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Catalysis by Pt(III) of Exchange Reactions of PtCl_4^- and PtCl_6^- 45737

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ABSTRACT

One path for the exchange of PtCl_6^- and Cl^- involves a chain mechanism. The reaction by this path is initiated by light, catalyzed by PtCl_4^- , inhibited by $\text{Fe}(\text{CN})_6^{3-}$, IrCl_6^- , 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 $\sim 0.01 \text{ M}$. The exchange of PtCl_4^- and Cl^- is induced by $\text{Ce}(\text{IV})$ but not by Cl_2 . The exchange of Pt between PtCl_4^- and PtCl_6^- is catalyzed by light, and inhibited by IrCl_6^- . These phenomena are explained by a common intermediate, a chloro complex of Pt(III). It is generated by the action of light on PtCl_6^- , by I_2^- oxidizing agents on PtCl_4^- , it can exchange associated Cl^- rapidly with Cl^- in solution, and can exchange oxidation state rapidly with PtCl_4^- and PtCl_6^- .

An experimental survey of the effect of oxidizing agents, reducing agents and of light on the exchange of Cl^- with PtCl_4^- and PtCl_6^- , and of Pt between PtCl_4^- and 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 PtCl_6^- and PtCl_4^- for exchange is apparently analogous to that demonstrated

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for Au(II) acting on AuCl_4^- .²⁾ The present system is the more interesting because both PtCl_4^- and 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 isotope³⁾. 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 - $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ This compound used for early work, was a commercial preparation, and was not further purified.

$\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$. A solution of platinum in aqua regia was treated by the method of Gilchrist and Wickers,⁴⁾ to remove Rh, Pd and Ir. The salt $(\text{NH}_4)_2\text{PtCl}_6$ was precipitated from the solution dissolved in aqua regia and subjected to several evaporations from concentrated HCl, then $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ 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 N Na_2PtCl_6 (found 0.498) containing also

²⁾ R.L. Rich & H. Imbe, J. Phys. Chem. 57, 6000 (1953)

³⁾ J.M. Cork, A.E. Stoddard, W.C. Rutledge, C.R. Branyan and J.M. LeBlanc., Phys. Rev., 77, 843 (1950)

⁴⁾ R. Gilchrist and E. Wickers, J. Am. Chem. Soc. 57, 2555 (1935)

0.1004 $\underline{\text{M}}$ HCl, 0.994 $\underline{\text{M}}$ HClO₄.

Radioactive K₂PtCl₆. "Pure" platinum which had been subjected to irradiation by neutrons was dissolved and treated⁴⁾ to remove impurities. Most of the activity was carried off as Au, Os and Ir. The residual platinum was then precipitated as K₂PtCl₆, recrystallized several times from dilute HCl, and dried at 110°.

K₂PtCl₆. The procedure in Inorganic Syntheses⁵⁾ was followed to prepare K₂PtCl₆. The salt was obtained as large well-formed crystals on recrystallization.

α -acetoxymercuri- β -methoxy hydrocinnamic methyl ester was prepared as described by Whitmore.⁶⁾

Separation Procedures

PtCl₆⁻ - 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, PtCl₆⁻ was precipitated as Ca₂PtCl₆, and separated from free chloride by filtration. The free chloride was then collected as AgCl, and dissolved in HCl for counting purposes. A modification giving results much more sensitive to small extents of exchange, was to reduce Ca₂PtCl₆ with Zn, and then count the chloride set free in this process. $\phi_4\text{As}^+$ 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 Hg^(II)_{X⁻} - Cl⁻ exchange, and the extractability by organic solvents of mercury complexes. In the simplest procedure, Hg(NO₃)₂ was added to the solution to be worked up, and the HgCl₂ was extracted. HgCl₂ can be salted completely into

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

⁶⁾F.C. Whitmore "Organic Compounds of Mercury", Chemical Catalog Co., N.Y., p. 311 (1921)

both ethyleyanacetate and phenylacetonitrile even with an excess of 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 Cl^- . The compound α -acetoxymercuri- β -methoxy hydrocinnamic methyl ester is easily prepared and works well. Using a solution of the mercuri compound in phenyl acetonitrile as solvent, Cl^- is extracted rapidly and quantitatively (< 2 min.) and no mercury can be detected in the water layer.

$\text{PtCl}_4^- - \text{Cl}^-$. $\phi_4\text{As}^+$ was used as precipitant to separate PtCl_4^- and Cl^- . The activity left in a solution (composition: 0.062 M HNO_3 , 0.0342 M in NaCl , $0.0125 \text{ M K}_2\text{PtCl}_4$) at exchange equilibrium stripped of PtCl_4^- and Cl^- was found to be 4% in excess of that expected for random distribution of activity between PtCl_4^- and Cl^- . The experiments to learn whether the excess is caused by incomplete precipitation or partial hydrolysis of PtCl_4^- have not been performed.

