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Registry No. $K_{12}H_6P_2W_{12}O_{50}$, 63950-53-8; $LiK_9P_2W_{17}O_{61}$, 63950-56-1; $K_6P_2W_{17}MoO_{62}$, 63950-62-9; $K_6P_2W_{16}Mo_2O_{62}$, 63950-61-8; $K_6P_2W_{12}Mo_6O_{62}$, 63950-60-7; $K_8H_2P_2W_{17}ZnO_{62}$, 63950-55-0; $Na_{10}H_4P_2W_{16}Zn_2O_{62}$, 63950-54-9; $Na_8HPW_9O_{34}$, 63950-57-2; $K_7PW_9Mo_2O_{39}$, 63950-58-3; $K_3PW_9Mo_3O_{40}$, 63956-77-4; $(NH_4)_6HPMo_{11}ZnO_{40}$, 11120-72-2; $Na_3H_6PMo_9O_{34}$, 51913-10-1; $Na_6P_2Mo_{18}O_{62}$, 50811-90-0; $K_3PMo_9W_3O_{40}$, 63950-63-0; $H_3PW_{11}MoO_{40}$, 63950-64-1; PW_{12}, 12534-77-9; PMo_{12}, 12379-13-4; PV_{12}, 12632-06-3; PW_{11}, 12412-84-9; PW_3Mo_9, 56646-36-7; P_2W_{18}, 12269-70-4; P_2W_{21}, 63950-52-7; P_3W_{18}, 63950-51-6; Na_2WO_4, 13472-45-2; H_3PO_4, 7664-38-2; Na_2MoO_4, 7631-95-0; $(NH_4)_6Mo_7O_{24}$, 12027-67-7; Na_2HPO_4, 7558-79-4; $(PW_{11}MoO_{40})^{4-}$, 12776-99-7; $H_6P_2W_{17}MoO_{62}$, 63950-59-4.

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Contribution from the Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439,
and Department of Chemistry, University of Missouri, Columbia, Missouri 65201

Reaction of Fluorine and Hypofluorous Acid with Some Substitution-Inert Complex Ions in Aqueous Perchloric Acid Solutions[1a]

RICHARD C. THOMPSON,[1b] EVAN H. APPELMAN,*[1c] and JAMES C. SULLIVAN[1c]

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This paper examines the reactions of F_2 and HOF with aqueous perchloric acid solutions containing various complexes of trivalent chromium. In no case is the chromium itself oxidized. The complex CrF^{2+} is unreactive toward either oxidant. $CrClO_3^{2+}$, $CrNO^{2+}$, $CrCl^{2+}$, and $CrBr^{2+}$ show increasing reactivity, with the formation of Cr^{3+} as the principal product. In the case of $CrBr^{2+}$ and $CrCl^{2+}$ there is evidence that F_2 can react with the substrate directly, as well as via the intermediate formation of HOF. This direct reaction produces some CrF^{2+} in addition to Cr^{3+}. Azidochromium(III), CrN_3^{2+}, is the most reactive of the complexes studied. It reacts directly with F_2 to form a mixture of Cr^{3+} and CrF^{2+}; it reacts with HOF to form $CrNO^{2+}$. Reaction mechanisms that can account for these observations are discussed.

Introduction

Although it has long been known that F_2 displays strong oxidizing power when passed into aqueous solutions,[2] the mechanism of its interaction with such solutions has never been elucidated. The recent isolation of hypofluorous acid, HOF,[3] has led to the suggestion that this molecule is the reactive intermediate that is responsible for the oxidizing properties of fluorine in aqueous media.[4] Support for this idea comes from the fact that the equilibrium

$$F_2 + H_2O \rightarrow HOF + HF \qquad (1)$$

lies very far to the right and from the observation that HOF and F_2 have generally similar oxidizing properties in aqueous solution.[4] Thus both reagents oxidize Ag^+ to Ag^{2+}, both oxidize water primarily to H_2O_2 in acid and primarily to O_2 in base, and both oxidize BrO_3^- to BrO_4^- in base only.[2d,4] It is therefore tempting to conclude that reaction 1 proceeds very rapidly and that all of the observed chemistry stems from subsequent reaction of HOF. There is, however, some evidence that this concept is an oversimplification. It is known, for example, that F_2 reacts with water to produce OF_2—small amounts in neutral or acid media and quite substantial amounts in base.[2d] The interaction of HOF with water, on the other hand, has never been observed to produce OF_2.[4]

If fluorine can react with aqueous substrates directly as well as through the intermediate formation of HOF, it is conceivable that under some circumstances different and distinguishable products will result from the two modes of reaction. The use of substitution-inert complex ions, such as those of trivalent chromium, would seem to constitute a promising way to search for such distinguishable products. In this article we wish to describe an aqueous reaction system in which oxidation of the complex CrN_3^{2+} by F_2 proceeds partly via HOF and partly by direct attack and in which the products of the two reaction paths are indeed different and distinguishable.

