terns. At 500° the sole product is tin(IV) fluoride, and conversion is complete. Tin(IV) oxide does not react with fluorine below 300°, at 400° conversion to tetrafluoride is about 80%, and at 500–550° conversion is complete.

The reaction with tin(II) oxide is thus similar to that with copper(I) oxide.[3] No evidence for an oxyfluoride was found.

Emeléus and Woolf[4] report a similar reaction between tin(II) oxide and bromine trifluoride, forming only tin(IV) oxide and fluoride.

Tin(II) sulfide reacts readily with fluorine, even at room temperature. At 400–500° reaction is so violent that much product is volatilized. Introduction of fluorine at room temperature, followed by gradual increase in temperature to 500°, gave complete conversion. X-Ray patterns of fluorination products from reactions at various temperatures showed only tin(IV) fluoride and unreacted sulfide. Tin(IV) sulfide does not react at 100° or below. Reaction is extensive at 200° and above. Fluorination over the range 25–300° gave complete conversion.

Experimental

The fluorinations were carried out as described previously.[5] All product transfers were made in the dry-box at a dewpoint of −25° or less. Stock C.P. tin and tin(IV) oxide were used. Tin(II) oxide was freshly prepared[6] to minimize possible contamination with tin(IV) oxide.

Anal. Calcd. for SnO: Sn, 88.12. Found: Sn, 88.07.

Tin(II) sulfide was prepared by precipitation from the chloride with hydrogen sulfide.[7] Tin(IV) sulfide was prepared by direct reaction between tin(II) chloride and sulfur.[8]

Anal. Calcd. for SnS: Sn, 78.73. Found: Sn, 78.54, 78.69. Calcd. for SnS_2: Sn, 64.93. Found: Sn, 64.73, 64.71.

Fluorination products of each run were also analyzed, Tin was determined as the oxide after treatment with nitric acid.

Anal. Calcd. for SnF_4: Sn, 60.96. Found: (Sn + F_2) Sn, 61.36, 61.18; (SnO + F_2, upper layer) Sn, 60.42, 60.88; (SnO_2 + F_2) Sn, 60.3, 61.5; (SnS + F_2) Sn, 61.27, 60.72; (SnS_2 + F_2) Sn, 61.09, 61.28.

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[3] H. M. Haendler, L. H. Towle, E. F. Bennett and W. L. Patterson, Jr., THIS JOURNAL, **76**, 2178 (1954).

[4] H. Emeléus and A. Woolf, *J. Chem. Soc.*, 164 (1950).

[5] H. M. Haendler and W. J. Bernard, THIS JOURNAL, **73**, 5218 (1951).

[6] W. Fraenkel and K. Snipischsky, *Z. anorg. Chem.*, **125**, 235 (1922).

[7] W. E. Henderson and W. C. Fernelius, "Inorganic Preparations," McGraw-Hill Book Co., Inc., New York, N. Y., 1935, p. 64.

[8] L. Vanino, "Handbuch der Präparativen Chemie," Vol. I, Enke Verlag, Stuttgart, 1925, p. 600.

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Non-exchange of Chlorine between Chloride and Hexachlorosmate(IV) Ions in Aqueous Solution[1]

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RECEIVED NOVEMBER 30, 1953

The generally encountered slowness of substitution reactions of osmium(IV) complexes may be expected to result in low rates of exchange between ligands coördinated to osmium(IV) and the corresponding free ligand ion or molecule in solution. In favorable cases such slow exchanges may be accessible to kinetic studies. We have examined the chloride–hexachlorosmate(IV) system for chloride exchange in nitric and sulfuric acid solutions, as well as determining the absorption spectrum of potassium hexachlorosmate(IV) in 1.32 *f* and 0.10 *f* nitric acid solution.

Experimental

Radiochlorine Tracer.—Radiochlorine-36 (half-life, 4×10^5 years), produced by (n,γ) reaction on potassium chloride, was supplied in a radiochemically purified form as a hydrochloric acid solution by the Oak Ridge National Laboratory on allocation by the U. S. Atomic Energy Commission.