$\text{PtCl}_4^- - \text{PtCl}_6^-$. The separation was made by precipitating Cs_2PtCl_6 .

Results and Discussion

The results of some of the experiments performed on the exchange $\text{PtCl}_6^- - \text{Cl}^-$ 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 chloroplatinate solutions which had been stored in the dark, performing the sensitive manipulations in the dark, or in red light.

Table I

The Exchange of Chloroplatinate with Chloride Ion
(Temperature 25.0°, but only approximately in expts. 1.21-1.24)

Formal Concentrations					Sep'n	Count	t	% ex.
No.	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	25 hr.	97
1.13	.048 ^a	.0106	.095		Hg ext.	HgCl ₂	48 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 ^c	Hg ext.	HgCl ₂	10 min.	100
1.24	.039 ^a	.0087	.078	diffuse light ^d	Hg ext.	HgCl ₂	5 min.	70
1.31	.024	.0048	.047	(0.01 Ba diphenylamine-) ^e	Cs ppt.	Zn, Cs, Cl	1 min.	48
1.32	.024	.0048	.047	sulfonate	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	25 hr.	25
1.51	.024	.0048	.047	0.01 K ₂ Fe(CN) ₆	Cs ppt.	orig. Cl ⁻	2 days	0
1.52	.024	.0048	.047	0.01 K ₂ Fe(CN) ₆	Cs ppt.	Zn, Cs, Cl	4 days	0.3
1.61	.024	.0048	.047	(0.01 K ₂ Fe(CN) ₆ + 0.01 K ₂ PtCl ₆)	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	0.024	0.0048	0.047	0.001 (NH ₄) ₂ IrCl ₆	Cs ppt.	Zn, Cs, Cl	5 hr.	4 or 0 ^f

^a Using the commercial K₂PtCl₆ rather than purified Na₂PtCl₆ 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 PtCl₆⁻.

^e PtCl₆⁻ added last as in other cases.

^f 4% for PtCl₆⁻ if no IrCl₆⁻ exchange, 0% for PtCl₆⁻ if slight IrCl₆⁻ 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 (exp. 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 ferrieyanide only a few percent 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 light⁷⁾. Evidently, absorption of light by PtCl_6^{2-} 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^{2-} obtained from commercial H_2PtCl_6 is much less than it is for K_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 (exp. 1.31). The catalyst is destroyed by reducing agents (exps. 1.32, 1.41, 1.42) and even more effectively by certain oxidizing agents. Although PtCl_4^{2-} is not the catalyst, the exchange of Cl^- with it, and the transfer between PtCl_4^{2-} and PtCl_6^{2-} being too slow for it to qualify (vide infra) it is helpful in generating the catalyst (compare exps. 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^{2-}), is as follows:

⁷⁾ H. Bell, Ann. phys., 2, 5 (1914).

Light is effective in generating the catalyst, presumably by causing dissociation 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. Chloroplatinite can generate the catalyst by the reaction

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 $\text{Fe}(\text{CN})_6^{4-}$. The ion IrCl_6^- , shown in exp. 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 Cl as the catalytic species. Chlorine can inhibit by the reaction

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_6^- . The experiments with inhibitor present show the reaction by this path to be very slow, no exchange being noted in 2 days with $\text{Fe}(\text{CN})_6^{4-}$ present. A slow substitution rate is expected for an ion of the electronic structure type of PtCl_6^- ⁸⁾. An experiment on the rate of substitution of Cl^- by Br^- was also performed. The reaction ^{was} followed by noting the increase in radioactivity of free chloride brought about by adding

⁸⁾ H. Tanabe, Chem. Reviews, 50, 69 (1952)

Br^- to a system with $\text{PtCl}_6^{2-} - \text{Cl}^-$ in exchange equilibrium. With Br^- in solution at 0.2 M, only a few percent of the associated chloride is replaced in 1/2 hour at room temperature (no added inhibitors, in the dark), although the equilibrium is favorable to the exchange.⁹⁾ Evidently Pt(III) does not provide a very effective path for the net replacement. A rationalisation 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

necessary for Pt(III) to function as catalyst in the $\text{Br}^- - \text{PtCl}_6^{2-}$ reaction will have a positive value of ΔH . Bromide ion as compared to chloride owes its higher affinity for Pt(IV) to its greater polarisability. The presence of five polarisable Br^- ions in place of Cl^- on Pt(III), will greatly lower its tendency to extract Cl from PtCl_6^{2-} . By analogy to the similar reaction in the $\text{Au(II)} - \text{AuCl}_4^{2-}$, the activation energy for reaction (1) 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 (1).

The mechanism discussed suggests that catalytic effects attributable to Pt(III) should also appear in the exchange of Cl^- with PtCl_4^{2-} . The results of a brief search for such effects are reported in Table II.

