

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

Chemical Consequences of the (n, γ) Reaction on Platinum Complexes¹BY B. C. HALDAR²

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Chemical consequences of the (n, γ) reaction on platinum in complex compounds have been studied. The 18-hour platinum activity is found distributed in three different fractions: (1) the original compound or its derivative, (2) anions removable by ion-exchange resins IRA-400 and IR-4B, (3) cations and neutral molecules different from the original compound. The retention of activity in complexes with bidentate groups varies from 4 to 7% and is less than that in complexes with monodentate groups. From the retention values it appears that two or more bonds are broken in 93 to 96% of the cases. A detailed analysis of the products from slow neutron bombardment of [Pt(en)₂]Cl₂ indicates that removable anion activity exists in three different forms—the first form (9%) extractable into butyl acetate from 6 N HCl without addition of stannous chloride, the second form (25%) extractable into butyl acetate only after addition of stannous chloride and the third form (15%) removable from solution only by anion exchange resins. It is observed that oxidation of bivalent to tetravalent platinum takes place as a result of the capture process. Of all the compounds studied in the present investigation, *trans*-[Pt(en)₂-Cl₂]Cl₂ seems to be most suitable for the preparation of high specific activity radioplatinum by the (n, γ) process.

Introduction.—Complex compounds of metals have been utilized for concentrating radioisotopes by the Szilard-Chalmers³ method. According to Steigman⁴ complex compounds which can be optically resolved are suitable for the Szilard-Chalmers reaction. This is supposed to be a sufficient though not a necessary condition. In working with cobalt complexes, Sue and Kayas⁵ observed that the recovery of active cobalt atoms as cobalt hydroxide from slow neutron irradiated solutions of hexamine, ethylenediamine and diethylenetriamine complexes of cobalt decreases with the increase in the number of coordinating linkages from a coordinating group. They interpreted their results by stating that with increase in the molecular complexity of the bombarded cobalt complex the bond rupture due to the (n, γ) reaction decreases, and thus the number of active cobalt atoms which leave the complex and can be separated as cobalt hydroxide decreases. This effect is very difficult to understand when one considers the large amount of energy given to the recoil atom by the (n, γ) reaction⁶ and that the recoil energy available for bond rupture⁷ is usually large compared to the bond energy. Due to emission of γ 's in opposite direction, recoil energies imparted to the active atom may cancel each other and so bond rupture may not take place, but this effect^{8,9} is presumed to be around 5%. Low energy γ 's emitted after neutron capture may, however, be internally converted and may cause electronic and vibrational excitations of the molecule which are very effective in bond breaking. The multiple charges produced by this internal conversion and the electronic energy may be distributed to the different parts of a complex ion so that the effective electronic and vibrational excitation of the central atom is reduced. Thus it is quite likely that the complexity, stability, molecular volume

and charge of the complex ion may have an effect on the breaking of bonds that would liberate the atom undergoing the (n, γ) reaction. It has been observed by Adamson and Grunland¹⁰ that in isomeric transitions of bromine where the γ 's are known to be internally converted, the retention of activity is dependent on the charge of the ion. Although it is known that γ 's emitted after neutron capture are internally converted^{11,12} it is not yet possible to measure separately the contribution of bond rupture by internal conversion in the (n, γ) process to the total effect observed.

In the present investigation the dependence of retention on the molecular complexity of the molecule and on the number of coordinating linkages from a single group for the (n, γ) reaction with different amino, chloroamino and diamino complexes of platinum has been studied. A detailed analysis of radioactive products may throw light on bond breaking by the (n, γ) process in a complex molecule and will lead to a choice of the most suitable platinum complex to be used for the preparation of high specific activity radioplatinum by the Szilard-Chalmers method.

