electrophilic. This is most simply illustrated for the case of HF catalysis

$$\overset{\delta+}{\mathrm{Cl}}\text{-}\overset{\delta-}{\mathrm{F}} + \mathrm{HF} \longrightarrow \overset{\delta\delta+}{\mathrm{Cl}}\cdots\overset{\delta-}{\mathrm{F}}\cdots\mathrm{H}\cdots\overset{\delta-}{\mathrm{F}} \qquad (6)$$

For the case of catalysis by the Lewis acids BF_3 and AsF_5, low-temperature complexes with ClF have been reported by several workers. Though the descriptions vary concerning the exact form of these complexes, there is general agreement that the chlorine bears enhanced positive charge.[8-10]

In any case, the Lewis acid interaction would be expected to occur much more readily in the case of the more polar (and more polarizable) chlorine monofluoride than in the case of fluorine. This description provides a satisfactory explanation of our observation that the acids effectively promoted chlorofluorination but failed to catalyze fluorination.

The use of the volatile Lewis acids as catalysts for R_fOCl synthesis presents advantages over the earlier use of metal fluorides. Considerable simplification is effected in manipulation of reaction systems, *i.e.*, drybox techniques and catalyst activation are not required,[1-3] and in the separation of less volatile hypochlorites[2] from the catalyst.

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The Oxidation of Neptunium(III) by Oxygen and Hydrogen Peroxide[1]

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The oxidation of transition metal ions by oxygen poses basic questions that have been succinctly formulated by Taube.[3] It is conceptually feasible to obtain information bearing on the question of a 1- and/or 2-equiv reaction step when Np(III) is used as the reductant. The products of such reactions, Np(IV) and Np(V), may be readily identified spectrophotometrically and do not undergo any additional mutual redox reaction. The reaction bewteen Np(III) and Np(V) proceeds at a measurable rate.[4]

This communication reports the results of a study of the products obtained when Np(III) is oxidized by oxygen and hydrogen peroxide in acidic perchlorate media.

Experimental Section

Reagents.—The preparation and standardization of perchloric acid, lithium perchlorate, Np(IV), and Np(V) solutions have been previously described.[4] Hydrogen peroxide solutions were prepared from Mallinckrodt AR 30% solutions and standardized with ceric sulfate. Np(III) solutions were prepared by Zn amalgam reduction as well as by electrolysis. The concentration of Np(III) and the total reducing power of the reaction mixtures were determined using a modification of the ceric sulfate titration procedure described by Newton.[5] The oxygen was obtained from the Liquid Carbonic Corp.

Procedures.—In the reactions with O_2, an aliquot of the reductant was injected by a syringe into a well-stirred O_2-saturated aqueous solution through which oxygen was vigorously bubbled. The reactions with hydrogen peroxide were studied in spectrophotometer cells using the familiar syringe–serum cap technique. The spectrophotometric analyses were performed with a Cary Model 14 MR recording spectrophotometer.

For the Np(III)–O_2 reaction, the acidity of the spent reaction mixture was determined by titration of an aliquot with 0.1086 M sodium hydroxide. Another aliquot of the spent reaction mixture was added to an absorption cell containing enough 2 or 4 M acid to bring the acidity to *ca.* 1 M. The absorbances measured at 9805 and 9605 Å were corrected for the presence of neptunium(IV) peroxide complex, whose apparent molar absorptivities in 1 M acid at these wavelengths are 143 and 86 M^{-1} cm^{-1}, respectively. The reducing power of the cell solution was determined at 3600 Å by ceric sulfate titration.

Results and Discussion

The results obtained in preliminary experiments to determine the products of the reaction between Np(III) and O_2 were internally inconsistent based on the assumption that such products were solely Np(IV) and Np(V). Evidence of a reaction between Np(IV) and H_2O_2 led to an explanation of this inconsistency.

The spectrum of Np(IV) in perchloric acid is drastically altered upon the addition of hydrogen peroxide.[6] In Figure 1 the spectra of the hydrated Np(IV) ion and of the complex are presented.

