. of 6 N nitric acid was washed around and warmed in the dish to take up any residue which may have remained (none was visible). This solution was diluted with 1 ml. of water and divided into two parts which were placed in two test tubes. One ml. of a saturated solution of hydrogen sulfide in water was added to each of the tubes. There was a very slight darkening showing the possibility of mercury. Known soltuions of mercury were tested to see the extent of darkening under similar circumstances. With 0.00024 milliequivalents of mercuric nitrate in one ml. of 3 N nitric acid the hydrogen sulfide solution gave a very similar darkening. Any larger amounts of mercury gave darker colors and precipitates. From this it was concluded that there is less than 0.00001 milliequivalents of mercury per ml. in the carbon tetrachloride. This small amount could be from dissolved water in the carbon tetrachloride, but for purposes of the equilibrium measurements there was a negligible quantity of mercury in the carbon tetrachloride phase.

Distributions at Low Acid Concentration over Extended Periods of Time.- In a 500 ml. two neck flask 100 ml. of 0.1907 F. mercuric nitrate solution and 300 ml. of carbon tetrachloride solution 0.0492 formal in cyclohexene were stirred for 25 minutes. The phases were allowed to separate for 35 minutes and two samples of each phase were taken and analysed. After the samples were taken the solutions were stirred again for 5 minutes, allowed to settle and two more samples of each phase analysed. This was continued until there were no more solutions remaining in the flask. There were several things noted about this set of data. The concentration of cyclohexene was decreasing in the water phase and increasing in the carbon tetrachloride phase, which should not be the case unless an equilibrium had been reached and a reaction was proceeding, because all the cyclohexene was initially in the carbon tetrachloride. Also the constants calculated were decreasing with time. (Table I and Plot 1.) Several runs were made varying the time of stirring. The time recorded was that from the start until the stirrer was stopped before each sample was taken. This included the time allowed for the separation of phases necessary for the abstraction of all preceding samples. The times were recorded thus, because if there were a reaction proceeding in the water phase, it would continue while there was no agitation, but no distribution would take place. Furthermore, redistribution would be permitted by the subsequent stirring. One run was made with stirring for only five minutes at the start, but equilibrium apparently had not been reached, because the constant was low (11.25), and on further stirring (five minutes, after six or seven minutes standing) the cyclohexene went from the carbon tetrachloride into the water phase giving higher constants (25.05, then 48.8, 61.0 and finally 63.3). Twenty minutes of stirring was taken to be about the minimum time for equilibrium to be established. Several determinations, indicated by ø in Table I and in Plot 1, were made in smaller flasks with only one analysis per flask, thus eliminating errors due to time of standing without stirring.

Table I

Time Change of K/K_D at 25° With (Hgt) = 0.1907 F
(HNO_3) = 0.0980 F μ= 1

Time	Conc'n. of Cyclohexene in CCl_4 $(B)_c$	$H_2O(Bt)$	K/K_D
25 min.	0.0161	0.1038	74.4
○ 1 hr. 16 min.	0.0161	0.1028	72.7
2 hr. 30 min.	0.0166	0.1010	68.0
3 hr. 33 min.	0.0169	0.1005	66.0
20 min.	0.0159	0.1033	74.5
56 min.	0.0158	0.1028	74.0
□ 1 hr. 40 min.	0.0161	0.1017	71.0
2 hr. 24 min.	0.0165	0.1005	67.0
3 hr. 06 min.	0.0173	0.1004	64.7
4 hr.	0.0172	0.0974	60.7
5 hr.	0.0175	0.0971	59.3
△ 8 hr. 25 min.	0.0178	0.0962	57.2
11 hr. 45 min.	0.0181	0.0961	56.2
15 hr. 50 min.	0.0183	0.0960	55.4
∅ 6 hr.	0.0184	0.0987	58.4
∅ 15 hr.	0.0192	0.0977	54.7
∅ 20 hr.	0.0194	0.0965	53.4
∅ 24 hr.	0.0188	0.0966	54.6
∅ 1 hr.	0.0163	0.1032	72.5