Preparation of the Various Compounds.—The platinum chloride for the preparation of the different complexes was J. T. Baker Analytical Reagent grade. Other chemicals employed were also of this grade whenever available, otherwise of c.p. quality. Technical grade butyl acetate was distilled and the fraction boiling between 124 and 126° was collected and then used for extraction experiments. The following platinum complexes were prepared according to the methods described in the literature: (1) K₂PtCl₄,¹³ (2) [Pt(NH₃)₄]Cl₂,¹³ (3) [Pt(en)₂]Cl₂,¹⁴ (4) *trans*-[Pt(en)₂Cl₂]Cl₂,¹⁴ (5) [Pt(en)Cl₂],¹⁴ (6) [Pt(en)Cl₄],¹⁴ (7) [Pt(NH₃)₅Cl]Cl₂,¹⁶ (8) [Pt(NH₃)₄]Cl₂,¹⁶ (9) *cis*-[Pt(NH₃)₂Cl₂],¹⁷ (10) *rac*-[Pt(en)₂]Cl₄·2½H₂O,¹⁸ (11) *rac*-[Pt(pn)₂]Cl₄·H₂O,¹⁹ (12) BaPtCl₄·3H₂O,²⁰ (13) *cis*-[Pt(NH₃)₂Cl₄].¹⁷ Attempts to pre-

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pare this last compound by oxidizing *cis*-[Pt(NH₃)₂Cl₂] with chlorine or nitric acid or aqua regia resulted in a lemon yellow compound which is described in the literature as the color of the *trans*-[Pt(NH₃)₂Cl₄]. *cis*-[Pt(NH₃)₂Cl₄] was prepared by the action of a concentrated solution of ammonium chloride on silver dihydroxychloroplatinate.¹⁷ The compound [Pt(en)₃](NO₃)₄ was prepared by adding the calculated quantity of silver nitrate to a known amount of [Pt(en)₃]Cl₄ in aqueous solution (en—ethylenediamine, pn—propylenediamine). The silver chloride was allowed to settle and the filtered solution was used for bombardment. The compounds prepared were purified by recrystallization from suitable solvents. The compound [Pt(NH₃)₃Cl]Cl₃ was purified by dissolving in the minimum quantity of water and then precipitating the original compound by adding concd. hydrochloric acid. The identity of each compound was checked by determining the platinum content.

Resins.—Amberlite IRA-400, a strong base anion-exchange resin manufactured by Rohm and Haas Company, and Amberlite IR-4B, a weak base anion-exchange resin supplied by Resinous Products and Chemical Company, were used to separate the anion activity from the platinum complex. Before use IRA-400 was converted into the hydroxy form by treatment with sodium hydroxide solution. IR-4B was obtained in the regenerated form, ready for use in the separation. In blank experiments it was found that IRA-400 could remove PtCl₆[−] and PtCl₄[−] ions quantitatively from their solution. It has been shown²¹ that IR-4B behaves similarly, and that the removal is quantitative was checked in this study. In the present experiments the recovery of the original compound after passage through the resins was quantitative.

Irradiations and Activity Measurements.—The complex (100 to 200 mg.) in the solid form or in aqueous solution, enclosed in a sealed quartz tube, was bombarded for one to two hours at an intensity of 1.3×10^{12} neutrons per cm² per second in the Argonne National Laboratory reactor CP-3. The gamma dosage during irradiations was approximately 500R per second. In one experiment the sample was bombarded in the thermal column of the reactor where the neutron and the gamma fluxes were 4×10^{11} per cm² per second and 8.3R per second, respectively. One gamma irradiation was made with the 300-curie cobalt source in this Laboratory at a dosage rate of approximately 80R per second.

The 18-hour platinum activity produced by the (n,γ) reaction with platinum was measured, after 24 hours from the end of bombardment, through an absorber of 105.2 mg. per cm² of aluminum which removed all gold activity. The total activity of the solid samples was determined in the standard way with a thin mica end-window Geiger-Müller counter. The activity of the solution was obtained by placing a constant volume of solution in the same beaker under constant geometry beneath the window of the Geiger-Müller counter. About 0.5 g. of IRA-400 or IR-4B resin was added to the solution of the bombarded sample. After 15 minutes the mixture was poured into a resin column. The solution was passed through the resin column until the activity of the solution was constant. When this solution was passed through a new resin column, the activity of the solution did not change further. The solution was then acidified with HCl and the volume was reduced by evaporation on a hot plate. The original compound was in general precipitated by addition of alcohol or alcohol-acetone mixture. The precipitate was then transferred into a weighed filter paper cup and was washed with alcohol and acetone, dried and counted. Previous experiments had shown that constant weight was obtained by this method. In a few experiments samples were counted on aluminum dishes. It may be mentioned here that active solutions were filtered through filter paper cups. The paper cups, after washing with water, alcohol and acetone, and after drying, were found to contain not more than 0.5% of the total activity. When active solutions were transferred from one glass vessel to another, no noticeable change in the specific activity of the solution was observed.

