[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORIES OF THE UNIVERSITY OF CHICAGO AND THE LOS ALAMOS SCIENTIFIC LABORATORIES]

Catalysis by Pt(III) of Exchange Reactions of $\mathrm{PtCl_4^=}$ and $\mathrm{PtCl_6^=}$

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One path for the exchange of $\mathrm{PtCl_6^=}$ and $\mathrm{Cl^-}$ involves a chain mechanism. The reaction by this path is initiated by light, catalyzed by $\mathrm{PtCl_4^=}$, inhibited by $\mathrm{Fe(CN)_6^\equiv}$, $\mathrm{IrCl_6^=}$, $\mathrm{Cl_2}$ and some reducing agents. The rate of exchange by non-chain paths is very slow, the exchange reaction in the presence of inhibitors having a half-life in excess of a week at 25° and at concentration level of ~ 0.01 *M*. The exchange of $\mathrm{PtCl_4^=}$ and $\mathrm{Cl^-}$ is induced by Ce(IV) but not by $\mathrm{Cl_2}$. The exchange of Pt between $\mathrm{PtCl_4^=}$ and $\mathrm{PtCl_6^=}$ is catalyzed by light, and inhibited by $\mathrm{IrCl_6^=}$. The catalyzed reactions are attributed to a common intermediate, a chloro complex of Pt(III). It is generated by the action of light on $\mathrm{PtCl_6^=}$, by $1e^-$ oxidizing agents on $\mathrm{PtCl_4^=}$, it can exchange associated $\mathrm{Cl^-}$ rapidly with $\mathrm{Cl^-}$ in solution, and can exchange oxidation state rapidly with $\mathrm{PtCl_4^=}$ and $\mathrm{PtCl_6^=}$.

An experimental survey of the effect of oxidizing agents, reducing agents and of light on the exchange of $\mathrm{Cl^-}$ with $\mathrm{PtCl_4^=}$ and $\mathrm{PtCl_6^=}$, and of Pt between $\mathrm{PtCl_4^=}$ and $\mathrm{PtCl_6^=}$ has exposed some remarkable and interesting induced effects in these systems. Rate laws have not been established but the present observations alone, covering as they do a wide range of interlocking phenomena, appear sufficient to show that the catalytic species generated by the various agents is a complex of Pt(III). The effect of the Pt(III) complex in labilizing $\mathrm{PtCl_6^=}$ and $\mathrm{PtCl_4^=}$ for exchange is apparently analogous to that demonstrated for Au(II) acting on $\mathrm{AuCl_4^-}$.[1] The present system is the more interesting because both $\mathrm{PtCl_4^=}$ and $\mathrm{PtCl_6^=}$ are inert to substitution, and the effect of the intermediate oxidation state in labilizing both can be observed. No compounds known to contain Pt in the +3 oxidation state have thus far been described in the literature.

Experimental

Activities.—The chlorine tracer was the isotope of mass 36, supplied by the Atomic Energy Commission. All counting of chlorine activity was performed on solutions. The activity was usually present in the free chloride initially. The radioactive platinum was prepared at Los Alamos. Our original plan was to use the long lived (82 day) platinum isotope.[2] However, this activity was found to follow iridium in the purification procedure, and is apparently the known 78 day iridium isotope. The 3 to 4 day activities were used as the tracer for Pt, and were counted in solution with a scintillation counter.

Chemicals.—$\mathrm{H_2PtCl_6 \cdot 6H_2O}$: This compound used for early work, was a commercial preparation, and was not further purified.

$\mathrm{Na_2PtCl_6 \cdot 6H_2O}$: A solution of platinum in aqua regia was treated by the method of Gilchrist and Wichers,[3] to remove Rh, Pd and Ir. The salt $\mathrm{(NH_4)_2PtCl_6}$ was precipitated from the solution dissolved in aqua regia and subjected to several evaporations from concentrated HCl, then $\mathrm{Na_2PtCl_6 \cdot 6H_2O}$ was precipitated by adding NaCl and cooling the solution. The salt was recrystallized several times from dilute HCl and dried at 55 to 60°. A stock solution was made up to contain 0.500 *M* $\mathrm{Na_2PtCl_6}$ (found 0.496) containing also 0.1004 *M* HCl, 0.994 *M* $\mathrm{HClO_4}$.