Experimental Section

Solutions of the perchlorates of CrF^{2+}, $CrCl^{2+}$, $CrBr^{2+}$, $CrClO_3^{2+}$, $CrNO^{2+}$, and CrN_3^{2+} were prepared by methods described previously[5,6] and were purified by ion exchange on Dowex 50. The total chromium content of these solutions was determined spectrophotometrically[7] after oxidation to chromate with alkaline hydrogen peroxide and destruction of the H_2O_2 by heating. The solutions were stored at −78 °C until needed. Xenon trioxide and trivalent rhodium were prepared by methods described in the literature.[8] The fluorine used was a 10 mol % mixture in argon, except for one gas-analysis experiment in which a ca. 50% mixture was used.

HOF was prepared by the reaction of F_2 with ice at −40 °C in a rapid recirculating flow system.[4] It was collected in a Kel-F U-tube at −183 °C, freed from more volatile impurities such as OF_2 by removing several volumes of vapor at −78 °C, and stored at −196 °C until ready for use. The preparations were contaminated with significant quantities of HF (about 0.5 mol of HF per mole of HOF).

Commercial OF_2 was used to prepare a saturated solution in 0.1 M $HClO_4$ at 0 °C (ca. 0.003 M).

Solutions of HOCl were prepared from reagent grade calcium hypochlorite, and solutions of H_2SO_5 were made from "Oxone", a product of Dupont Co. containing a mixture of K_2SO_5 and K_2SO_4.

Distilled water was redistilled first from alkaline permanganate and then from dichromate–sulfuric acid before use.

In a typical experiment ca. 1 mmol of F_2 (in 40 min) or 1.5 mmol of HOF (in 5 min) was bubbled into a test tube containing ca. 20 cm^3 of a solution of the complex in $HClO_4$ at 0 °C. The fluorine was introduced via a Teflon bubbler with a 1-mm orifice connected to a Monel reservoir equipped with a valve and pressure gauge. The amount of fluorine used was estimated from the change in pressure of the reservoir, which was of known volume. If the total amount of fluoride in the product solution was to be measured the reaction was carried out in a Kel-F test tube instead of a glass one.

When it was desired to measure the gaseous products of a reaction, a mixture of fluorine and argon was added to 1–3 cm^3 of aqueous solution in a 38-cm^3 glass bulb closed with a Teflon valve. The solution was stirred magnetically until reaction appeared complete, after which a sample of the gases present was analyzed mass spectrometrically.

Hypofluorous acid was introduced into reaction solutions by passing argon through a U-tube containing the HOF and then into the solution via a Kel-F bubbling tube with a 2-mm orifice. The U-tube was initially cooled with liquid oxygen and was allowed to warm slowly to room temperature during the course of the reaction. The amount introduced was determined by carrying out a duplicate preparation, passing the HOF into a 2 M NaI solution at 0 °C via an argon stream, and titrating with standardized thiosulfate.

The products of reactions with the various complexes were at least partially separated by ion exchange on Dowex 50 columns at 3 °C. The total chromium content of each fraction was determined spectrophotometrically after oxidation to chromate. Fractions containing $CrNO^{2+}$ and CrF^{2+} were analyzed by three different methods which gave essentially the same results. (1) The $CrNO^{2+}$ was determined by addition of excess Ce(IV), followed by back-titration of the excess, along with any dichromate that had been formed, with Fe^{2+}.[9] An authentic sample of $CrNO^{2+}$ was found to consume 3.89 ± 0.02 equiv of Ce(IV) per mole, corresponding fairly closely to the stoichiometry

$$2H_2O + CrNO^{2+} + 4Ce^{4+} \rightarrow Cr^{3+} + NO_3^- + 4Ce^{3+} + 4H^+$$

(2) The $CrNO^{2+}$ was converted quantitatively to Cr^{3+} by treatment with BrO_3^-, and the CrF^{2+} and Cr^{3+} were separated by ion exchange. (3) The optical density of the mixture at 445 nm was determined. At this wavelength, $CrNO^{2+}$ and CrF^{2+} have extinction coefficients of 120 and 9.4 M^{-1} cm^{-1}, respectively.[10] Hence, if the total chromium content is known, the composition of the mixture can be resolved. However, this is the least accurate of the three methods. Mixtures of CrN_3^{2+}, $CrNO^{2+}$, and CrF^{2+} were analyzed by method 2 after quantitative conversion of the CrN_3^{2+} to Cr^{3+} by treatment with HNO_2[11] and removal of this Cr^{3+} by ion exchange. HNO_2 is unreactive toward $CrNO^{2+}$ and CrF^{2+}. Mixtures of CrF^{2+} with $CrBr^{2+}$ or $CrCl^{2+}$ were analyzed by the liberation and titration of F^- (vide infra).