PLOT NO 1
Time Change of $\frac{K_E}{K_0}$ with (Hg t) = 0.1907
added HNO_3 = 0.0980
μ = 1
$\frac{K}{K_0}$
80
75
70
65
60
55
50
2
4
6
8
10
12
14
16
18
20
22
24
Time in hours

As a result of these figures it was thought that cyclohexene formed a complex quite rapidly with mercuric ion. This reaction takes place in the first twenty minutes of stirring. At the same time and later there is a secondary reaction which is much slower, as indicated by the decrease in the value of the constant. The reaction probably is not reversible. The trend of the concentrations of cyclohexene in the water phase from 0.1083 mol per liter to 0.0960 mol per liter and the trend of concentrations in carbon tetrachloride from 0.0161 mol per liter to 0.0183 mol per liter indicate apparently that the concentrations are approaching values which would result from a stable compound of two mercury ions with one molecule of cyclohexene; namely 0.0953 mol per liter in the water phase and 0.0174 mol per liter in the carbon tetrachloride phase.

Further Study of the Secondary Reaction.- Compounds formed between olefins and mercuric acetate in alcohol solution can be titrated with potassium thiocyanate.(4e) Each mercury compound of this type reacts with one equivalent of thiocyanate instead of with two, as mercuric ion does. With this in mind a sample of the water phase of one of the distributions was titrated with potassium thiocyanate. There was a lower amount of mercuric ion shown by titration than was present at the start of the distribution.

The following experiment was undertaken to follow the concentration of mercury in the presence of cyclohexene over a period of time. Two ml. of cyclohexene were dissolved in 100 ml. of 0.286 formal mercuric nitrate. solution. (The cyclohexene dissolved completely and gave a clear solution.) The air above the liquid was displaced with nitrogen and the flask was shaken vigoously for several seconds. 10 ml. samples were withdrawn from time to time and titrated with potassium thiocyanate solution. The results are shown in Table II.

Table II

Time Effect of Cyclohexene on Apparent Mercuric Ion Concentration

Time	ml. of 0.1090 N KSCN used per 10 ml. sample	(b) apparent (Hg^{++})	(c) Corrected for Hg^{+} (Hg^{++})	(Hg^{+})
0 min.	52.47	0.286	0.286	0.000 (a)
7 min.	50.86	.2775	..2690	.0085
35 min.	48.39	.2640	.2420	.0220
1 hr. 32 min.	45.38	.2472	.2076	.0396
3 hr. 15 min.	42.31	.2305	.1750	.0555
4 hr. 47 min.	40.89	.2230	.1600	.0630
11 hr. 10 min.	37.29	.2033	.1206	.0827
13 hr. 20 min.	37.05	.2020	.1180	.0840

(a) These are for titration of mercuric nitrate solution without cyclohexene and have not been corrected for volume of added cyclohexene. Corrected values would be 51.44 ml. and 0.2804 mol per liter.

(b) Assuming Hg^{++} only reacts with thiocyanate.

(c) Hg = 0.286 minus subsequent values.

The mixture of cyclohexene in mercuric nitrate solution had a very foul odor and caused headaches. There was no odor of cyclohexene. When this was titrated with potassium thiocyanate the sweet odor of cyclohexene developed. In the last few samples when drops of potassium thiocyanate were added, there was a dark precipitate formed which became lighter as the titration was continued. The last titration mixture remained dark and the end point was very difficult to see.

A similar experiment was performed with 0.1232 mol per liter of cyclohexene in 0.286 formal mercuric nitrate. In this case the samples were taken and analysed for cyclohexene by bromination. There was an apparent increase in cyclohexene concentration which is unexplainable. The samples analysed for mercury at the same time showed the tendency of mercury to decrease as before. The last titration mixture gave no definite end point.

Table III

Time Effect on Apparent Concentrations of Cyclohexene and Mercuric Ion in Water Solution at 25°.