Exp. 2.11 shows that the spontaneous exchange of PtCl_4^{2-} and Cl^- is slow. The $1e^-$ oxidising agent Ce(IV) , even when added in amounts sufficient to oxidise only 3% of the PtCl_4^{2-} , induces almost complete exchange of PtCl_4^{2-} and Cl^- . The reaction of PtCl_4^{2-} and Ce(IV) is very rapid at least in the early stages. If the reaction is 2nd order in Ce(IV) , the reaction 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^{2-} , although

⁹⁾ H.I. Schlesinger and R.E. Palmiter, J.Am.Chem.Soc., 52, 4316 (1930).

Table II

Induced Exchange in the System $\text{PtCl}_4^{2-} + \text{Cl}^-$

((PtCl_4^{2-}) = 0.0125 M; (NaCl) = 0.0842 M; (HNO_3) = 0.002 M, Temp., 0°;
in ordinary laboratory light)

No.	Time in min.	Inducing agent	Conc. Ind. ag.	% Exchange
2.11	30.0	-	-	1.2
2.21	0.5	Co(IV)	5.5×10^{-4}	62.
2.22	4.0	"	"	87.
2.23	140.0	"	"	95.
2.24	5.0	Cl_2	6.5×10^{-4} M	1 or -2 ^a
2.25	10.0	PtCl_6^{2-}	2.5×10^{-4} M	2.0

^a1% if Cl_2 reacts before it exchanges with Cl^- ; -2% if exchange with Cl^- is complete before reaction.

this ion does have the ability to generate the catalyst at low concentration. The observations again point to Pt(III) as the catalyst. With Co(IV) as oxidizing agent, the catalyst is generated by the reaction:

As suggested earlier, PtCl_5^{2-} reaches isotopic equilibrium with the solution rapidly. The lability is transferred to another PtCl_4^{2-} by the reactions:

Although Cl_2 was added in amounts equivalent to twice the amount of Co(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^{2-} . This view is strengthened as a conclusion on consideration of the observation that the immediate product of the reaction is not PtCl_6^{2-} , but $\text{PtCl}_5\text{OH}^{2-}$. 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, Ce^{IV} 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; 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 0.0387 g.; that expected for the net change: $PtCl_4^{2-} + Cl_2 + H_2O \rightarrow PtCl_5OH^- + H^+ + Cl^-$ was 0.0411 g.; that expected for: $PtCl_4^{2-} + Cl_2 \rightarrow PtCl_6^{2-}$, none. A subsequent slower reaction: $PtCl_5OH^- + H^+ + Cl^- \rightarrow PtCl_6^{2-} + H_2O$ does eventually deliver $PtCl_6^{2-}$ 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 $PtCl_4^{2-}$, and simultaneously, OH^- derived from a water molecule, completes the coordination number of 6.

Chloride is added to $PtCl_4^{2-}$ fairly efficiently by the oxidizing system $Ce(IV) + Cl^-$. When the reaction takes place at 0° in 0.04 M Cl^- , 1.4 mole Cl^- is added per mole of $PtCl_4^{2-}$ 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:

The interpretations advanced for the induced effects in the exchange $PtCl_5^- - Cl^-$, $PtCl_4^{2-} - Cl^-$ require as corollary that $Pt(III)$ catalyze the exchange between $PtCl_4^{2-}$ and $PtCl_5^-$ via the reactions already assumed:

The half-time for the exchange between PtCl_6^{2-} and PtCl_4^{2-} 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^{3-} 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^{2-} and PtCl_6^{2-} , may also be catalysed by Pt(III) , which is produced by the interaction of PtCl_4^{2-} and PtCl_6^{2-} , or by the nuclear radiation.

The compound Ca_2PtCl_5 is described in the literature¹⁰⁾. It is formed when Cl_2 is passed into a cold solution of Ca_2PtCl_4 , with PtCl_4^{2-} kept in excess, but not by mixing PtCl_6^{2-} and PtCl_4^{2-} in the presence of Ce^{4+} . The compound was prepared and tested as a catalyst for the exchange of PtCl_4^{2-} and PtCl_6^{2-} . 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 Ca_2PtCl_5 does not yield PtCl_5^{2-} 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 coordination numbers with approximately the same energy. Along the series PtCl_6^{2-} , PtCl_5^{2-} , PtCl_4^{2-} , there is compensation for the energy required to remove Cl^- , because the odd electron finds itself left in orbitals of increasing stability. Alternation between a pair of these may

¹⁰⁾ L. Wöhler and F. Martin, Ber. 42, 3933 (1909).

account for the rapid exchange. The first two would seem particularly suitable because the ion PtCl_6^{2-} makes all Cl's equivalent.

The induced exchange effects demonstrated should be a useful tool in diagnosing mechanisms of reduction of PtCl_6^{2-} and of oxidation of PtCl_4^{2-} . The reactions studied in this brief survey are only a few of those which suggest themselves for investigation.