Hexaaquorhodium(III) was determined spectrophotometrically.

Fluoride was determined by titration with La^{3+} or Th^{4+}, using either a fluoride electrode and a potentiometric endpoint or a visual endpoint with "Amadec-F" indicator. Fluoride bound to chromium was first liberated by oxidation of the chromium with alkaline hydrogen peroxide. Very small amounts of fluoride were determined colorimetrically with "Amadec-F".

Nitrate was determined by reduction to ammonia with FeO in the presence of Ag_2O, followed by distillation and titration with acid.

Hydrogen peroxide was determined by titration with a standard solution of ceric sulfate in the presence of excess Th^{4+} to complex fluoride. Br_3^- and H_2SO_5 were determined by reaction with I^- and titration of the resulting I_3^- with thiosulfate.

Results

General Observations on the Reactions of F_2 and HOF with Perchloric Acid Solutions. When 110–450 standard cm^3 of 10 mol % F_2 in argon (0.5–2 mmol of F_2) were passed into 4 to 50 cm^3 of 1–2 M $HClO_4$ at 0 °C and at flow rates between three and ten standard cm^3/min, some 40–60% of the fluorine was retained in the solution as HF. The retention dropped to about 25% in 0.1 M $HClO_4$. Substantial quantities of hydrogen peroxide are formed in these solutions, but the yield of H_2O_2 is always less than would be predicted for the reaction

$$F_2 + 2H_2O \rightarrow 2HF + H_2O_2$$

which would call for the formation of 1 mol of H_2O_2 for every 2 mol of HF. The H_2O_2 yield decreases as the amount of fluorine added per volume of solution increases. For example, in typical experiments the addition of 0.51 mmol of F_2 (10 mol % in argon) to 50 cm^3 of 1 M $HClO_4$ formed 0.62 mmol of HF and 0.28 mmol of H_2O_2, corresponding to a peroxide yield of 90%, whereas the addition of 0.52 mmol of F_2 to 4 cm^3 of 1 M $HClO_4$ formed 0.50 mmol of HF and 0.16 mmol of H_2O_2, corresponding to a peroxide yield of 64%, while the addition of 2.1 mmol of F_2 to 4 cm^3 of 1 M $HClO_4$ formed 1.57 mmol of HF and 0.35 mmol of H_2O_2, corresponding to a peroxide yield of only 45%. We have calculated these peroxide yields relative to the HF production, which we take to be a measure of the fluorine absorbed, inasmuch as no HOF is expected to escape from these solutions (vide infra). (We have neglected the small amount of OF_2 that is probably produced.[2d]) The peroxide formation that we observe is in general agreement with the observations of earlier workers.[2b]

In contrast to the incomplete retention in perchloric acid solutions, when fluorine is bubbled into 0.4 M NaI, essentially all of the fluorine introduced can be accounted for by the reaction

$$F_2 + 3I^- \rightarrow 2F^- + I_3^-$$

In a typical result 0.95 mmol of F_2 was passed into 27 cm^3 of 0.4 M NaI to give 0.93 mmol of I_3^-. Analogously, the introduction of 1.00 mmol of F_2 into 27 cm^3 of 0.4 M NaBr yielded 0.98 mmol of Br_3^-. The deviations of these results from exact stoichiometry may reflect a slight systematic error in the volumetric measurement of the fluorine or they may indicate the presence of an impurity in the fluorine used.

When hypofluorous acid is passed into aqueous perchloric acid solutions nearly all of the added HOF is converted to H_2O_2 in accordance with the reaction

$$HOF + H_2O \rightarrow HF + H_2O_2 \qquad (2)$$

Decreasing the solution volume per mole of HOF added decreases the yield of H_2O_2 slightly. Thus in typical experiments the addition of 1.3 ± .07 mmol of HOF to 16 cm^3 of 1 M $HClO_4$ produced 1.35 mmol of H_2O_2, while the addition of the same amount of HOF to 3 cm^3 of 1 M $HClO_4$ only produced 1.07 mmol of H_2O_2.

