volume changes attending solution for the two hydrates to be nearly equal.

The small heat effect and the relatively high viscosity of saturated solutions of magnesium dichromate also give a reason why measurement of the transition temperature with precision is difficult. The average temperature of the heating and cooling "breaks" is 49.0 ± 1.3°, but two solid phases were identified unequivocally only at 48.2° and 48.4°. The best estimate available appears to be 48.5 ± 0.5° for the transition temperature, at a solubility of 61.16% $MgCr_2O_7$. The transition occurs exceptionally slowly, twenty-four hours agitation being required for equilibration in the tests described above. These same characteristics explain why $MgCr_2O_7 \cdot 6H_2O$, actually the stable phase at room temperature, went so long undiscovered.

While visual examination of the solubility curve shows no apparent break, statistical methods were also used to verify this point. Over the temperature range 39.4 to 60.2°, the equation $S = 53.73 + 0.15325T$ fits the data with an average deviation of 0.05% solubility and a maximum error of 0.13%. An appreciably better fit cannot be obtained by the use of curves of higher order, and the precision of fit of the above straight line is substantially the same as the precision of the solubility data itself.

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BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE SPECTROSCOPY LABORATORIES AT CANISIUS COLLEGE]

Niobium and Tantalum 8-Quinolinolates[1]

BY HERMAN A. SZYMANSKI AND JOHN H. ARCHIBALD[2]

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A preparative technique was developed for an interaction of niobium and tantalum compounds with 8-quinolinol (8-hydroxyquinoline) which minimized contamination of the product with basic salts. A modification of the originally proposed method for the preparation of niobium 8-quinolinolate was used and a new formula for the compound of niobium 8-quinolinolate proposed. Infrared spectroscopy was utilized to verify some of the results. Products with the empirical formula $MO(C_9H_6ON)_3$ and $M(C_9H_6ON)_5$ have been prepared in the pure form.

Discussion

The compounds of 8-quinolinol with niobium or tantalum have been described as of indefinite or of inadequately described structures.[3] Niobium 8-quinolinolate was first prepared by Sue[4] and a formula was proposed.

$$Nb_2O_5 \cdot 5.5(C_9H_6ON) \cdot 4(H_2O)$$

Schwarz[5] reported having prepared niobium and tantalum 8-quinolinolates in connection with an analytical study of niobium and tantalum but no formulas were proposed. Doan and Duval[6] reported from a thermogravimetric study that the compound of niobium 8-quinolinolate as prepared by Sue has no definite composition.

Experimental

Niobium 8-Quinolate.—One-tenth g. of very high purity niobium oxide was fused with 5 g. of potassium bisulfate. The melt dissolved in 100 ml. of 10% sulfuric acid solution containing 1 g. of oxalic acid. 8-Quinolinol (1.5 g.) in 12% acetic acid solution was then added. Upon neutralizing with ammonium hydroxide a finely crystalline yellow precipitate of niobium 8-quinolinolate formed. After digesting for one hour, the precipitate was filtered on a weighed glass-frit crucible and washed with hot water. To produce a substance free of water and excess 8-quinolinol, the precipitate was dried overnight at 155°.

Anal. Calcd. for $NbO(C_9H_6ON)_3$: Nb, 17.16; C_9H_6ON, 79.88. Found: Nb, 17.1; C_9H_6ON, 80.3.

Anal. Calcd. for $NbO(C_9H_6ON)_3$: Nb, 17.16; C_9H_6ON, 79.88. Found: Nb, 17.1; C_9H_6ON, 80.3.

Tantalum 8-Quinolinolate from Tantalum Pentachloride.—A small excess of a benzene solution of 8-quinolinol was added to a benzene solution of tantalum pentachloride. A bright, orange-yellow precipitate was formed which was filtered and washed with benzene.

Anal. Calcd. for $Ta(C_9H_6ON)_5 \cdot 5HCl$: Ta, 16.7; C_9H_6ON, 66.5; HCl, 16.8. Found: Ta, 18.4; C_9H_6ON, 66.1; HCl, 15.2.

Niobium and Tantalum 8-Quinolinolates from Mixed Oxides.—Equal weights of niobium and tantalum oxides were mixed and fused with potassium bisulfate. The same procedure by which niobium 8-quinolinolate was prepared, was followed. The yellow precipitate which formed was digested, then filtered and dried overnight at 155°.

Anal. Calcd. for $TaO(C_9H_6ON)_3$ and $NbO(C_9H_6ON)_3$: Ta + Nb, 21.9; C_9H_6ON, 75.4. Found: Ta + Nb, 22.2; C_9H_6ON, 74.0.

Analysis of Compounds.—The determination of niobium in niobium 8-quinolinolate was determined from the weight of the starting material. The niobium oxide starting material was determined by X-ray fluorescence analysis to be 99.5+% pure. In the mixed compounds of niobium and tantalum and in the tantalum compound prepared from tantalum pentachloride, weighed portions of the final products were ignited to the oxides. The 8-quinolinol content was determined by a volumetric titration with sodium bromate solution as recommended by Berg.[7] The hydrogen chloride content of the tantalum compound was determined by a Volhard titration of the chloride.[8]

The infrared spectrum of the dry compounds (made in Nujol-mull) showed no bands for water and free 8-quinolinol and no shift in bands of the complex as water was removed.

A change in the technique of precipitation of niobium 8-quinolinolate was used to avoid contamination of the final product with basic salts. When a pure compound, free of

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(1) Supported in part by a grant from Research Corporation, New York, N. Y.