All activity measurements were made under identical conditions and were corrected for coincidence losses, back-

ground, radioactive decay, chemical yield, self-absorption and self-scattering. Chemical recovery varied from 50 to 90%.

Separation of the Various Compounds.—A detailed analysis of the products from neutron bombardment of solid [Pt(en)₂]Cl₂ was done as follows. To the solution of the bombarded solid, after treatment with anion-exchange resin, [Pt(en)Cl₂] was added in solid form. After a half hour the solid was removed by filtration. The filtrate was then treated with solid [Pt(en)Cl₄] and the solution was again filtered after a half hour. Excess of potassium chloroplatinite solution was added to the filtrate and the precipitated [Pt(en)₂]PtCl₄ was removed. *trans*-[Pt(en)₂Cl₂]Cl₂ was added to the solution and after a few minutes a precipitate of [Pt(en)₂Cl₂]PtCl₄ was separated. The remaining solution was acidified with 2 N HCl, reduced with magnesium powder, and metallic platinum collected on filter paper. The separated solids were then prepared for activity measurements.

In the extraction experiment the bombarded solid was dissolved in 20 cc. of 6 N HCl previously shaken with butyl acetate and the solution was extracted four times with 5-cc. portions of butyl acetate. Two drops of 10% stannous chloride solution in 2 N HCl was added to the aqueous phase and the solution was again extracted with butyl acetate as before. The activity of the 6 N HCl solution was measured after each butyl acetate extraction. The solution was treated as above in order to obtain the activity associated with [Pt(en)₂]PtCl₄, with [Pt(en)₂Cl₂]PtCl₄ and with the metallic platinum.

The irradiated solution of [Pt(en)₂]Cl₂ was divided into two portions. One portion was evaporated to dryness on a weighed aluminum cup. The solid was moistened with alcohol and acetone, dried to constant weight and counted. The other portion of the solution was treated in the same manner as in solid irradiations.

Bombarded solid *cis*-[Pt(NH₃)₂Cl₂] and solid *cis*-[Pt(NH₃)₂Cl₄] were dissolved in 30 cc. of warm water and the solutions acidified with a few drops of 2 N HCl. It was observed that when yellow solutions of *cis*-[Pt(NH₃)₂Cl₂] and of *cis*-[Pt(NH₃)₂Cl₄] were passed through an anion-exchange column, the solutions became colorless. This was possibly due to the transformation of the original compounds into new compounds which could be removed from the solution by the anion exchange.²¹ Bombarded solid [Pt(NH₃)₄]Cl₂ was dissolved in 5 cc. of water and the solution, after passing through an anion-exchange column, was scavenged with solid *cis*-[Pt(NH₃)₂Cl₂] and [Pt(NH₃)₄Cl₂]Cl₂. The original compound was then precipitated by adding 10 volumes of alcohol-acetone mixture or the solution was treated with excess of potassium chloroplatinite to precipitate [Pt(NH₃)₄]PtCl₄, and the precipitate was washed, dried and counted. In one experiment, the solution of [Pt(en)₃]Cl₄, after the resin treatment, was reduced to a small volume and then treated with solid ammonium tartrate. The white solid which separated was washed with water and dissolved in the minimum quantity of 6 N HCl. The original compound was then precipitated by adding alcohol and the activity of the precipitate determined.

Results and Discussion

The results of the determination of the distribution of activities in the original substances and the various products are summarized in Tables I and II. The percentages are based on the activity in the original bombarded target or the solution of the target as 100% as indicated.

It is quite evident from a comparison of bombardment 4 with 8, 9 or 10 in Table I that the retention of activity by a complex does not increase with increase in the number of coördinating linkages from a coördinating group. On the other hand retention values of compounds containing monodentate groups are slightly greater than those of compounds with bidentate groups, except for 8, 9 and 10 which are discussed later. The difference of the retention values in column 2 and 3 of Table I gives the retention due to active degraded products