Time	Apparent Conc'n. of C_6H_{10}	Apparent Conc'n. of $Hg(NO_3)_2$
0 min.	0.1232*	0.286#
34 min.	0.1236	0.2684
1 hr. 31 min.	0.1228	0.2700
3 hr.	0.1275	0.2497
4 hr. 3 min.	0.1330	0.2330
9 hr. 17 min.	0.1530	0.2246
16 hr. 50 min.	0.1728	0.2537

* A weighed amount of cyclohexene was dissolved in the solution to give this value.

This value not corrected for volume of added cyclohexene.

The apparent increase of cyclohexene and the apparent decrease of mercuric nitrate indicated more conclusively that a more complicated reaction of mercuric ion and cyclohexene was taking place. This secondary reaction had very little similarity to the silver coordination complexes with unsaturated compounds. Because the primary reaction, which was apparently quite rapid, was like that of silver ion, and because the original purpose of this research was to study the similarities of mercuric ion complexes to the silver ion complexes, attention was focused on the primary reaction, which could be studied even though there were a secondary reaction.

Complex Formation Between Mercuric Ion and Cyclohexene.- The calculated constants K/K_D at the shorter times were considered to be due almost entirely to the primary reaction. These constants were used to study the reaction and were obtained in the following manner. Three distributions were made for each concentration with stirring one half hour, one hour, and one and one half hours respectively. The constants K/K_D calculated for these three runs were extrapolated to zero time. The calculated constants were not the same for different concentrations of mercuric nitrate. The more dilute solutions of mercuric nitrate were prepared by diluting the stock solution with 1 N potassium nitrate to keep the ionic strength at 1μ. In this way the acid was also being diluted and the effect might have been due to acid concentration. A series of determinations was made at one concentration of mercuric nitrate but with different acid concentrations. The calculated constant changed as shown in Table IV. At the higher acid concentrations there was no drift of the constant with time of stirring, but at the lower acid concentrations the drift was the same as indicated in Plot 1, a decrease with time.

Table IV

Values of K/K_D Obtained by Distribution at 25° of Cyclohexene Between CCl_4 and $Hg(NO_3)_2 + HNO_3 + KNO_3$ Aq. at 1μ.

(Hgt)	(HNO_3)	Extrapolated $(B)_{\underline{o}}$	(Bt)	K/K$_D$ ½ hr.	1 hr.	1½ hr.	Extrap.
0.0477	0.2731	0.0320	0.0271	41.4	41.6	40.6	41.2
0.0954	0.0490	0.0135	0.0558	108.5	105.8	103.2	~~110.~~ 111.2
0.0954	0.0963	0.0153	0.0529	83.6	81.2	79.5	85.6
0.0954	0.2740	0.0209	0.0449	42.4	42.2	42.5	42.4
0.0954	0.2740	0.00805	0.0256	45.6	44.5	46.5	45.5
0.0954	0.2740	0.00364	0.0137	45.0	46.3	46.5	45.9
0.0954	0.5490	0.0252	0.0376	24.9	25.8	26.3	25.7
0.1907	0.0980	0.0158	0.1040				76.0*
0.1907	0.2756	0.01001	0.0606	45.5	47.7	47.4	46.8

* Values taken from Table I and Plot 1.

From this it was seen that acid affected the constant, so pH readings were made with a Beckmann pH meter to see if hydrogen ion was formed when cyclohexene was dissolved in mercuric nitrate. Readings were taken on a mercuric nitrate solution, then the solution was saturated with cyclohexene and readings again taken. Table V shows these readings.

Table V

Change of pH of Mercuric Nitrate Solutions When Cyclohexene was Added.

pH of Mercuric Nitrate Solution	pH Immediately after Addition of C_6H_{10}	pH after Approx. 3 hours
1.55	1.16	1.04
1.30	1.07	0.77
1.19	0.92	0.77 (a)

(a) Two hours for this value.