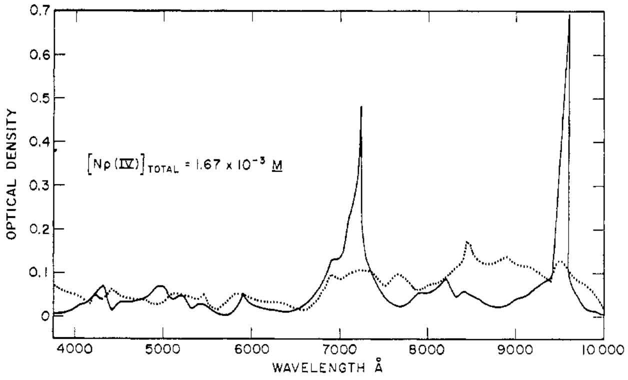

Figure 1.—Spectra of Np(IV) (——) and the complex (···) in 0.1 M $HClO_4$ at 25°. [Np[IV)] = 1.67×10^{-3} M in both systems; 2-cm cell; $[H_2O_2] = 0.01$ M.

Values have been calculated for the equilibrium constant

$$K = [C]/[Np(IV)]^2[H_2O_2] \qquad (1)$$

from spectrophotometric measurements.[7] At 25°, 1.0 M $HClO_4$, $[IV]^t = (0.66\text{–}1.70) \times 10^{-3}$ M, and $[H_2O_2]^0$

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Participant in the A. C. M. Honors Program from Lawrence University.

(3) H. Taube, *J. Gen. Physiol.*, **49** (1), Part 2, 29 (1965).

(4) R. C. Thompson and J. C. Sullivan, *J. Amer. Chem. Soc.*, **89**, 1098 (1967), and earlier references therein cited.

(5) T. W. Newton and N. A. Daugherty, *J. Phys. Chem.*, **71**, 3768 (1967).

(6) (a) R. Sjoblom and J. C. Hindman, *J. Amer. Chem. Soc.*, **73**, 1744 (1951). (b) It is important to note that under the concentration conditions employed for these spectrophotometric studies the oxidation of Np(IV) to Np(V) is negligible. For example, the Ce(IV) titers of aliquots of an Np(IV) and H_2O_2 stock were 5.26×10^{-2} and 2.37×10^{-2} ml, respectively. Similar titers of mixtures (irrespective of order of addition) were 7.56×10^{-2} ml.

= (0.53–10.9) × 10^{-3} *M* values were computed from eight data sets, each set containing from five to seven observations. The results were (3.28 ± 1.70) × 10^4 and (3.43 ± 0.87) × 10^4, respectively, from observations at 7240 and 9605 Å.

The reaction of O_2 (saturated solution in 1.0 *M* $HClO_4$ at 25°) with Np(III) (*ca.* 2 × 10^{-4} *M*) is complete within the 10-sec time of mixing and initial observation. The reaction of Np(IV) with O_2 is measurable but orders of magnitude slower. For example, after *ca.* 16 hr (concentration of O_2 kept constant at saturation in 0.01 *M* $HClO_4$, 25°) a solution originally 9.81 × 10^{-4} *M* in Np(IV) decreased to 5.92 × 10^{-4} *M* Np(IV).[8]

Table I contains a summary of pertinent experimental results. It is of interest to note that (a) the major product is Np(IV), (b) the most important path that results in the production of Np(V) is not strongly dependent on hydrogen ion concentration, and (c) for initial concentrations of Np(III) less than 9 × 10^{-4} *M* the reducing power of the spent reaction mixture is the same as that of the original solution.

TABLE I

PER CENT Np(V) PRODUCED FROM THE REACTION Np(III) + O_2[a]

[$HClO_4$], *M*	*I*[c]	10^4[Np(III)],[b] *M*	% Np(V)[d]	Exptl redn power × 10^3, ml/mequiv	Calcd redn power × 10^3,[e] ml/mequiv
0.029	0.029	19.3	43.7 ± 0.05	3.84 ± 0.15	5.33
0.015	0.015	11.6	40.0 ± 0.6	2.26 ± 0.15	2.70
0.0076	0.0076	5.32	36.0 ± 0.1	1.32 ± 0.05	1.39
0.0070	1.0	5.55	29.2 ± 2.5	1.30 ± 0.09	1.39
0.121	1.0	5.29	19.0 ± 0.3	1.33 ± 0.03	1.39
0.714	1.0	5.61	16.0 ± 0.1	1.56 ± 0.01	1.50
1.1	1.1	4.36	17.5 ± 0.2	1.24 ± 0.01	1.27
1.1	1.1	5.15	18.0 ± 0.1	1.39 ± 0.01	1.39
1.1	1.1	14.7	21.6 ± 0.1	4.70 ± 0.07	5.33
4.4	4.4	20.5	2.14 ± 1.4	4.80 ± 0.04	5.33

[a] Average of two or three determinations; uncertainty is average deviation from mean. [b] Initial concentration in reaction vessel. [c] Maintained with $LiClO_4$. [d] % Np(V) = [Np(V)]/([Np(IV)] + [Np(V)]) × 100. [e] Based on calculated initial [Np(III)], in sample titrated.