Radioactive $\mathrm{K_2PtCl_6}$: "Pure" platinum which had been subjected to irradiation by neutrons was dissolved and treated[3] to remove impurities. Most of the activity was carried off as Au, Os and Ir. The residual platinum was then precipitated as $\mathrm{K_2PtCl_6}$, recrystallized several times from dilute HCl, and dried at 110°.

$\mathrm{K_2PtCl_4}$: The procedure in reference 4 was followed to prepare $\mathrm{K_2PtCl_4}$. The salt was obtained as large well-formed crystals on recrystallization.

α-Acetoxymercuri-β-methoxyhydrocinnamic methyl ester was prepared as described by Whitmore.[5]

Separation Procedures.—$\mathrm{PtCl_6^=}$–$\mathrm{Cl^-}$: The early experiments on the exchange gave erratic results. In the course of establishing control over the system, several separation procedures were developed, some of which are outlined. All of them work, but they differ somewhat in convenience and precision.

In some experiments, $\mathrm{PtCl_6^=}$ was precipitated as $\mathrm{Cs_2PtCl_6}$, and separated from free chloride by filtration. The free chloride was then collected as AgCl, and dissolved in $\mathrm{NH_3}$ for counting purposes. A modification, giving results much more sensitive to small extents of exchange, was to reduce $\mathrm{Cs_2PtCl_6}$ with Zn, and then count the chloride set free in this process. $\mathrm{(C_6H_5)_4As^+}$ is a good precipitant but was used for only one experiment at the end of the work.

Solvent extraction procedures were developed exploiting the lability of the $\mathrm{Hg^{(II)}x^-}$–$\mathrm{Cl^-}$ exchange, and the extractability by organic solvents of mercury complexes. In the simplest procedure, $\mathrm{Hg(NO_3)_2}$ was added to the solution to be worked up, and the $\mathrm{HgCl_2}$ was extracted. $\mathrm{HgCl_2}$ can be salted completely into both ethyl cyanoacetate and phenylacetonitrile even with an excess of $\mathrm{Hg^{++}}$ present, but the latter solvent is preferable since it is less soluble in water. A modification of the procedure was made, providing a separation method which is more generally applicable because it keeps Hg out of the aqueous phase. The mercury is incorporated in an organic molecule, leaving one bond to an anion, this group then being exchangeable with $\mathrm{Cl^-}$. The compound α-acetoxymercuri-β-methoxyhydrocinnamic methyl ester is easily prepared and works well. Using a solution of the mercury (II) compound in phenylacetonitrile as solvent, $\mathrm{Cl^-}$ is extracted rapidly and quantitatively (<2 min.) and no mercury can be detected in the water layer.

$\mathrm{PtCl_4^=}$–$\mathrm{Cl^-}$: $\mathrm{(C_6H_5)_4As^+}$ was used as precipitant to separate $\mathrm{PtCl_4^=}$ and $\mathrm{Cl^-}$. The activity left in a solution (composition: 0.062 *M* $\mathrm{HNO_3}$, 0.0342 *M* in NaCl, 0.0125 *M* $\mathrm{K_2PtCl_4}$) at exchange equilibrium stripped of $\mathrm{PtCl_4^=}$ and $\mathrm{Cl^-}$ was found to be 4% in excess of that expected for random distribution of activity between $\mathrm{PtCl_4^=}$ and $\mathrm{Cl^-}$. The experiments to learn whether the excess is caused by incomplete precipitation or partial hydrolysis of $\mathrm{PtCl_4^=}$ have not been performed.

$\mathrm{PtCl_4^=}$–$\mathrm{PtCl_6^=}$: The separation was made by precipitating $\mathrm{Cs_2PtCl_6}$.

Results and Discussion

The results of some of the experiments performed on the exchange $\mathrm{PtCl_6^=}$–$\mathrm{Cl^-}$ are summarized in Table I. Several additional experiments not reported in detail in the table are referred to in the text, and the conditions obtaining for them are implied by the comparisons made. With the exceptions noted in Table I, the experiments were done using hexachloroplatinate(IV) solutions which had been stored in the dark, performing the sensitive manipulations in the dark, or in red light.