Passage of the effluent gas from an HOF reaction solution into aqueous iodide showed that even in the absence of reducing substrate no significant oxidizing power was being carried out of the reaction mixtures. From this we may

Table I. Reactions of F_2 and HOF with Aqueous Reductants[a]

Reductant				
Species	Initial concn,[b] 10^3M	Oxidant[c]	[$HClO_4$], M	Products (% of total Cr)
Cr^{3+}	17.1	F_2	0.19	100% Cr^{3+}
Cr^{3+}	17.1[d]	F_2	0.19	99% Cr^{3+}
Cr^{3+}	17.1	HOF	0.19	99% Cr^{3+}
Rh^{3+}	9.7	F_2	0.2	102% Rh^{3+}
Rh^{3+}	9.7	HOF	0.2	100% Rh^{3+}
CrF^{2+}	7.9	F_2	1.0	100% CrF^{2+}
CrF^{2+}	7.9	HOF	1.0	100% CrF^{2+}
$CrClO_3^{2+}$	6.4	F_2	1.0	90% $Cr(ClO_3)^{2+}$,[e] 10% Cr^{3+}
$CrClO_3^{2+}$	6.4	HOF	1.0	91% $Cr(ClO_3)^{2+}$,[e] 9% Cr^{3+}
$CrNO^{2+}$	9.2	F_2	0.24	84% $CrNO^{2+}$, 16% Cr^{3+}
$CrNO^{2+}$	9.2	HOF	0.24	70% $CrNO^{2+}$, 30% Cr^{3+}
$CrCl^{2+}$	7.6	F_2	1.0	62% $CrCl^{2+}$,[e] 38% Cr^{3+}
$CrCl^{2+}$	7.6	HOF	1.0	60% $CrCl^{2+}$,[e] 40% Cr^{3+}
$CrBr^{2+}$	6.4	F_2	2.0	96% Cr^{3+}
$CrBr^{2+}$	6.4	F_2	0.20	99% Cr^{3+}
$CrBr^{2+}$	6.4	HOF	2.0	100% Cr^{3+}
$CrBr^{2+}$	176[f]	F_2[g]	2.0	93% Cr^{3+}[i]
$CrBr^{2+}$	176[f]	F_2[h]	2.0	93% Cr^{3+}[i]

[a] Reactions conducted at 0 °C. Ca. 40 min bubbling time for F_2 and 5 min bubbling time for HOF. [b] With 15–28 cm^3 used unless otherwise specified. [c] About 1 mmol of F_2 and 1.5 mmol of HOF were used unless specified otherwise. [d] With 0.052 M XeO_3 present. [e] The +2 fraction was assumed to consist entirely of unreacted reductant. [f] A 1.06 mmol total in 6 cm^3. [g] With 2 mmol of F_2. [h] With 4 mmol of F_2. [i] Remainder of Cr was in a +2 fraction that showed an absorption spectrum different from that of either $CrBr^{2+}$ or CrF^{2+}. The spectrum was not the same in the two experiments.

conclude that not only does no HOF escape from such solutions but that no appreciable amounts of OF_2 are formed. Even when HOF is passed into alkaline solutions, there is no detectable formation of OF_2.

Reactions of Ions and Complexes with H_2O_2. Because of the known formation of hydrogen peroxide in our experiments, the reaction of H_2O_2 with chromium complexes was examined under comparable conditions. No reaction was observed on the time scale of our experiments.

Reactions of Ions and Complexes Other Than CrN_3^{2+}. These results are summarized in Tables I and II. Cr^{3+}, Rh^{3+}, and CrF^{2+} show no sign of reaction with either F_2 or HOF. Even the addition of XeO_3 as a scavenger of H_2O_2 does not lead to oxidation of Cr^{3+} by F_2. $CrClO_3^{2+}$, $CrNO^{2+}$, $CrCl^{2+}$, and $CrBr^{2+}$ show progressively increasing reactivity toward both F_2 and HOF, the principal product in all cases being Cr^{3+}. (The slight reaction observed for $CrClO_3^{2+}$ could result from aquation during the analysis of the reaction mixture. $CrClO_3^{2+}$ aquates slowly but more rapidly than many other Cr(III) complexes.)

Table II summarizes the reactions of F_2 with excess $CrBr^{2+}$ and $CrCl^{2+}$. The 0.3 M $CrBr^{2+}$ solution retains essentially all of the added fluorine. The retention of fluorine by the other solutions is significantly less, but it is still much greater than the ca. 50% retention found in the absence of reducing substrates. In addition to Cr^{3+}, CrF^{2+} is formed as a product of these experiments.