From this it was evident that hydrogen ion was formed. In order to make calculations of this effect it was necessary to know the exact concentrations in the mercuric nitrate solutions. The acid in the stock solution of mercuric nitrate was determined by precipitating the mercury with hydrogen sulfide, filtering and washing the precipitate, boiling the filtrate and washings to remove the excess hydrogen sulfide, and titrating the total acid with standard sodium hydroxide. Since the concentration of mercuric nitrate was known, the amount of added acid, which was the sum of the amount actually added and that originally in the mercuric nitrate, could be calculated.

Table IV also includes results from varying the concentrations of mercuric nitrate, cyclohexene and acid.

Discussion of the Data

Treatment I.- Since acid concentration has such a large effect on K/K_D and since it has been shown that dissolving cyclohexene in mercuric nitrate solution liberates acid, equation I suggests itself for the reaction

$$Hg^{++} + B + H_2O \overset{K_1}{\rightleftarrows} Hg\cdot B\cdot OH^+ + H^+ \qquad \text{(I)}$$

taking place when cyclohexene and mercuric ion form a complex. The equilibrium constant for the reaction represented by equation I is given in equation II.

$$K_1 = \frac{(Hg\cdot B\cdot OH^+)(H^+)}{(Hg^{++})(B)} \qquad \text{(II)}$$

If we define K_o as K_1/K_D then K_o is given by equation III if equation I represents the true state of affairs.

$$K_o = K_1/K_D = \frac{K}{K_D}(H^+) \qquad \text{(III)}$$

(H) in this treatment is given by equation IV. This treatment seems to fit the data quite satisfactorily.

$$(H^+) = (HNO_3) + (BT) \qquad \text{(IV)}$$

The values for K_o given by equations III and IV are listed in Table VI.

Table VI

Values of K_o Obtained by Using Equation I

(Hgt)	$(B)_c$	(Bt)	K/K_D	(HNO_3)	$(H^+)=(Bt)+(HNO_3)$ Equation IV	$K_o=K/K_D(H^+)$
0.0954	0.0135	0.0558	111.2 ~~110.~~	0.0490	0.1048	11.7 ~~11.5~~
.0954	.0153	.0529	85.6	.0963	.1492	12.8
.0954	.0209	.0449	42.4	.2740	.3189	13.5
.0954	.00805	.0256	45.5	.2740	.2996	13.5
.0954	.00304	.0137	45.9	.2740	.2877	13.0
.0954	.0252	.0376	25.7	.5490	.5866	15.1
.1907	.0158	.1040	76.0	.0980	.2020	15.4
.1907	.01001	.0606	46.8	.2756	.3362	15.7
.0477	.0320	.0271	41.2	.2731	.3002	12.4

Mean-13.7

Mean Deviation± 1.2

These values vary from 11.5 to 15.7, the mean being 13.7 and the mean deviation being ± 1.2.

Treatment II.- When silver nitrate forms complexes with cyclohexene there is no acid liberated. (1) Even though mercury salts like to hydrolyze, it seems probable that there is a complex formed similar to the silver cyclohexene complex and represented by equation V.

$$B + Hg^{++} \overset{K_1'}{\rightleftarrows} B\cdot Hg^{++} \qquad (V)$$

With the assumption of two complexes the dataare better correlated than by treatment I (Table VI). Assuming both reactions represented by equations I and V and defining $K'_o = \frac{K\dashv}{K_D}\,)\,\frac{K}{K_D}$ depends on hydrogen ion concentration as shown by equation VI.

$$K/K_D = K'_o + \frac{K_o}{(H^+)} \qquad \text{VI}$$

Using the series of runs with (Hgt) = 0.0954 a first approximation to K'_o was obtained by plotting K/K_D against $\frac{1}{(H^+)}$ using corrected (H^+) from Table VI. The first approximation was five. Then this value of K'_o was used to obtain a better approximation to the hydrogen ion concentration with the relation shown in equation VII.

$$(H^+) = (HNO_3) + (Bt) \times \left(\frac{K/K_D - K'_o}{K/K_D}\right) \qquad \text{(VII)}$$

K/K_D against the better corrected (H^+) is shown in Plot 2. The value of K'_o from this plot is the same as the first approximation. Table VII shows the constancy in K_o obtained by using $K'_o = 5$ in connection with equations VI and VII.