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(1) R. L. Rich and H. Taube, *J. Phys. Chem.*, **58**, 6 (1954).

(2) J. M. Cork, A. E. Stoddard, W. C. Rutledge, C. R. Branyan and J. M. LeBlanc, *Phys. Rev.*, **77**, 843 (1950).

(3) R. Gilchrist and E. Wichers, THIS JOURNAL, **57**, 2565 (1935).

(4) W. C. Fernelius, "Inorganic Syntheses," Vol. II, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 247.

(5) F. C. Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1921, p. 311.

TABLE I

THE EXCHANGE OF HEXACHLOROPLATINATE(IV) WITH CHLORIDE ION

Temperature 25.0°, but only approximately in expt. 1.21–1.24.

No.	Formal concentrations				Sepn.	Count		Exch., %
	$PtCl_6^{=}$	Cl^-	H^+	Other				
1.11	0.048[a]	0.0106	0.095		Hg ext.	$HgCl_2$	1 hr.	62
1.12	.048[a]	.0106	.095		Hg ext.	$HgCl_2$	23 hr.	97
1.13	.048[a]	.0106	.095		Hg ext.	$HgCl_2$	49 hr.	100
1.21	.039[a]	.0087	.078	(Darkness)	Hg ext.	$HgCl_2$	20 min.	20
1.22	.039[a]	.0087	.078	Diffuse light[b]	Hg ext.	$HgCl_2$	20 min.	100
1.23	.039[a]	.0087	.078	Diffuse light[b]	Hg ext.	$HgCl_2$	10 min.	100
1.24	.039[a]	.0087	.078	Diffuse light[c]	Hg ext.	$HgCl_2$	5 min.	70
1.31	.024	.0048	.047	0.01 Ba diphenyl-[d]	Cs ppt.	Zn, Cs, Cl	~1 min.	43
1.32	.024	.0048	.047	amine sulfonate[e]	Cs ppt.	Zn, Cs, Cl	~1 min.	<0.5
1.41	.024	.0048	.047	0.02 hydroquinone	Cs ppt.	Zn, Cs, Cl	~1 min.	<0.4
1.42	.024	.0048	.047	0.02 hydroquinone	Cs ppt.	Orig. Cl	23 hr.	25
1.51	.024	.0048	.047	0.01 $K_3Fe(CN)_6$	Cs ppt.	Orig. Cl^-	2 days	0
1.52	.024	.0048	.407	0.01 $K_3Fe(CN)_6$	Cs ppt.	Zn, Cs, Cl	4 days	<0.3
1.61	.024	.0048	.047	0.01 $K_3Fe(CN)_6$ and 0.01 K_2PtCl_4	Cs ppt.	Zn, Cs, Cl	22 hr.	6
1.71	.024	.0048	.047	0.001 Cl_2	Cs ppt.	Zn, Cs, Cl	40 hr.	<0.7
1.81	.024	.0048	.047	0.001 $(NH_4)_2IrCl_6$	Cs ppt.	Zn, CS, Cl	5 hr.	4 or 0[f]

[a] Using the commercial H_2PtCl_6 rather than purified Na_2PtCl_6 as in the others. [b] In open window on a sunny day. [c] In an open window on a cloudy day. [d] Inhibitor added immediately after $PtCl_6^{=}$. [e] $PtCl_6^{=}$ added last as in other cases. [f] 4% for $PtCl_6^{=}$ if no $IrCl_6^{=}$ exchange, 0% for $PtCl_6^{=}$ if slight $IrCl_6^{=}$ exch.