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TABLE I

Solid cpd. bombarded	Activity retained by soln. after passing through anion-exchange resins, %	Activity retained by original cpd. or its derivative	Difference of columns 2 and 3
1 <i>cis</i> -[Pt(NH ₃) ₂ Cl ₄]	11.4 ± 2	...
2 <i>cis</i> -[Pt(NH ₃) ₂ Cl ₂]	16.5 ± 2	...
3 [Pt(NH ₃) ₂ Cl] ₂	40.7 ± 2	20.7 ± 2	20.0
4 [Pt(NH ₃) ₄]Cl ₂	76.6 ± 3	40.2 ± 2	36.4
5 [Pt(en) ₂]Cl ₂ ·2½H ₂ O	40.0 ± 2	5.6 ± 2	34.4
6 [Pt(en) ₂]Cl ₂ ·H ₂ O	59.3 ± 2	4.2 ± 2	55.1
7 <i>trans</i> -[Pt(en) ₂ Cl ₂]Cl ₂	13.8 ± 0.5	6.8	7.0
8 [Pt(en) ₂]Cl ₂	51.2 ± 2	23.0 ± 3	28.2
9 [Pt(en) ₂]Cl ₂	58.8	26.6	32.2 ^a
10 [Pt(en) ₂]Cl ₂	57.8	26.6	31.2 ^b

^a Bombarded in the thermal column of the pile and the aqueous solution exposed to γ's from the cobalt source for 2 hours. ^b Bombarded in the thermal column of the pile.

TABLE II

Cpd. bombarded in aqueous soln.	Activity retained by soln. after passing through anion-exchange resins, %
1 [Pt(en) ₂]Cl ₂	96 ± 3
2 [Pt(en) ₂](NO ₃) ₄	88 ± 2
3 [Pt(NH ₃) ₄]Cl ₂	92.0 ± 1

which cannot be removed from solution by anion-exchange resins IRA-400 and IR-4B. As noted earlier, 4 to 7% retention by bidentate complexes is possibly due to chance cancellation of γ's emitted in opposite directions. The retention value above 4 to 7% in the case of a monodentate complex is possibly due either to adsorption on the recovered original compound of active degraded products formed as a result of the (nγ) reaction or the re-formation of the parent compound by thermal as well as hot processes. In a thermal process the average energy of the reactants is less than the chemical bond energy while in a hot process the average energy of one of the reactants is above the chemical bond energy and is not temperature dependent. These retention values of the solid bidentate complexes would seem to suggest that at least two bonds are broken in 93 to 96% of the cases.

The activity of precipitated [Pt(NH₃)₄]PtCl₄, the derivative of 4 in Table I, was found to give retention varying from 39 to 75%. But when the solution of the bombarded solid, after removing activities by anion exchange resins, was scavenged with solid *cis*-[Pt(NH₃)₂Cl₂] and [Pt(NH₃)₄Cl₂]Cl₂, the retention in [Pt(NH₃)₄]Cl₂ was found to be reproducible within 2% in independent experiments. The scavengers were washed with water, alcohol and acetone, dried and examined for activity. Only 2.2 and 3.3% of the total activity were associated

with the scavengers *cis*-[Pt(NH₃)₂Cl₂] and [Pt(NH₃)₄Cl₂]Cl₂, respectively. This indicates that possibly the scavengers removed from the solution other active species different in chemical nature.

It is to be noticed from Tables I and II that when an aqueous solution of a complex is irradiated with slow neutrons the percentage of activity removable by anion-exchange resins is less than in the case of irradiation of the solid. That is to say, initial active degraded products, before being degraded completely into platinous or platinic ions which would form anions, react with water molecules or other groups and radicals to form active products which are not removable by anion exchange resins. When solid samples are irradiated, the initial degraded products either degrade further, due to excess recoil energy, into platinous or platinic ions or are thermalized. On dissolving the irradiated sample in water, the thermalized products react at least in part with water and change into anions. It might be possible, in the case of irradiation in aqueous solution, that by the action of the background γ's of the pile on water molecules new products are formed, which react in a different manner than water molecules with the thermalized active degraded products of the complex. The results of Table I (No. 9 and 10), however, indicate that the difference in the retention values obtained for irradiation in aqueous solution (Table II) and in solid form (8, Table I) is not due to the reaction between thermalized active degraded products and the substances produced by the action of γ's on water molecules.

The distribution of activities in various fractions formed in the neutron bombardment of [Pt(en)₂]Cl₂ is summarized in Table III.