Reactions of CrN_3^{2+}. The results for CrN_3^{2+} are presented in Tables III, IV, and V. With F_2 as the oxidant, CrF^{2+}, $CrNO^{2+}$, and Cr^{3+} are found as reaction products. The

Table II. Reaction of Fluorine with Excess $CrBr^{2+}$ and $CrCl^{2+}$[a]

Substrate			Amt of F_2 added, mmol	Amt of "retained F",[b] mmol	Amt of substrate reacted, mmol	Product dist (% of total product)	
Species	Initial concn, M	Initial mmol				CrF^{2+}	Cr^{3+}
$CrBr^{2+}$[c]	0.0308	0.616	0.25	0.46	0.348	5	95[d]
$CrBr^{2+}$	0.308	3.08	1.24	2.56	2.19	4	96
$CrCl^{2+}$	0.597	4.78	2.15	3.7	1.48	19	81

[a] At 0 °C; [$HClO_4$] = 2.0 M unless otherwise specified; F_2 (10% in Ar) introduced at a rate of 0.025–0.03 mmol/min. [b] "Retained F" is the sum of free HF and complexed fluoride in the product solution. If OF_2 formation is neglected, the number of mmol of F_2 reacting with the solution is equal to half the "retained F". [c] $HClO_4$ = 1.0 M. [d] With 10% of chromium unaccounted for.

Table III. Reactions of CrN_3^{2+} with Excess F_2, HOF, and Other Selected Oxidants[a]

	Initial [CrN_3^{2+}]		Oxidant		[$HClO_4$], M	% products		
Expt	10^3M	mmol	Species	mmol		CrF^{2+}	$CrNO^{2+}$	Cr^{3+}
1[b]	9.1	0.182	F_2	1.1	2.0	28.2 ± 1.0	45.5 ± 1.3	26.4 ± 0.6
2	6.0	0.121	F_2	1.1	0.20	14	65	21
3	4.4	0.122	F_2	1.1	0.57	16	62	22
4	6.5	0.117	F_2	1.1	1.0	19	53	28
5	6.5	0.117	F_2	1.1	2.0	24	42	34
6	20.1	0.121	F_2	1.1	1.2	34	29	39
7	20.1	0.363	F_2	3.2	1.2	37	23	40
8[c]	8.3	0.149	F_2	1.1	1.2	25	48	27
9[d]	8.3	0.149	F_2	1.1	1.2	29	44	27
10[e]	8.3	0.149	F_2	1.1	1.2	35	37	28
11	8.3	0.149	F_2	0.65	1.2	19	60	21
12[f]	9.9	0.228	F_2	0.75	2.0	28	47	24
	9.9	0.228	F_2	1.3	2.0	30	37	33
13	7.6	0.214	HOF	1.5	0.57		83	17
14	0.95	0.091	OF_2	0.3[g]	2.0			~100
15	19.2	0.418	HOCl	2.0[h]	2.0			~100
16	46.4	0.418	H_2SO_5	1.2[i]	2.0		81	19
17	46.4	0.418	H_2SO_5	2.3[j]	2.0		45	55

[a] Reactions carried out at 0 °C. Ca. 40 min bubbling time for F_2 and 5 min for HOF unless otherwise specified. The CrN_3^{2+} was completely consumed in all experiments. [b] Performed in triplicate; uncertainties are mean deviations. All other experiments were performed only once. [c] A 10-min bubbling time. [d] A 120-min bubbling time. [e] 0.20 M HF present initially. [f] A total of 43% of the mixture was taken and analyzed at the visual stoichiometry point (0.7 mmol of F_2). Another 0.5 mmol of F_2 was then added to the remainder of the mixture, after which it was analyzed again. [g] Ca. 0.003 M OF_2, 1 h reaction time. [h] Rapid reaction at 20 °C. [i] After 2 h reaction time at 20 °C, 0.30 mmol of CrN_3^{2+} was consumed. [j] After 2 h reaction time at 20 °C, 0.35 mmol of CrN_3^{2+} was consumed.

Table IV. Reactions of F_2 and HOF with Excess Aqueous CrN_3^{2+} [a]

	Initial [CrN_3^{2+}]		Oxidant		[$HClO_4$],	Amt of CrN_3^{2+} consumed,	Product dist (% of total product)		
Expt	10^3M	mmol	Species	mmol	M	mmol	CrF^{2+}	$CrNO^{2+}$	Cr^{3+}
18	8.3	0.149	F_2	0.32	1.2	0.115	22	56	22
19	16.6	0.298	F_2	0.32	1.2	0.206	44	23	33
20[b]	21.3	0.447	F_2	0.32	1.2	0.297	52	12	36
21	24.8	0.596	F_2	0.32	1.2	0.295	58	3	39
22	113	0.791	F_2	0.50	1.1	0.508	58	3	39
23	38.6	0.811	F_2	0.43	2.0	0.392	56	4	40
24	38.1	0.761	F_2	0.43	0.5[d]	0.328	53	9	38
25[c]	38.7	0.851	F_2	0.43	0.10[d]	0.323	41	11	48
26	11.4	0.228	HOF	0.22	2.0	0.125		93	7
27	22.8	0.455	HOF	0.235	2.0	0.235		91	9
28	22.8	0.455	HOF	0.23	0.20	0.228		94	6