Potassium Hexachlorosmate(IV).—This substance was synthesized by heating a mixture of C.P. osmium(VIII) oxide, iron(II) chloride and concentrated hydrochloric acid in a pressure flask, followed by precipitation with potassium chloride, in a manner similar to that employed by Dwyer and Hogarth[2] for the preparation of the ammonium salt. The potassium salt was recrystallized from 3 *f* hydrochloric acid, cooled to 0°, filtered and washed with 1 *f* hydrochloric acid and finally with 95% ethanol. The crystals were dried over phosphorus(V) oxide in a vacuum desiccator. Weighed portions of the dried crystals were analyzed by reduction to metallic osmium in a stream of hydrogen at 400°, the hydrogen chloride formed being absorbed in an excess of standard silver nitrate solution which was later back-titrated with standardized potassium thiocyanate solution by the Volhard method. The residue, consisting of metallic osmium and an equivalent amount of potassium chloride, was transferred in a nitrogen atmosphere into a weighing vessel and weighed, then the potassium chloride leached out with water and this chloride determined as above.

Anal. Calcd. for K_2OsCl_6: Os, 39.5; Cl, 44.2. Found: Os, 39.8; Cl, 44.4.

Other reagents were C.P. or reagent grade and were used without further purification.

Separation Method.—The hexachlorosmate(IV) ion was separated from chloride ion by precipitation with excess ammonium nitrate. Experiments showed that precipitation from a solution 25 *f* in ammonium nitrate gave a rapid and quantitative separation. Two-gram portions of ammonium nitrate were added to the 1-ml. aliquots of the exchange mixtures, and the ammonium hexachlorosmate(IV) precipitates centrifuged and washed with saturated ammonium nitrate solution.

Exchange Runs.—Exchange mixtures (10-ml. volumes) were synthesized by weighing out potassium hexachlorosmate(IV) and dissolving in solutions volumetrically synthesized from standardized sodium chloride, sodium nitrate (used to adjust the ionic strength, μ), and nitric or sulfuric acid solutions. The mixtures were brought to the reaction temperature in a bath thermostated to $\pm 0.2°$, and exchange initiated by admixture with 50 μl. of radiochlorine tracer solution known to be in the form of chloride ion. One-ml. aliquots were removed at definite time intervals and subjected to the above separation procedure. All exchange runs were carried out in the absence of light.

Specific Activity Determinations.—In some cases the precipitated ammonium hexachlorosmate(IV) fraction was dissolved in 3 *f* sodium hydroxide and transferred to a cell used for radioassay with a dip-type Geiger–Mueller tube and associated scale-of-64 circuit. In other cases, the solution fractions were transferred directly to cells. These solutions were diluted in the cells to a volume of *ca.* 20 ml. and had essentially the same density so that self absorption and self-scattering corrections were unnecessary. Background corrections (*ca.* 30 c./min.) were applied, and the background with dip tube and cell determined just prior to each radioassay to check their decontamination.

Spectrophotometric Runs.—Certain exchange solutions were diluted 250-fold with solvent of the same composition as the exchange mixture except for the omission of the po-

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[1] These investigations were carried out under contract AT-(11-1)-34, Project 12, between the University of California and the U. S. Atomic Energy Commission.

[2] F. P. Dwyer and J. W. Hogarth, *J. Proc. Roy. Soc. N. S. Wales*, **84**, 194 (1951).

TABLE I

EXCHANGE OF Cl* BETWEEN Cl^- AND $OsCl_6^=$ IONS IN ACID SOLUTION (DARK RUNS)

K_2OsCl_6, f	NaCl*, f	HNO_3, f	μ	Temp., °C.	Exch. time, d.	Cl^- fr., c./min.	$OsCl_6^=$ fr., c./min.	Exch., %
0.059	0.060	1.00	1.6	25.1	0	786 ± 10		0
					0.8	785 ± 10		0
					4.0	751 ± 15		5
		1.32[a]	2.0	49.6	0	902 ± 10		0
					1.0	901 ± 24	0 ± 4	0
					9.8	932 ± 30		0
					13.0		2 ± 3	0
		0.10[a]	0.4		0	(831 ± 10)		
					7.1		0 ± 2	0
					56		0 ± 2	0
0.064	0.12	2.0[b]			0	831 ± 10		0
					1.2	825 ± 10		1
					63		12 ± 3	2

[a] Exchange mixtures examined spectrophotometrically at 25° after 250-fold dilution. [b] H_2SO_4.

tassium hexachlorosmate(IV). These solutions were examined at 25° with a Model 11 PMS Cary recording spectrophotometer, using quartz cells of 1-cm. path length.