The higher retention by the original compound in this case compared to that of other bidentate complexes is possibly due either to the re-formation of the original compound by reaction between degraded products and ethylenediamine or to adsorbed active impurity. It is to be expected that if the retention is due to adsorbed active impurity then a change in the nature of the precipitate should change the retentivity value calculated from the activity of the precipitate. In three experiments in which an aqueous solution of [Pt(en)₂]Cl₂ was bombarded with neutrons, [Pt(en)₂]Cl₂ was removed, subsequent to the resin treatment, by precipitating it (1) as [Pt(en)₂]PtCl₄ by addition of K₂PtCl₄ and (2) as [Pt(en)₂]Cl₂ by addition of an alcohol-acetone mixture. The percentage retentions obtained by the two procedures were 46 and 48%, respectively. Thus it is inferred that retention is due to the re-formation of the original compound. In support of this is the observation that practically no activity was associated with the

TABLE III
DISTRIBUTION OF RECOIL PRODUCTS FROM NEUTRON BOMBARDMENT OF [Pt(en)₂]Cl₂

Condition of bombardment (1)	Activity retained by soln. after passing through anion-exchange resin (2)	% activity as				Pt* metal (7)	Total of 5,6,7
		[Pt*(en)Cl ₂] (3)	[Pt*(en)Cl ₄] (4)	[Pt*(en) ₂]PtCl ₄ (5)	[Pt*(en) ₂]Cl ₂ (6)		
Solid, 1-2 hr., 1.3 × 10 ¹² neutrons/cm. ² /sec.	51.2	0.88	0.19	23.0	6.0	18.7	47.7
Soln., 2 hr., 1.3 × 10 ¹² neutrons/cm. ² /sec.	96	0.22	0.26	46.0	13.9	35.4	95.3
Soln., 2 hr., 1.3 × 10 ¹² neutrons/cm. ² /sec.	97	0.2	0.16	43.9	Not separated	37.4	

fraction recovered as $[\text{Pt}(\text{en})\text{Cl}_2]$. The latter, which would be formed from a degradation product such as $[\text{Pt}(\text{en})]^{+2}$, must therefore have reformed the original compound $[\text{Pt}(\text{en})_2]\text{Cl}_2$. It might be suggested that the active form of $[\text{Pt}(\text{en})\text{Cl}_2]$, produced in tracer quantity as a result of the capture process, reacts with the anion-exchange resin and is removed from the solution. However, this is not the case. In one experiment when the solution of bombarded $[\text{Pt}(\text{en})_2]\text{Cl}_2$, before passing through the anion-exchange column, was treated with solid $[\text{Pt}(\text{en})\text{Cl}_2]$ and solid $[\text{Pt}(\text{en})\text{Cl}_4]$, and then the solids removed, only 0.2 and 0.3%, respectively, of the total activity was obtained.

In the irradiation of an aqueous solution of $[\text{Pt}(\text{en})_2]\text{Cl}_2$, 14% of the activity is associated with $[\text{Pt}(\text{en})_2]\text{Cl}_2$. This would indicate that as a result of the capture process oxidation of bivalent to tetravalent platinum takes place along with the rupture of the coordinating bonds, provided the activity is not due to adsorbed active degraded products. In a blank experiment it was observed that metallic platinum could not be separated by reducing with magnesium powder a hydrochloric acid solution of inactive *trans*- $[\text{Pt}(\text{en})_2]\text{Cl}_2$. If the activity associated with the fraction $[\text{Pt}(\text{en})_2]\text{Cl}_2$ were due to adsorbed active impurity, which otherwise would have separated with the metallic platinum fraction, then the activity of the metallic platinum produced by reduction of the bombarded solution of $[\text{Pt}(\text{en})_2]\text{Cl}_2$ by magnesium powder before adding *trans*- $[\text{Pt}(\text{en})_2]\text{Cl}_2$ and separating the precipitate of $[\text{Pt}(\text{en})_2]\text{Cl}_2$ should be greater than that associated with the platinum obtained by reduction after the addition of *trans*- $[\text{Pt}(\text{en})_2]\text{Cl}_2$. The results in column six of Table III show that no such increase, within experimental error, is observed. It seems therefore that the retention of activity by the fraction $[\text{Pt}(\text{en})_2]\text{Cl}_2$ is true retention, rather than due to adsorbed impurity, and platinum has been oxidized from the bivalent to the tetravalent state.