[a] Reactions carried out at 0 °C. Ca. 40 min bubbling time for F_2 and 5 min for HOF. [b] In a duplicate of this experiment 0.62 mmol of total fluoride ([HF] + [CrF^{2+}]) was found in the solution. [c] In a duplicate of this experiment 0.68 mmol of total fluoride ([HF] + [CrF^{2+}]) was found in the solution. [d] $NaClO_4$ added to make [$HClO_4$] + [$NaClO_4$] = 2 M.

Table V. Gas Evolution in the Reaction of F_2 with Aqueous CrN_3^{2+} [a]

[$HClO_4$],	Amt of added reagents, mmol		Amt of CrN_3^{2+} consumed,	Products, mmol					
M	CrN_3^{2+}	F_2	mmol	N_2	N_2O	O_2	CrF^{2+}	$CrNO^{2+}$	Cr^{3+}
2.0	0.0683	0.0309	0.0281	0.0287	0.0093	0.0013	0.0154	<0.001	0.0127
2.0	0.0228	0.144[b]	*c*	0.0213	<0.001	0.0209	*c*	*c*	*c*
0.10[d]	0.0629	0.0328	0.0262	0.0253[e]	0.0058	0.0016	0.0104	0.0040	0.0119

[a] A total of 1-3 cm^3 of 0.023 M CrN_3^{2+} solution was agitated at 0 °C with ca. 36 cm^3 of an argon-fluorine mixture at an initial total pressure of 140-160 Torr. Ar:F_2 = 9 unless otherwise specified. A sample of one of the Ar-F_2 mixtures was agitated with mercury and analyzed mass spectrometrically. No significant amounts of N_2 or O_2 were found. [b] Ar:F_2 = 1.1. [c] Not determined. [d] 0.9 M $NaClO_4$. [e] Trace of N_2F_2 observed in product gas.

distribution of these products varies with the experimental conditions. The perchloric acid and initial CrN_3^{2+} concentrations have an appreciable effect, while the bubbling rate and volume of reactants result in only a small variation. The initial presence of HF (experiment 10) increases the yield of the CrF^{2+} product at the expense of $CrNO^{2+}$. However, the HF concentration in experiment 10 was considerably greater than the average concentration present in the other experiments during the time the CrN_3^{2+} was reacting. In the experiments with excess CrN_3^{2+}, the yield of CrF^{2+} increases while the yield of $CrNO^{2+}$ decreases markedly as the initial CrN_3^{2+} concentration increases. At high concentrations of CrN_3^{2+} in 1–2 M $HClO_4$ 1 mol of F_2 consumes 1 mol of CrN_3^{2+} to give a mixture of CrF^{2+} and Cr^{3+} (experiments 20–23). Under such conditions, with CrN_3^{2+} in excess, nearly all of the added fluorine is retained in the solution (Table IV, note b).

At perchloric acid concentrations below 1 M, the reaction produces more $CrNO^{2+}$ and less CrF^{2+} and Cr^{3+}. In low acid solutions containing excess CrN_3^{2+}, the retention of fluorine decreases substantially, but the ratio of retained fluorine to consumed CrN_3^{2+} still appears to be near unity (see experiment 25 and note c in Table IV). Under the static conditions of the experiments in Table V, however, the consumption of CrN_3^{2+} in 0.1 M acid is significantly less than the amount of F_2 reacted (vide infra).

Experiment 12 indicates that about a fourth of the Cr^{3+} formed in experiments with excess F_2 results from further reaction of the $CrNO^{2+}$ that is formed initially. This effect may explain the high yield of $CrNO^{2+}$ in experiment 11, in which a relatively slight excess of F_2 was used.

The experiments of Table V show that the reaction of 1 mol of fluorine with excess CrN_3^{2+} in 2 M $HClO_4$ consumes 0.91 mol of CrN_3^{2+} and produces 0.93 mol of N_2, 0.30 mol of N_2O, and 0.04 mol of O_2, while the reaction of 1 mol of CrN_3^{2+} with excess fluorine in 2 M $HClO_4$ produces 0.93 mol of N_2 and less than 0.05 mol of N_2O, along with a great deal of oxygen from the reaction of the excess fluorine with water. The reaction of 1 mol of fluorine with excess CrN_3^{2+} in 0.1 M $HClO_4$ consumes 0.80 mol of CrN_3^{2+} and produces 0.77 mol of N_2, 0.18 mol of N_2O, and 0.05 mol of O_2.

