TABLE I

X-RAY POWDER DIFFRACTION DATA

TaF_5		$TaF_5 \cdot XeF_6$		$TaF_5 \cdot 2XeF_6$	
d, Å	Intens	*d*, Å	Intens	*d*, Å	Intens
5.05	w	4.70	vs	5.08	vs
4.44	w	4.17	s	4.48	s
4.32	w	4.07	s	4.10	vs
4.06	s	3.77	vs	3.91	s
3.96	s	3.13	vs	3.78	s
3.59	w	2.86	w	3.60	vs
3.35	s	2.68	m	3.07	m
2.74	w	2.52	w	2.94	m
2.38	m	2.40	m	2.78	w
2.26	w	2.34	m	2.70	vw
2.13	m	2.26	m	2.55	vw
2.02	m	2.23	vw	2.46	vw
1.99	vw	2.154	m	2.28	s
1.97	vw	2.090	m	2.16	vw
1.890	w	1.984	m	2.12	s
1.838	w	1.945	m	2.08	s
1.779	w	1.912	w	2.06	vw
1.729	w	1.836	w	1.94	vw
1.684	w	1.796	s	1.88	vw
1.607	w	1.701	vw	1.84	vw
1.481	w	1.684	vw	1.802	m
1.460	w	1.638	w	1.698	m
		1.622	vw	1.610	w
		1.573	w	1.577	w
		1.555	vw	1.537	m
		1.538	vw	1.500	m
		1.504	vw	1.419	w
		1.455	vw	1.363	m
		1.439	w		

valve to −183° and unreacted F_2 was removed. This step was followed by pumping for a few minutes with the vessel at −60°. The weight of product, 1.6381 g, corresponded to the weight remaining in the reactor of 6.167 mmol of XeF_6 and 1.006 mmol of $MnF_{3.67}$. (In another similar run a ratio of F/Mn of 3.25 was found.) These data suggest that the manganese was either in the III or the IV oxidation state. Experimental error (mainly a loss of a small amount of XeF_6 remaining in the valve and removed by pumping while the tube was cold) could easily have been large enough to allow either number to be correct. The vessel was then held at 0° while XeF_6 was removed by pumping. From time to time, the vessel was removed and weighed. Figure 2 shows the relationship between time of pumping and weight of product remaining in the reactor. The weight fell rapidly until the ratio of XeF_6 to MnF_3 (or MnF_4) was a little less than 4; then the weight remained about constant. This indicated existence of a compound which was either $4XeF_6 \cdot MnF_3$ or $4XeF_6 \cdot MnF_4$. Pumping was then continued at 40, 50, 60, and finally 70° as shown in Figure 2. During these operations xenon hexafluoride was removed at a decreasing rate, as shown in the figure, until a constant weight of 0.4070 g was reached at an Xe:Mn ratio a little greater than 1. The product was found by analysis to contain about 10.7 g-atoms of F/g-atom of Mn (average of two determinations, 10.4 and 11.1). It also reacted with potassium iodide solution liberating 4.0 mol of I_2/g-atom of Mn (average of two determinations, 3.95 and 4.05).

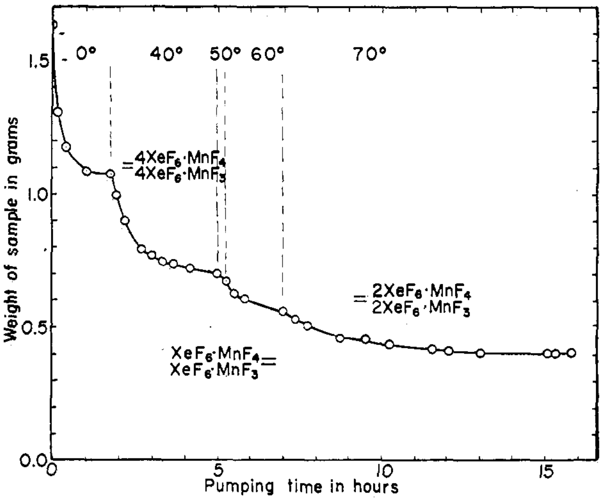

Figure 2.—Removal of XeF_6 under vacuum.

Other experiments gave results similar to the above. One of the runs involved the use of Mn, XeF_6, and F_2. While the formulas for the compounds have not been definitely established, the authors feel strongly that the first compound is $4XeF_6 \cdot MnF_4$ and that this decomposes when heated under vacuum to give XeF_6 and a product of composition close to $XeF_6 \cdot MnF_4$. The final material was found to be pink (suggesting the presence of MnF_5^-) and to react vigorously at 25° with water but not with $(CF_2CFCl)_n$ polymer oil. It could be stored without decomposition under nitrogen in glass but became brown in air containing water vapor. Data regarding the X-ray powder pattern can be furnished by the authors.

System XeF_6–UF_6.—A mixture of XeF_6 with UF_6 in the molar ratio 6.66 was held at 70° in a Monel metal reactor for 65 hr. A second mixture in the ratio 4.79 was held in another reactor for 17 hr at 100°. In each case subsequent pumping from the reactor when held at 0° allowed one to draw a smooth curve for weight of sample *vs.* time. No plateau existed in the curve. The whole sample was pumped away. These experiments gave no indication of compound formation by combination of the two hexafluorides.