Experiments 1.21 to 1.24 show that the rate of the exchange is greatly increased by light. The striking effect exerted by light at ordinary laboratory intensities (expt. 1.24) indicates long reaction chains. This is confirmed as a conclusion by the strong inhibitory effects on the photo-induced exchange which are observed. In the presence of hydroquinone or ferricyanide only a small percentage exchange takes place in diffuse daylight within an hour. The great sensitivity to light is peculiar to the exchange reaction. Although the rate of hydrolysis is increased by light, the quantum yield is small, much less than unity for blue light.[6] Evidently, absorption of light by $PtCl_6^{=}$ generates a catalyst peculiarly effective for the exchange reaction. The exchange reaction in the dark also shows effects attributable to a catalyst. The spontaneous exchange rate for $PtCl_6^{=}$ obtained from commercial H_2PtCl_6 is much less than it is for Na_2PtCl_6, purified from iridium and other possible inhibitors. Even in the dark, with the purer preparation, the exchange was 43% complete during the few seconds elapsed before the inhibitor was added (expt. 1.31). The catalyst is destroyed by reducing agents (expt. 1.32, 1.41, 1.42) and even more effectively by certain oxidizing agents. Although $PtCl_4^{=}$ is not the catalyst, the exchange of Cl^- with it, and the transfer between $PtCl_4^{=}$ and $PtCl_6^{=}$ being too slow for it to qualify (*vide infra*), it is helpful in generating the catalyst (compare expt. 1.51 and 1.61).

If the phenomena described are interrelated, they require the effective catalyst to be an ion containing Pt(III). The mechanism for the catalytic effect exerted by Pt(III) (assumed for the sake of concrete discussion to be $PtCl_5^{=}$) is

$$PtCl_5^{=} + Cl^{*-} \rightleftarrows PtCl_5^{*=} + Cl^- \qquad (1)$$

$$PtCl_5^{*=} + PtCl_6^{=} \longrightarrow PtCl_5{}^*Cl^{=} + PtCl_5^{=} \qquad (2)$$

Light is effective in generating the catalyst, presumably by causing dissociation of $PtCl_6^{=}$ to $PtCl_5^{=}$ and Cl. The initiator in the spontaneous change may be radiation emitted by the radioactive chloride, or traces of the catalyst generated in the handling. Tetrachloroplatinate (II) can generate the catalyst by the reaction

$$PtCl_4^{=} + PtCl_6^{=} \rightleftarrows 2PtCl_5^{=} \qquad (3)$$

The experiments give no clue to the nature of the chain-breaking steps in the absence of inhibitors. In view of the instability of Pt(III), the equilibrium in reaction 3 lying far to the left, the species is expected to be easily oxidized and reduced. Of particular interest is the inhibitory effect of an oxidizing agent as weak as $Fe(CN)_6^{≡}$. The ion $IrCl_6^{=}$, shown in expt. 1.81 to be an inhibitor, can account for the difference in behavior of commercial H_2PtCl_6 and the more refined compound. The observation that Cl_2 is an inhibitor seems to eliminate atomic chlorine as the catalytic species. Chlorine can inhibit by the reaction

$$PtCl_5^{=} + Cl_2 \longrightarrow PtCl_6^{=} + Cl$$

The fate of Cl is left undetermined except for the specification that it is not efficient in generating new chains.

A path for the exchange must exist in the absence of Pt(III), which involves hydrolysis of $PtCl_5^{=}$. The experiments with inhibitor present show the reaction by this path to be very slow, no exchange being noted in two days with $Fe(CN)_6^{≡}$ added. A slow substitution rate is expected for an ion of the electronic structure type of $PtCl_6^{=}$.[7] An experiment on the rate of substitution of Cl^- by Br^- also was performed. The reaction was followed by noting the increase in radioactivity of free chloride brought about by adding Br^- to a system with $PtCl_6^{=}$–Cl^- in exchange equilibrium. With Br^- in solution at 0.2 *M*, only a small percentage of the associated chloride is replaced in 0.5 hour at

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(6) M. Boll, *Ann. phys.*, **2**, 5 (1914).

(7) H. Taube, *Chem. Revs.*, **50**, 69 (1952).

room temperature (no added inhibitors, in the dark), although the equilibrium is favorable to the exchange.[8] Evidently Pt(III) does not provide a very effective path for the net replacement. A rationalization for the difference in the catalytic effect of Pt(III) on the exchange reaction, and that involving net replacement, is the following: A change such as reaction 2 takes place with $\Delta H = 0$, but the reaction

$$PtBr_5^{=} + PtCl_6^{=} \longrightarrow PtBr_5Cl^{=} + PtCl_5^{=} \quad (4)$$

necessary for Pt(III) to function as catalyst in the Br^-–$PtCl_6^=$ reaction will have a positive value of ΔH. Bromide ion as compared to chloride owes its higher affinity for Pt(IV) to its greater polarizability. The presence of five polarizable Br^- ions in place of Cl^- on Pt(III) will greatly lower its tendency to extract Cl from $PtCl_6^=$. By analogy to the similar reaction in the Au(II)–$AuCl_4^-$, the activation energy for reaction 2 is expected to be small; an unfavorable ΔH for reaction 4 will impose a greater activation energy at least of this magnitude for reaction 4 as compared to reaction 2.