A reaction mixture similar to experiment 1 was analyzed for nitrate after the chromium species had been removed by ion exchange. A total of 0.0334 mmol of nitrate was found.

In contrast to the complex mixture resulting from the reaction of CrN_3^{2+} with F_2, the reaction with HOF yields only $CrNO^{2+}$ as the primary product, along with small amounts of Cr^{3+} but *no detectable* CrF^{2+}. (A large part of the Cr^{3+} formed in experiment 13 probably resulted from further reaction of $CrNO^{2+}$). At sufficiently high concentrations of CrN_3^{2+}, it appears that 1 mol of HOF consumes 1 mol of complex.

The experiments with OF_2 and HOCl indicate Cr^{3+} to be the principal reaction product, whereas H_2SO_5, like HOF, produces $CrNO^{2+}$ in good yield. The large yield of Cr^{3+} in experiment 17 would appear to result from further reaction of $CrNO^{2+}$ with H_2SO_5.

Discussion

The observed reactions of fluorine and HOF with acidic aqueous solutions may be rationalized by the following scheme.

$$F_2 + H_2O \rightarrow HOF + HF \tag{1}$$

$$HOF + H_2O \rightarrow H_2O_2 + HF \tag{2}$$

$$F_2 + H_2O_2 \rightarrow 2HF + O_2 \tag{3}$$

$$HOF + H_2O_2 \rightarrow HF + H_2O + O_2 \tag{4}$$

$$F_2 + R \rightarrow R' \tag{5}$$

$$HOF + R \rightarrow R'' \tag{6}$$

Here R is a reducing substrate, while R′ and R″ are reaction products that may or may not be distinguishable. In addition, there is the unknown reaction that produces small quantities of OF_2. A possible candidate for this process is

$$F_2 + HOF \rightarrow OF_2 + HF \tag{7}$$

If R′ and R″ are reactive, a further complication is introduced, inasmuch as they are subject to reduction by the H_2O_2 formed in reaction 2. Here, then, we confront the central enigma of aqueous fluorine reactions. If a substrate appears to react, is it reacting with F_2 or with HOF? If it appears not to react, is this only because the reaction product is being reduced back to the starting material by H_2O_2?

An example of the second ambiguity is found in the apparent failure of either F_2 or HOF to oxidize Cr^{3+}. It is certainly conceivable that higher oxidation states of chromium are actually produced but are reduced back to Cr^{3+} by the H_2O_2. The reduction of chromium(VI) by H_2O_2 in acid solution is a frequently used method for preparing hexaaquochromium(III). Two additional results indicate strongly that, in fact, no oxidation of Cr^{3+} is occurring. First, the presence of XeO_3 is without effect, even though XeO_3 is known to react very rapidly with hydrogen peroxide.[12] Second, solutions of CrF^{2+} are unaffected by treatment with substantial amounts of F_2 or HOF. If Cr^{3+} is being oxidized, we would expect CrF^{2+} to be oxidized also. This would result in release of the fluoride ligand because of the substitution lability of Cr(IV) and Cr(V).[13]

The question of what is reacting with the substrate confronts us when we consider the reactions of $CrClO_3^{2+}$, $CrNO^{2+}$, $CrCl^{2+}$, and $CrBr^{2+}$ with F_2 and HOF. In all cases the principal chromium-containing product is Cr^{3+}. Is there any way in which we can tell whether there is substantial direct reaction of these complexes with F_2? The CrF^{2+} formed in relatively low yield from the reaction of F_2 with excess $CrCl^{2+}$ and $CrBr^{2+}$ (Table II) can logically be taken to indicate a small amount of direct reaction, but might not the Cr^{3+} also be formed directly as well as via the intermediate production of HOF?

One approach to making this distinction is a kinetic one. When fluorine is bubbled through perchloric acid solutions, a substantial fraction escapes before it can react to form HOF. A substrate that is sufficiently reactive toward F_2 should reduce the amount that escapes. Thus the fact that fluorine reacts quantitatively with iodide and bromide solutions to form I_3^- and Br_3^-, respectively, draws us to the conclusion that there must be direct reactions of F_2 with I^- and Br^-. Similarly, the nearly complete retention of fluorine by the $CrBr^{2+}$ and $CrCl^{2+}$ solutions of Table II also implies a substantial degree of direct reaction. Such extensive retention of fluorine cannot be accounted for by the small amount of CrF^{2+} that is formed, and we must conclude that F_2 reacts directly with $CrBr^{2+}$ and $CrCl^{2+}$ to form Cr^{3+} as well as CrF^{2+}.