(2) Abstracted from the Master's Thesis of John H. Archibald.

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(6) V. M. Doan and C. Duval, *Anal. Chim. Acta*, **6**, 83 (1952).

(7) R. Berg, *Pharm. Ztg.*, **71**, 1542 (1926).

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water and excess 8-quinolinol, was obtained analysis showed the composition $NbO(C_9H_6ON)_3$. The same technique by which niobium 8-quinolinolate was prepared failed to produce a compound from a pure tantalum solution. When pure tantalum and niobium were mixed however, tantalum appeared to have formed a similar compound. When tantalum pentachloride and 8-quinolinol were combined in benzene solutions, a stable addition compound containing about 5 moles of 8-quinolinol was formed. Niobium pentachloride appeared to form a compound similar to the tantalum addition compound with 8-quinolinol but which was quite unstable.

Niobium 8-quinolinolate shows a strong characteristic band at about 10.9 μ in the infrared spectra that apparently is due to the "NbO" group.[9,10]

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BUFFALO, N. Y.

[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY]

Kinetics of the Neptunium(III)–Neptunium(V) Reaction in Perchlorate Solution[1]

BY J. C. HINDMAN, J. C. SULLIVAN AND DONALD COHEN

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The kinetics of the Np(III)–Np(V) reaction in perchlorate solution have been investigated. The rate law for the forward reaction can be written as $-\partial[NpO_2^+]/\partial t = k_1[Np^{+3}][NpO_2^+][H^+]$. At 25° and $\mu = 2.0$, $k_1 = 2590$ l.^{2} mole^{-2} min.$^{-1}$. The rate is slightly decreased in a deuterated medium. The experimental activation energy is 6.5 ± 0.5 kcal. in $HClO_4$ solution and 5.6 ± 0.5 kcal. in $DClO_4$ solution. Possible mechanisms for the reaction are considered.

Reactions which involve the oxidation of Np(IV) to Np(V) appear to proceed through hydrolyzed species of the lower state.[2-4] Similar behavior is noted for reactions of the analogous species of U(IV)[5] and plutonium (IV).[6] It has been suggested[4] that the mechanism of such reactions involves the formation of species which can readily be converted to the XO_2^+ or XO_2^{++} ions. It is of considerable interest to examine the mechanism for the reverse situation, *i.e.*, the reduction of an oxygenated cation to an ion of a lower unhydrolyzed oxidation state. The reaction studied in the present investigation was the reduction of Np(V) by Np(III), yielding Np(IV) quantitatively.

Two investigations have been made of the reduction of Np(V) by Fe(II).[2,7] The rate law for the reaction appeared to be given by the expression $d(NpO_2^+)/dt = k[NpO_2^+][Fe^{++}][H^+]$. A similar rate law has been indicated for the reduction of PuO_2^+ by Pu^{+3}.[6] The role of the hydrogen ion in these reactions is of particular interest. For this reason the present investigation has been carried out both in H_2O and D_2O solutions.

Experimental

The general aspects of the experimental techniques and preparation of reagents have been described in previous papers.[3,4] Two methods were employed in the preparation of the Np(III) solutions. The first method used was a reduction of the Np(V) stock solutions with hydrogen gas at a platinized platinum catalyst.

Considerable difficulty was experienced in obtaining consistent results with these solutions. More reproducible results were obtained if the Np(III) solutions were prepared by electrolytic reduction.

The instability of Np(III) with respect to air oxidation necessitated working under an inert atmosphere. Deaerated Np(V) solutions of the desired composition were transferred to five-cm. quartz absorption cells, modified by addition of an extra opening for the insertion of a gas bubbler assembly. Gas was kept flowing through the cell until temperature equilibrium was reached (*ca.* two hours) after which the Np(III) was transferred under nitrogen to the absorption cell and mixed. The course of the reaction was followed by spectrophotometric monitoring of the 7230 Å. absorption band of Np(IV). The temperature in the absorption cell compartment of the Cary spectrophotometer was maintained to ±0.1°.

Results and Discussion

Molecularity of the Reaction.—The molecularity of the reaction with respect to the metal and hydrogen ions was determined by experiments in which the concentrations of the species were varied in the reaction mixture. The reaction was found to be bimolecular with respect to the metal ions. Data for a typical experiment are summarized in Table I. The apparent rate constant, k', was calculated by the integrated equation for a bimolecular process. No correction for the back reaction is necessary since at equilibrium the concentrations of Np(III) and Np(V) are negligible. Data on the effect

TABLE I

THE RATE OF REACTION OF Np(III) WITH Np(V) AT 16.1 ± 0.1°

$\mu = 2.0$, $[H^+] = 0.31$ *M*, Np(III) = Np(V) = 6.90×10^{-4} *M*

Time, min.	$D_{obs.}$ 7230 Å.	Apparent rate constant k', l. mole^{-1} min.$^{-1}$	Time, min.	$D_{obs.}$ 7230 Å.	Apparent rate constant k', l. mole^{-1} min.$^{-1}$
0.25	0.092	614.5	2.00	0.437	605.8
.50	.170	623.8	2.25	.466	607.9
.75	.233	619.7	2.50	.492	609.8
1.00	.282	603.0	2.75	.518	618.0
1.25	.331	610.0	3.00	.540	621.5
1.50	.371	609.0	∞	.960	
1.75	.405	604.7			
				Av.	612.3 ± 6.0

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

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