The mechanism discussed suggests that catalytic effects attributable to Pt(III) should also appear in the exchange of Cl^- with $PtCl_4^=$. The results of a brief search for such effects are reported in Table II.

TABLE II

INDUCED EXCHANGE IN THE SYSTEM $PtCl_4^= + Cl^-$

(($PtCl_4^=$) = 0.0125 *M*; (NaCl) = 0.0342 *M*; (HNO_3) = 0.062 *M*; temp., 0°; in ordinary laboratory light).

No.	Time in min.	Inducing agent	Concn. inducing agent	Exch., %
2.11	30.0	....	....	1.2
2.21	0.5	Ce(IV)	5.5×10^{-4}	62
2.22	4.0	Ce(IV)	5.5×10^{-4}	87
2.23	140.0	Ce(IV)	5.5×10^{-4}	95
2.24	5.0	Cl_2	6.5×10^{-4} *M*	1 or −2[a]
2.25	10.0	$PtCl_6^=$	2.5×10^{-4} *M*	2.0

[a] 1% if Cl_2 reacts before it exchanges with Cl^-; −2% if exchange with Cl^- is complete before reaction.

Experiment 2.11 shows that the spontaneous exchange of $PtCl_4^=$ and Cl^- is slow. The $1e^-$ oxidizing agent Ce(IV), even when added in amounts sufficient to oxidize only 3% of the $PtCl_4^=$, induces almost complete exchange of $PtCl_4^=$ and Cl^-. The reaction of $PtCl_4^=$ and Ce(IV) is very rapid at least in the early stages. If the reaction is second order in Ce(IV), it will become very slow toward the end. This may account for the tailing off noted in the data of experiments 2.21–2.23. Experiment 2.25 shows that the catalyst is not $PtCl_6^=$, although this ion does have the ability to generate the catalyst at low concentration. The observations again point to Pt(III) as the catalyst. With Ce(IV) as oxidizing agent, the catalyst is generated by the reaction

$$Ce(IV) + PtCl_4^{=} (+ Cl^-) \longrightarrow Ce^{+++} + PtCl_5^{=}$$

As suggested earlier, $PtCl_5^=$ reaches isotopic equilibrium with the solution rapidly. The lability is transferred to another $PtCl_4^=$ by the reaction

$$PtCl_4^{=} + PtCl_5^{*=} \longrightarrow PtCl_4Cl^{*=} + PtCl_4^{*=} \quad (5)$$

Although Cl_2 was added in amounts equivalent to twice the amount of Ce(IV) added, no exchange was induced by it. This observation indicates (but does not prove) that the stage Pt(III) is bypassed in the reaction of Cl_2 and $PtCl_4^=$. This view is strengthened as a conclusion after consideration of the observation that the immediate product of the reaction is not $PtCl_6^=$, but $PtCl_5OH^=$. The experiment establishing this observation was conducted at 0°, using freshly dissolved K_2PtCl_4 (0.025 *M*) in 0.1 *M* HNO_3, and adding to it a slight excess of a solution of Cl_2 in 0.1 *M* HNO_3. After reaction, which is apparently complete on mixing, the excess Cl_2 was removed by a stream of air, $CsNO_3$ was added and the precipitate removed. The chloride ion left in solution was determined as AgCl. The precipitate was contaminated slightly by a silver chloroplatinate (IV) and a correction for the impurity was applied, based on the Pt content of the precipitate. The amount of Cl^- left was observed to be 0.0397 g.; that expected for the net change: $PtCl_4^= + Cl_2 + H_2O = PtCl_5OH^= + H^+ + Cl^-$ was 0.0411 g.; that expected for: $PtCl_4^= + Cl_2 = PtCl_6^=$, none. A subsequent slower reaction: $PtCl_5OH^= + H^+ + Cl^- = PtCl_6^= + H_2O$ does eventually deliver $PtCl_6^=$ as product. A simple interpretation of the non-inducing effect and the observed stoichiometry with Cl_2 as oxidizing agent is that, in effect, Cl^+ is transferred to $PtCl_4^=$ and, simultaneously or subsequently, OH^- derived from a water molecule completes the coordination number of 6.