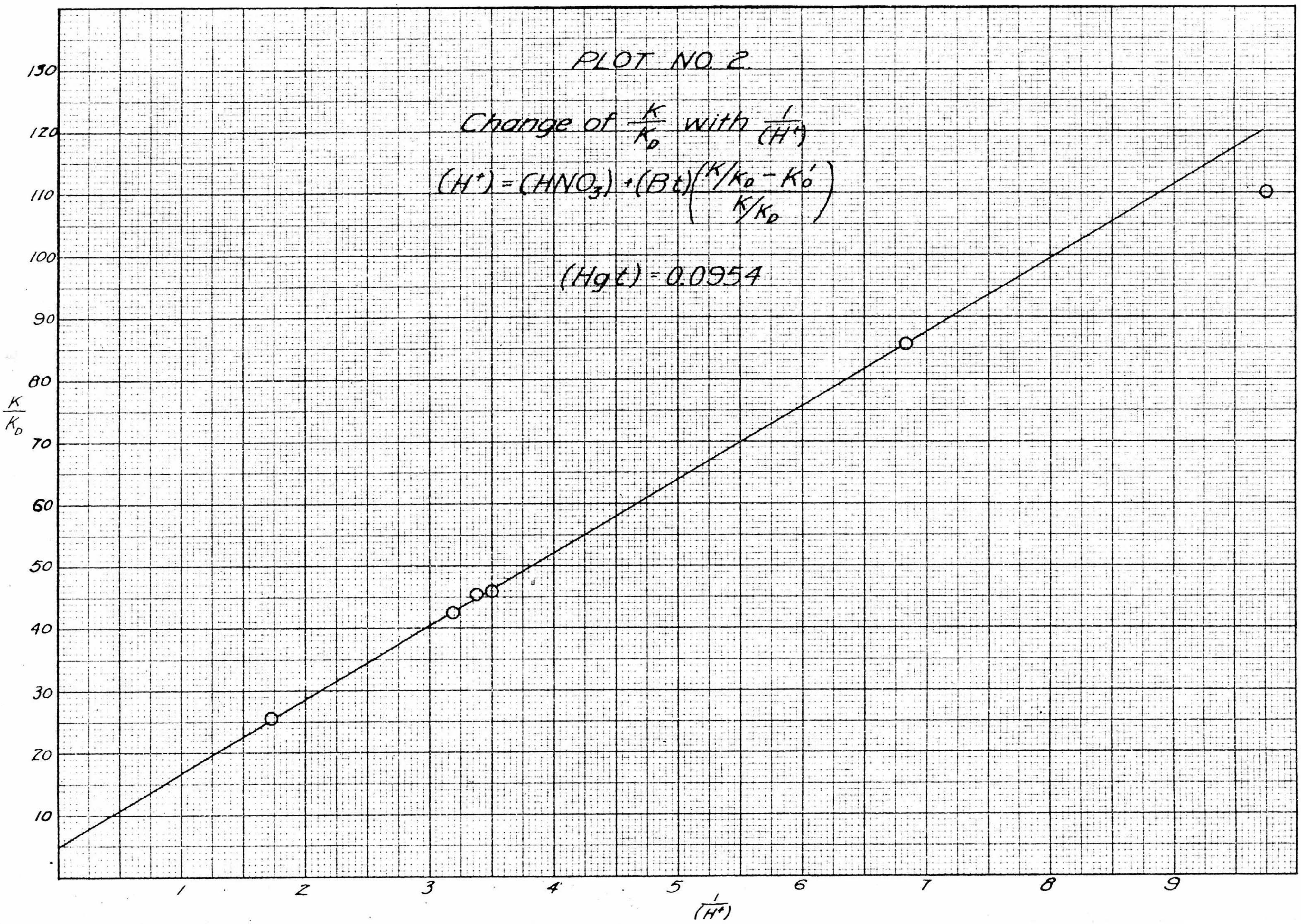
Table VII

Values of K_o Obtained by Treatment II for Runs With (Hgt) = 0.0954

(Hgt)	$(B)_c$	(Bt)	K/K_D	(HNO_3)	(H^+) Equation VII	$K_o = (K/K_D - 5)(H^+)$
0.0954	0.0135	0.0558	~~110~~ 111.2	0.0490	0.1023	~~10.7~~ 10.9
.0954	.0153	.0529	85.6	.0963	.1461	11.8
.0954	.0209	.0449	42.4	.2740	.3136	11.7
.0954	.00805	.0256	45.5	.2740	.2968	11.9
.0954	.00304	.0137	45.9	.2740	.2862	11.7
.0954	.0252	.0376	25.7	.5490	.5793	11.8

Mean 11.6

Mean Deviation ± 0.3



PLOT NO 2

Change of $\frac{K}{K_D}$ with $\frac{1}{(H^+)}$

$(H^+) = (HNO_3) + (Bt)\left(\frac{K/K_D - K_D'}{K/K_D}\right)$

$(Hgt) = 0.0954$

Thus at constant mercuric nitrate concentration, treatment of the data assuming two kinds of complexes handles very well the effect of acid concentration. The low value of K_o for the first run in Table VII could be explained in this manner. It had a relatively low initial acid concentration which might not have been exactly right due to the fact that mercuric nitrate may hydrolyze slightly to form more acid. A higher value for the corrected acid concentration would give a value of K_o nearer to that of the other runs.

With $K_o' = 5$, similar calculations of K_o for other concentrations of mercuric nitrate disclose a trend in K_o with concentration of mercuric ion, as shown in Table VIII.

Table VIII

Variation of K_o Obtained by Treatment II With (Hgt)

(Hgt)	$K_o = (K/K_D - 5)(H^+)$
0.0477	10.6
.0954	11.6[(a)]
.1907	13.7[(b)]

(a) Average of values in Table VII.

(b) Average of two values 13.8 and 13.6.

If it is assumed that mercuric nitrate has a different salt effect than potassium nitrate and nitric acid these results are logical.