Results and Discussion

The exchange results are given in Table I. The per cent. exchange was calculated assuming the six chlorine atoms in the hexachlorosmate(IV) ion are equivalent. The errors given for the counting rates include only the standard deviation of the counting statistics. The over-all error in the per cent. exchange is estimated to be 5%.

Within the 5% estimated experimental error there is no exchange between chloride ion and hexachlorosmate(IV) ion in acid solution even at 50° and for exchange times up to 63 days. Assuming as much as 5% exchange at the longest time for each exchange system studied, and assuming the exponential exchange law and a bimolecular rate law, the bimolecular rate constants are $<4 \times 10^{-9}$ and $<6 \times 10^{-8}$ liter $mole^{-1}$ $sec.^{-1}$ at 50 and 25°, respectively, under the experimental conditions. It does not appear feasible to extend measurements over significantly longer time periods or at higher temperatures because of net decomposition (hydrolysis and/or aquation) of the hexachlorosmate(IV) ion.

These non-exchanges (or slow exchanges) are consistent with the slow substitution reactions of "inner orbital" complex ions of the "inert" type, to which Os(IV) complexes belong, in accordance with the postulation of Taube.[3]

Two of the nitric acid exchange mixtures were examined spectrophotometrically at zero time and after one week in order to note if there was evidence for decomposition of the hexachlorosmate(IV) ion during the exchange runs, as well as to obtain the absorption spectrum of this ion in aqueous solution, which does not appear to have been previously reported.[4] The absorption spectra were essentially identical within the experimental error, and only a single curve is shown in Fig. 1. Thus, there is no indication of chemical changes within one week from either the spectrum or exchange observations. A solution from the 0.10 f HNO_3 exchange run (Table I) was examined spectrophotometrically under somewhat different conditions after 56 days at 50° and there was evidence that the optical density had decreased considerably without any wave length shifts. The possible formation of the pentachloroaquo ion of osmium(IV) cannot be deduced or ruled out from the observed spectral change inasmuch as this ion has apparently not been characterized and its absorption spectrum is not known. Further spectrophotometric studies were not undertaken because of our main interest in the exchange reactions which have proved too slow for convenient kinetic study.

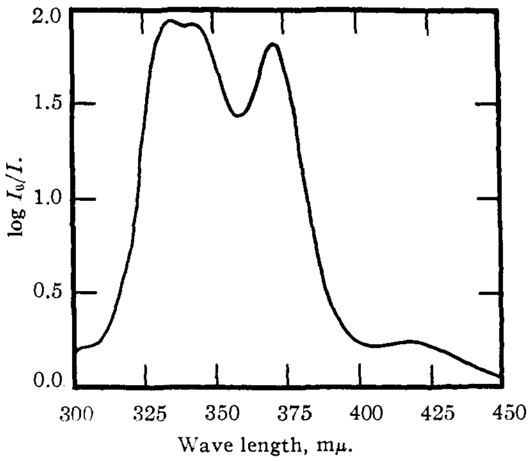

Fig. 1.—Absorption spectrum of K_2OsCl_6 in HNO_3 solution at 25°. The optical density is zero from 475 to 750 mμ. The absorption due to all species except the K_2OsCl_6 has been experimentally subtracted off. The same spectrum was found for solutions 0.000236 f in K_2OsCl_6 and 0.060 f in NaCl and either 1.32 f or 0.10 f in HNO_3, observed at zero time and after 250-fold dilution of identical nitric acid solutions 0.059 f in K_2OsCl_6 which had been at 50° for seven days (see Table I).

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[3] H. Taube, *Chem. Revs.*, **50**, 69 (1952).

[4] The absorption spectrum of a substance alleged to be $OsCl_4$ in water and in hydrochloric acid was reported by S. Karim and R. Samuel, *Bull. Acad. Sci. United Provinces Agra Oudh, India*, **2**, 157 (1933). This spectrum is different from that found by us for K_2OsCl_6 in nitric acid solution.