Chloride is added to $PtCl_4^=$ fairly efficiently by the oxidizing system Ce(IV) + Cl^-. When the reaction takes place at 0° in 0.04 *M* Cl^-, 1.4 moles of Cl^- is added per mole of $PtCl_4^=$ oxidized. Simple stoichiometry is not expected for a system involving Pt(III) as an intermediate. Even if $PtCl_5^=$ is the formula at ordinary chloride concentrations, the composition of the final product will be determined by the result of competition between the paths

$$PtCl_5^{=} + Ce(IV) \longrightarrow$$
$$PtCl_5^{=} + Ce(IV) + Cl^- \longrightarrow$$

The interpretations advanced for the induced effects in the exchange $PtCl_6^=$–Cl^-, $PtCl_4^=$–Cl^- require as corollary that Pt(III) catalyze the exchange between $PtCl_4^=$ and $PtCl_6^=$ *via* the reactions already assumed

$$\begin{array}{l} PtCl_5^{=} + Pt^*Cl_4^{=} \longrightarrow PtCl_4^{=} + Pt^*Cl_5^{=} \\ \underline{Pt^*Cl_5^{=} + PtCl_6^{=} \longrightarrow PtCl_4^{=} + Pt^*Cl_6^{=}} \\ \text{net: } Pt^*Cl_4^{=} + PtCl_6^{=} = PtCl_4^{=} + Pt^*Cl_6^{=} \end{array}$$

The half-time for the exchange between $PtCl_6^=$ and $PtCl_4^=$ at 25° with the ions at 0.005 *M* and in 0.01 *M* HCl is observed to be about 1 hour. When a reaction mixture of similar composition is exposed to a source of ultraviolet light, the exchange is approximately 100% complete in 5 min. The ion $IrCl_6^=$ inhibits the photo-exchange. When it is present at 10^{-5} *M* the photo-induced exchange in 5 min. is only 60% complete. These observations bear out the expectations based on the mechanism at least qualitatively. The spontaneous exchange, which seems remarkably rapid for ions of such dissimilar geometry at $PtCl_4^=$ and $PtCl_6^=$, may also be catalyzed by Pt(III), which is produced by the

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[8] H. I. Schlesinger and R. E. Palmitaer, THIS JOURNAL, **52**, 4316 (1930).

interaction of $PtCl_4^=$ and $PtCl_6^=$, or by the nuclear radiation.

The compound Cs_2PtCl_5 is described in the literature.[9] It is formed when Cl_2 is passed into a cold solution of Cs_2PtCl_4, with $PtCl_4^=$ kept in excess, but not by mixing $PtCl_6^=$ and $PtCl_4^=$ in the presence of Cs^+. The compound was prepared and tested as a catalyst for the exchange of $PtCl_4^=$ and $PtCl_6^=$. Even when used in amounts representing 12% of the total Pt in the system, no catalytic effect is observed in 5 min. We consider this observation not to weaken the case which has been presented for reactions of Pt(III), but rather to show that Cs_2PtCl_5 does not yield $PtCl_5^=$ in solution, probably because it does not contain this ion.

An interesting question is the reason for the exceptional exchange lability of Pt(III). It is considered to be caused by the existence of this ion in states of different coördination numbers with approximately the same energy. Along the series $PtCl_6^{\equiv}$, $PtCl_5^=$, $PtCl_4^-$, there is compensation for the energy required to remove Cl^-, because the odd electron finds itself left in orbitals of increasing stability. Alternation of Pt(III) between a pair of these structures may account for the rapid exchange. The first two would seem particularly suitable because the ion $PtCl_6^{\equiv}$ makes all Cl's equivalent.

The induced exchange effects demonstrated should be a useful tool in diagnosing mechanisms of reduction of $PtCl_6^=$ and of oxidation of $PtCl_4^=$. The reactions studied in this brief survey are only a few of those which suggest themselves for investigation.