There are several reasons why treatment II is better than treatment I. In treatment I the K_o varies with both acid concentration and mercuric nitrate concentration, while in treatment II K_o varies only with mercuric nitrate concentration. It seems right to assume that treatment II is correct because the drift of K_o with mercuric nitrate concentration is similar to the drift of the constant for the silver-cyclohexene complex.(1) Also there is the similarity of the reaction, shown by equation V in treatment II to the reaction of silver nitrate with cyclohexene.

One could argue that the differences in salt effects of nitric acid, potassium nitrate and mercuric nitrate would cause the variations of K_o found by treatment I. However, Lucas and Eberz (5) found that potassium nitrate has the same salt effect as nitric acid upon isobutene. It seems logical that this would also be true with other olefins such as cyclohexene. This equality of salt effect is indicated in treatment II by the constancy of K_o at a constant mercuric nitrate concentration. Potassium nitrate and nitric acid must have equal salt effects if K_o remains constant with variation in nitric acid at constant mercuric nitrate concentration.

Summary

Coordination complexes of the mercuric ion with cyclohexene have been studied chiefly by the distribution of cyclohexene between carbon tetrachloride and solutions, at ionic strength of 1μ, containing mercuric nitrate, nitric acid and potassium nitrate.

Evidence has been presented for assuming there are complex ions of two types, viz., $Hg\cdot B\cdot OH^+$, formed according to the equation $Hg^{++}+B+H_2O \rightleftharpoons Hg\cdot B\cdot OH^+ + H^+$, and $B\cdot Hg^{++}$, formed according to the equation $Hg^{++}+B \rightleftharpoons B\cdot Hg^{++}$.

Equilibrium constants have been calculated for the formation of these complexes.

Two methods of treating results have been considered and the superiority of one method has been demonstrated on the basis of the probable validity of the results which it affords.

Experimental data, from which it was deduced that a slow secondary reaction was proceeding concurrently with the other two, were obtained.

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