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Perhaloalkyl Hydrochlorites and Pentafluorosulfur Hypochlorite. III. Lewis Acid Catalyzed Synthesis

BY D. E. YOUNG,* L. R. ANDERSON, AND W. B. FOX

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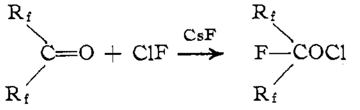
Recent publications have described the synthesis of perfluoroalkyl hypochlorites, R_fOCl, a new class of compounds prepared by the metal fluoride catalyzed addition of chlorine monofluoride to perfluorinated carbonyl compounds[1-3]



(1)

These may be regarded as base-catalyzed oxidative additions to the carbonyl group, where the first step

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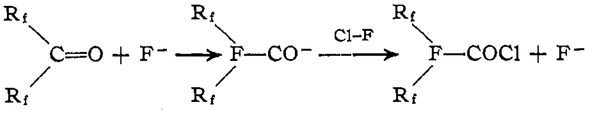
* To whom correspondence should be addressed.

(1) D. E. Gould, L. R. Anderson, D. E. Young, and W. B. Fox, *Chem. Commun.*, 1564 (1968).

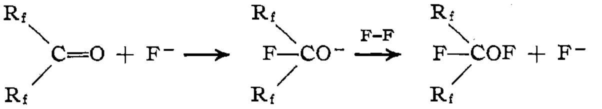
(2) D. E. Gould, L. R. Anderson, D. E. Young, and W. B. Fox, *J. Amer. Chem. Soc.*, **91**, 1310 (1969).

(3) C. J. Schack and W. Maya, *ibid.*, **91**, 2902 (1969).

is attack by the base (fluoride ion) on the electrophilic carbon of the carbonyl group to form a fluoroalkoxide "salt" intermediate. The latter is in turn oxidized by chlorine monofluoride to form the hypochlorite product and regenerate fluoride ion[2,3]


(2)

An analogous mechanism is believed operative in the synthesis of fluoroxy derivatives by the metal fluoride catalyzed addition of fluorine to fluorinated carbonyl compounds[4,5]


(3)

We have found that the formation of perfluoroalkyl hypochlorites by the addition of ClF to substrate carbonyl groups is also catalyzed by strong Lewis acids, the volatilities of which offer certain advantages over nonvolatile catalysts.

Experimental Section

Standard vacuum line procedures with a nickel–Monel–Kel-F vacuum system were used throughout. The reaction vessels were 30-cm³ Hoke 304SS cylinders fitted with appropriate needle valves.

Reagents.—Carbonyl fluoride was prepared by the high-temperature (150°) reaction of phosgene and NaF in a 500-cm³ stainless steel cylinder and was purified by vacuum-line fractionation. Trifluoroacetyl fluoride and hexafluoroacetone were obtained from Peninsular ChemResearch and Allied Chemical Corp. (Specialty Chemicals Division), respectively, and were used with no further treatment. Anhydrous hydrogen fluoride and boron trifluoride were obtained from the Matheson Co., and arsenic pentafluoride was obtained from the Ozark-Mahoning Co. The BF_3 and AsF_5 were carefully fractionated through −111° traps several times before use.

Chlorofluorinations.—Since we have recently shown that cylinders in which metal fluoride coatings have been formed promote ClF additions in perfluoroalkyl hypochlorite synthesis,[6] a standard sequence of experiments was carried out with each Lewis acid to ensure that the acid and not the cylinder wall was indeed the catalyst.

First, the reactor was charged with 8–10 mmol of the appropriate carbonyl compound (F_2CO, CF_3CFO, or $(CF_3)_2CO$) and a slight excess of ClF at −196°. The mixture was then allowed to stand for 10–20 hr at −20°. At this point, before any Lewis acid was added to the reactants, the mixtures were carefully separated by vacuum line fractionation using appropriate cold traps. Not only were the reactants quantitatively recovered, *i.e.*, the total volumes of the separated fractions equaled the total volumes of the starting materials, but thorough examination of the fractions by infrared spectroscopy revealed only starting materials and showed that no hypochlorite formation had occurred.

Then, using the same cylinder, the reactants were recombined, 1–2 mmol of the Lewis acid (HF, BF_3, AsF_5, or PF_5) was added to the reaction mixture at −196°, and the contents were again held at −20° for 10–20 hr. Using this procedure, carbonyl fluoride was quantitatively converted to trifluoromethyl hypochlorite, CF_3OCl, in the presence of HF, BF_3, or AsF_5. The weaker acid PF_5 was ineffective as a catalyst. Trifluoroacetyl fluoride and hexafluoroacetone were quantitatively converted to pentafluoroethyl hypochlorite, CF_3CF_2OCl, and heptafluoroisopropyl hypochlorite, *i*-C_3F_7OCl, respectively, using HF catalysis (BF_3, AsF_5, and PF_5 were not tried). In the cases where hypochlorites were formed, fractionation of the reaction mixture revealed the appropriate loss of ClF. Each hypochlorite was identified by its infrared spectrum and through derivatization by reaction with carbon monoxide in separate reaction cylinders.[7] The measured amounts of chloroformates produced in the CO reactions indicated that the yields of the hypochlorites were at least 90%.