The chemical nature of the substance (or substances) whose activity is removed as metallic platinum, after removing activities in other possible forms, is difficult to deduce. Active degraded products which do not exchange or exchange only very slowly with the added carrier would appear with the metallic platinum fraction. Further work is needed to establish the exact nature of this fraction of the activity. Formation of active polymeric products of platinum should also be considered.

In neutron bombardment of aqueous solutions of $[\text{Pt}(\text{en})_2]\text{Cl}_2$, the activities separated with $[\text{Pt}^*(\text{en})_2]\text{PtCl}_4$, $[\text{Pt}^*(\text{en})_2]\text{Cl}_2$ and metallic platinum are greater than those obtained with bombardments of solid. This suggests that the formation of the active products $[\text{Pt}^*(\text{en})_2]\text{Cl}_2$ and $[\text{Pt}^*(\text{en})_2]\text{Cl}_2$ and the active products separated as metallic platinum are favored in thermal processes in solution.

The fraction of activity removable by butyl acetate extraction is only 34% compared to 49% by anion-exchange resins. The extractable activity can be separated in two steps, one fraction (9%)

TABLE IV
DISTRIBUTION OF RECOIL PRODUCTS FROM NEUTRON BOMBARDMENT OF $[\text{Pt}(\text{en})_2]\text{Cl}_2$

Condition of bombardment (1)	Activity retained by soln. after extraction with butyl acetate, %		% activity as		Pt* metal (6)	Total of 4, 5, 6 (7)
	Without SnCl_2 (2)	With SnCl_2 (3)	$[\text{Pt}^*(\text{en})_2]\text{PtCl}_4$ (4)	$[\text{Pt}^*(\text{en})_2]\text{Cl}_2$ (5)		
Solid, 2 hr., 1.3×10^{13} neutrons/ cm. ² /sec.	91	65.75	25.2	6	30	61.2

without addition of stannous chloride and the other fraction (25%) after addition of stannous chloride. The products, of unknown composition, of the reduction of H_2PtCl_4 and H_2PtCl_6 by stannous chloride in aqueous solution may be extracted by butyl acetate. The nature of the fraction extracted without reduction by stannous chloride is not known. It may be mentioned that attempts were made to extract into organic solvents chloroplatinous acid prepared in solution by (1) reduction of chloroplatinic acid with sulfur dioxide, (2) addition of perchloric acid to potassium chloroplatinite and (3) addition of sulfuric acid to barium chloroplatinite. Table V summarizes the results of the extraction experiments.

TABLE V
EXTRACTION OF CHLOROPLATINOUS ACID BY ORGANIC SOLVENTS

Platinum before extraction, mg.	HCl in soln., N	Platinum in aqueous layer after extraction, mg.	Organic solvent
27.6	1.4	26	Ethyl acetate
27.6	4.2	28	Ethyl acetate
30.1	8.4	30.1	Ethyl acetate
30.1	1.4	29.2	Ether
30.1	4.2	29.7	Ether
30.1	8.4	27.7	Ether
50.0	6.0	49.0	Butyl acetate

It is known that the red colored complex produced by reduction of chloroplatinic acid with stannous chloride solution can be extracted easily into ether,²³ ethyl acetate^{22,23} and butyl acetate²¹ and it is commonly stated that chloroplatinous acid is extracted into organic solvents. However, in the light of the above experimental results it must be concluded that chloroplatinous acid cannot be extracted into ether, ethyl acetate or butyl acetate. It would be interesting to determine the nature of the complex formed by reduction of chloroplatinic acid with stannous chloride solution and extracted into organic solvents.

It has been noted already that 49% (Table III, column 2) of the total activity can be removed by anion-exchange resins. The difference (15%) between the fraction of activity removable by anion-exchange resins and by butyl acetate extraction represents a new form of anion activity different

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(23) E. B. Sandell, "Colorimetric Determination of Traces of Metals," Vol. B, 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1950.

from the other two mentioned before, provided it is assumed that no chemical reaction takes place between the resins and active degraded products. Thus, three different kinds of anion activities are formed as a result of the (n, γ) reaction on $[\text{Pt}(\text{en})_2]\text{Cl}_2$.