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[9] L. Wöhler and F. Martin, *Ber.*, **42**, 3958 (1909).

[CONTRIBUTION OF THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

Antimony(V) Species in Hydrochloric Acid Solution[1]

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Analysis of the ultraviolet spectra of solutions of antimony(V) in hydrochloric acid solutions, ranging in concentration from 2 to 12 *M*, has allowed determination of the kind and amounts of the various species present. The spectrum characteristic of $SbCl_6^-$ has been observed in solutions of hydrated $HSbCl_6$ in ether, and in antimony(V) solutions in concentrated HCl. With decreasing acidity the presence of $Sb(OH)Cl_5^-$, $Sb(OH)_2Cl_4^-$, etc., has been demonstrated, and the amounts of each determined for various acidities. The $Sb(OH)Cl_5^-$ ion is the predominant form in 8 *M* acid; $Sb(OH)_2Cl_4^-$, in 6 *M* acid. Below 5 *M* acid $Sb(OH)_3Cl_3^-$ and the more hydrolyzed species are the most important.

There has been little evidence available concerning the nature of the species present when antimony(V) is dissolved in hydrochloric acid, and this lack of information has made difficult the interpretation of many experiments concerned with such solutions. It has been the belief for some time that solutions of antimony(V) in moderately concentrated hydrochloric acid contain the antimony primarily as the ion $SbCl_6^-$ but the existence of this ion in solution had not been demonstrated. Both polarographic[2] and spectrophotometric[3] work indicated that hydrolysis of $SbCl_6^-$ is probably important at lower acidities, but the hydrolytic species remained unidentified. It was clear from Bonner's work[4] on the radioactive exchange between Sb(III) and Sb(V) that some knowledge of the species involved would be necessary to interpret the exchange results. As a preliminary then to an investigation of the radioactive exchange a study has been made of the ionic species of Sb(V) present in hydrochloric acid solutions.

This study has primarily utilized spectrophotometric[5] methods. The spectrum of $SbCl_6^-$ was established by use of ether solutions of salts. Comparison of this spectrum with the spectra of aqueous hydrochloric acid solutions has allowed decomposition of the spectra into their component parts. As a result, the ions present have been identified, and the amounts of each determined as a function of acidity.

Experimental

Spectral Measurements.—All measurements were made with a Beckman Model DU spectrophotometer using fused silica cells having a light path of one cm. The cells were maintained at constant temperature in the spectrophotometer by means of a water jacket. The spectra of equilibrium mixtures in hydrochloric acid were obtained from 215 to 400 mμ. Absorbency values were obtained at 5 mμ intervals, except in the regions of maxima where readings were taken at 2 mμ intervals. A large slit width was necessary, varying from 2.0 mm. at 215 mμ to 0.4 mm. at 400 mμ. So that the spectra of solutions of varying acidity would be comparable the slit width was maintained constant for a given wave length for all solutions.

Solutions 2.01×10^{-4} *M* in Sb(V) were prepared in acids ranging from 2 through 12 *M* by adding 100 microliters of a 0.1005 *M* stock solution to 50 ml. of HCl of approximately the desired concentration. It was necessary to allow the solutions to stand for several days; equilibrium was considered to be reached when no change in the spectrum was observed over a period of 48 hours. After equilibrium had been attained the acidity was determined by titration. Solutions 4.02×10^{-5} *M* were also prepared by using a 20-microliter portion of stock solution. The stock solution was prepared from "J. T. Baker Analyzed" antimony pentachloride and hydrochloric acid. Solvent blanks for the spectrophotometer were prepared in a manner analogous

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[1] Presented in part at the Chicago Meeting of the American Chemical Society, September, 1953.

[2] J. J. Lingane and F. Nishida, THIS JOURNAL, **69**, 530 (1947).

[3] J. Whitney and N. Davidson, *ibid.*, **69**, 2076 (1947); **71**, 3809 (1949).

[4] N. A. Bonner, *ibid.*, **71**, 3909 (1949).

[5] The nomenclature used here for spectrophotometric terms is that given in Letter Circular LC-857 of the National Bureau of Standards.