The last point noted, as well as the spectrophotometric observations, is consistent with the interpretation that hydrogen peroxide is produced in the course of the reaction between oxygen and Np(III). A further implication is that hydrogen peroxide does not compete favorably as an oxidant with oxygen under these experimental conditions.

A summary of the results obtained from some observations on the reaction between H_2O_2 and Np(III) is presented in Table II. It should be noted that it was not possible to describe either the rate of disappearance of Np(III) nor the rate of appearance of Np(V) by simple first- or second-order rate laws. The concentration of Np(V) as a function of time (monitored at 9805 Å) increased to a maximum value before reaching the final value.

TABLE II

THE Np(III)–H_2O_2 SYSTEM[a]

10^4 [Np(III)], *M*	[Np(IV)]/([Np(III)] + [Np(IV)])	[H_2O_2]/([Np(III)] + [Np(IV)])	% Np(V)[c]	*K*,[d] M^{-1} sec^{-1}
4.28[b]	0.363	0.520	60.5 ± 1.1	36, 31[e]
3.12–4.90	0.260–0.530	0.530	14.1 ± 1.5	38
1.26–6.63	0.023–0.530	1.06	23.4 ± 1.8	35, 34[e]
4.23[b]	0.530	1.06	78.3 ± 3.1	

[a] 25°, 1.0 *M* $HClO_4$; uncertainties are average deviations from mean. Initial concentrations of Np(III), Np(IV), and H_2O_2 were used in calculation of ratios. [b] In 0.10 *M* $HClO_4$. [c] % Np(V) = ([Np(V)] formed)/([Np(III)] + [Np(IV)]) × 100. [d] Calculated from limiting slopes at 9805 Å. Rate parameters are defined as $(d[Np(V)]/dt)_{t=0} = k[H_2O_2] = -(d[Np(III)]/dt)_{t=0}$. Uncertainties of 10% associated with these rate constants: see A. Zielen, J. C. Sullivan, D. Cohen, and J. C. Hindman, *J. Amer. Chem. Soc.*, **80,** 5632 (1958), for vicissitudes encountered in the calculation of rate parameters from limiting slopes. [e] Calculated from limiting slopes at 2670 Å.

The salient points to be noted from these data are (a) the percentage of Np(V) formed is not directly proportional to increased ratio of peroxide to initial concentrations of Np(III) and Np(IV), (b) the percentage of Np(V) formed is not dependent upon the mole fraction of Np(IV) originally present, and (c) the initial rate parameters for the disappearance of Np(III) or appearance of Np(V) are the same within the limitation noted.

The data that have been presented are consistent with the following comments. (1) The oxidation of Np(III) by oxygen can be described in terms of either an initial 1- or 2-equiv change. There is no compelling evidence presented that would serve as a basis for discrimination between these mechanisms. (2) The oxidation of Np(III) by hydrogen peroxide may involve a minor path of sequential 1-equiv changes. The major path may well be

$$Np(III) + H_2O_2 \xrightarrow{k_1} Np(V) + 2H^+$$

$$Np(III) + Np(V) \xrightarrow{k_2} 2Np(IV)$$

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[7] The data were not consistent with a model based on the formation of a 1:1 complex. Indirect support for the formulation advanced is provided by analogy with the Pu(IV)–H_2O_2 system as discussed by R. E. Connick and W. H. McVey, *J. Amer. Chem. Soc.*, **71**, 1534 (1949).

[8] It should be noted that although *ca.* 40% of the Np(IV) was oxidized, the reducing powers of aliquots of the initial and final reaction mixtures (measured by Ce(IV) consumption) were identical.

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Base-Induced Configurational Changes in Titanium(III) D-(−)-1,2-Propylenediaminetetraacetate[1]

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Complexes of d^1 metals, although labile, can be

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