Of all the compounds investigated in the present research, *trans*- $[\text{Pt}(\text{en})_2\text{Cl}_2]\text{Cl}_2$ appears to be most suitable for preparing high specific activity radio-platinum by the (n, γ) process, assuming that radiation decomposition due to γ 's from the pile is about the same in all the compounds.

The present investigation indicates that in the

(n, γ) reaction with complex compounds of platinum a considerable fraction of the total activity exists as degraded products. The formation of active degraded products which have different stabilities toward caustic soda can explain the difference in retention values observed by Sue and Kayas⁵ with cobalt complexes containing mono, bi and tridentate groups.

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NOTRE DAME, INDIANA

NOTES

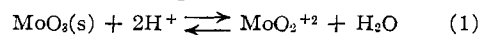
State of Mo(VI) in Acid Solutions

BY MARK M. JONES

RECEIVED APRIL 23, 1954

The fact that molybdenum trioxide dissolves in aqueous solutions of strong mineral acids has been known for many years.¹⁻⁴ That molybdenum trioxide forms compounds with sulfuric acid has also been demonstrated by the isolation of $\text{MoO}_3 \cdot \text{SO}_4$ and several related substances.^{2,3,5} These compounds have led to the postulation of the ion MoO_2^{+2} in these compounds and in acidic solutions of molybdic anhydride⁶ and it was to test this that the present work was undertaken.

If molybdenum trioxide dissolves in acids to form the ion MoO_2^{+2} and water, this reaction may be represented by the equilibrium



which has an equilibrium constant

$$K = \frac{a_{\text{MoO}_2^{+2}} a_{\text{H}_2\text{O}}}{a_{\text{MoO}_3(\text{s})} a_{\text{H}^+}^2} \quad (2)$$

This expression may be simplified by making use of the fact that the activity of the molybdenum trioxide will be a constant at any given temperature and that the activity of the water in dilute solutions will also remain constant. If the molybdenum in solution is present as MoO_2^{+2} , then the relationship between the solubility of the trioxide and the concentration of acid will be determined by equation 2. If we take logarithms of equation 2 we obtain after simplification

$$2 \log a_{\text{H}^+} + \log K^1 = \log a_{\text{MoO}_2^{+2}} \quad (3)$$

Here $K^1 = K(a_{\text{MoO}_3(\text{s})}/a_{\text{H}_2\text{O}})$. If we make the further assumption that $a_{\text{MoO}_2^{+2}}$ is equal to the

solubility of the trioxide in the acid solutions we obtain

$$2 \log a_{\text{H}^+} + \log K^1 = \log S \quad (4)$$

where S is the concentration of molybdenum in moles per liter. Thus if the molybdenum trioxide dissolving in an acid solution is present as MoO_2^{+2} , a plot of the logarithm of the solubility as ordinate against logarithm of the hydrogen ion activity as abscissa should be a straight line with slope of 2.⁷

Experimental.—The solubility of molybdenum trioxide was determined in aqueous perchloric acid solutions of various concentrations. The molybdenum trioxide used was the Merck & Co., Inc., A.C.S. Reagent. The perchloric acid solutions were prepared by dilution of 72% perchloric acid from the G. F. Smith Chemical Co. and were analyzed by titration against a standard sodium hydroxide solution. To prepare a solubility sample, 10 g. of molybdenum trioxide and 100 ml. of the perchloric acid solution were put into a 250-ml. flask. The flask was then tightly stoppered and put into a constant temperature bath at $25 \pm 0.5^\circ$ and shaken frequently. The solutions were allowed to equilibrate a minimum of two weeks before analysis. For analysis a sample was removed through a filter paper into a 25-ml. pipet. The sample was then put into a tared container, evaporated to dryness and the residue weighed. The solid obtained upon evaporation of these solutions was the yellow hydrated oxide, $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$,⁸⁻¹¹ and was weighed as such. Samples taken from the same solution, a week or more apart, showed no significant differences or trends.

Results and Discussion.—The results are presented in Table I. The hydrogen ion activity in these solutions was obtained from data in Conway.¹² In Fig. 1 a plot of $\log S$ versus $\log a_{\text{H}^+}$ (equation 4) is given. Although a fair straight line may be drawn through these points its slope is not 2 but rather 0.68. It is possible to make a correction for the activity coefficient of the MoO_2^{+2} ion in this solution, basing it upon data for the UO_2^{+2} ion in

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