Following the removal of hypochlorite products in the reactions described above, the evacuated hypochlorite reaction cylinder was recharged with fresh carbonyl compound and excess ClF and held at −20° as before. In each case, the starting materials were recovered unchanged, verifying that the prior formation of hypochlorite products was catalyzed by the Lewis acid rather than by a fluoride coating on the reactor walls.

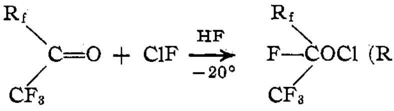
Fluorinations.—A reaction cylinder was charged with carbonyl fluoride (8 mmol) and HF (1 mmol) at −196°; a slight excess of fluorine was added and the reactor was held at −20° for 20 hr. No CF_3OF was formed and the COF_2 was unchanged. A similar experiment in which hexafluoroacetone was treated with fluorine in the presence of HF produced substantial cleavage of carbon–carbon bonds (about 50% of the ketone was converted to $CF_3C(O)F$, COF_2, and CF_4) but no OF products. Similar treatment of a 20% solution of hexafluoroacetone in HF (monitored by ^{19}F nmr and infrared spectroscopy) again resulted only in cleavage products.

Results and Discussion

With carbonyl fluoride, quantitative addition of chlorine monofluoride occurred readily at low temperature in the presence of hydrogen fluoride

$$F_2CO + ClF \xrightarrow[-20°]{HF} CF_3OCl \qquad (4)$$

Although boron trifluoride and arsenic pentafluoride were equally effective catalysts, the weaker Lewis acid phosphorus pentafluoride failed to promote the chlorofluorination. Hydrogen fluoride catalysis was also demonstrated with hexafluoroacetone and trifluoroacetyl fluoride


(R_f = CF_3 or F) (5)

and it seems likely that the other fluorinated carbonyl compounds and thionyl tetrafluoride which were previously shown to afford hypochlorites by base-catalyzed chlorofluorination[1-3] should also be amenable to acid-catalyzed chlorofluorination.

It is of interest that fluorine addition to the carbonyl group (to produce corresponding R_fOF compounds) was not effected by acid catalysis.

One possible explanation of the role of the Lewis acid in catalysis of hypochlorite formation involves a polarizing interaction of the Lewis acid with chlorine monofluoride in a manner that enhances the "positive" character of the chlorine, *i.e.*, lowers the activation energy for oxidation by making the chlorine more

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(4) J. K. Ruff, A. R. Pitochelli, and M. Lustig, *J. Amer. Chem. Soc.*, **88**, 4531 (1966).

(5) F. A. Hohorst and J. M. Shreeve, *ibid.*, **89**, 1809 (1967).

(6) D. E. Young, L. R. Anderson, and W. B. Fox, *Inorg. Nucl. Chem. Lett.*, **6**, 341 (1970).

(7) D. E. Young, L. R. Anderson, D. E. Gould, and W. B. Fox, *Tetrahedron Lett.*, 723 (1969).

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.

[8] M. Schmeisher, paper presented at the Symposium on Inorganic Fluorine Chemistry, Argonne, Ill., Sept 1963; summarized in *Science*, **143**, 1058 (1964).

[9] K. O. Christie and W. Sawodny, *Inorg. Chem.*, **8**, 213 (1969).

[10] R. J. Gillespie and M. J. Morton, *ibid.*, **9**, 811 (1970).

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

BY C. S. BURGENER[2] AND J. C. SULLIVAN*

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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.

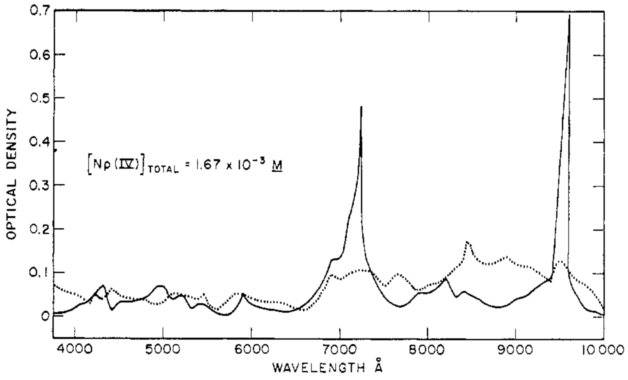

Figure 1.—Spectra of Np(IV) (——) and the complex (···) in 0.1 *M* $HClO_4$ at 25°. [Np[IV)] = 1.67×10^{-3} *M* in both systems; 2-cm cell; $[H_2O_2]$ = 0.01 *M*.

Values have been calculated for the equilibrium constant

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

from spectrophotometric measurements.[7] At 25°, 1.0 *M* $HClO_4$, $[\mathrm{IV}]^4 = (0.66\text{–}1.70) \times 10^{-3}$ *M*, and $[\mathrm{H_2O_2}]^0$

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* To whom correspondence should be addressed.

[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.