It is presumably possible to reduce the concentrations of these substrates to such an extent that the direct reaction (eq 5) can no longer compete with reaction 1, and it seems likely that at the relatively low concentrations of most of the experiments in Table I the indirect reaction (eq 6) does, in fact, predominate.

We should note that this interpretation depends on the irreversibility of reaction 2.[4] Because of this irreversibility, reactions of substrate with HOF cannot lead to increased retention of fluorine, and we must therefore attribute such increased retention to direct reaction of the substrate with F_2.

Concentrations of CrN_3^{2+} in excess of about 0.02 M are able to trap F_2 essentially quantitatively in 1–2 M $HClO_4$, indicating direct reaction. In addition, it is evident that the reaction of CrN_3^{2+} with F_2 produces products that are different from those of its reaction with HOF. The latter produces $CrNO^{2+}$ as the principal chromium-containing product, and on the basis of the stoichiometry with excess CrN_3^{2+}, we may write the initial reaction

$$CrN_3^{2+} + HOF \rightarrow CrNO^{2+} + N_2 + HF \qquad (8)$$

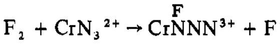
The small amount of Cr^{3+} formed may represent a minor path or may result from further reaction of $CrNO^{2+}$.

The reaction with fluorine appears more complex, with $CrNO^{2+}$, CrF^{2+}, and Cr^{3+} all being formed. However, with an excess of CrN_3^{2+} at a substantial concentration, little or no $CrNO^{2+}$ is produced, and we may conclude that the *direct* reaction with F_2 forms only CrF^{2+} and Cr^{3+}. On the basis of the stoichiometry with excess CrN_3^{2+} and the analyses of the evolved gases, we may write the initial direct reaction in 1–2 M $HClO_4$ as

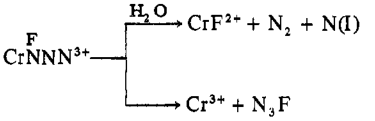
$$F_2 + CrN_3^{2+} \xrightarrow{H_2O} 0.6CrF^{2+} + 0.4Cr^{3+} + 1.4HF + N_2 + N(I) \qquad (9)$$

The data in Table V indicate that with excess CrN_3^{2+} in 2 M $HClO_4$, two-thirds of the N(I) ends up as N_2O. The rest may form the relatively stable $H_2N_2O_2$. An excess of F_2 may be expected to oxidize N(I) to higher oxidation states. It is therefore not surprising that we find nitrate in solutions of CrN_3^{2+} that have been treated with excess F_2 and that such reaction mixtures evolve very little N_2O (see Table V).

The mixture of chromium-containing products may reflect alternate modes of reaction of an intermediate, e.g.



$$F_2 + CrN_3^{2+} \rightarrow Cr\overset{F}{N}NN^{3+} + F^- \qquad (10)$$



$$Cr\overset{F}{N}NN^{3+} \xrightarrow{H_2O} CrF^{2+} + N_2 + N(I) \qquad (11a)$$

$$Cr\overset{F}{N}NN^{3+} \longrightarrow Cr^{3+} + N_3F \qquad (11b)$$

$$N_3F + H_2O \rightarrow N_2 + HF + N(I) \qquad (12)$$

The trace of N_2F_2 observed in the low acid experiment of Table V could result from an alternate decomposition of N_3F[14]

$$2N_3F \rightarrow 2N_2 + N_2F_2$$

In place of reactions 11b and 12, an alternate means of forming Cr^{3+} is the sequence

$$N(I) + F_2 + H_2O \rightarrow HNO_2 + 2HF \qquad (13)$$

$$H^+ + CrN_3^{2+} + HNO_2 \rightarrow Cr^{3+} + N_2 + N_2O + H_2O \qquad (14)$$

The last reaction of this series is the known oxidation of CrN_3^{2+} by HNO_2.[11,15]

It would thus appear that CrN_3^{2+} is an unusual reagent in that its reactions with F_2 and HOF yield different and readily distinguishable products.

Many questions arise from the results of this study. Why is Cr(III) not oxidized by either F_2 or HOF? Why does CrN_3^{2+} react so readily with F_2 to form CrF^{2+} as a major product? Why does HOF oxidize CrN_3^{2+} to $CrNO^{2+}$, whereas most other oxidants, such as HNO_2, HOCl, and OF_2, split off all of the nitrogen with formation of Cr^{3+}?

When comparing HOF and F_2 with other oxidants, one must bear in mind that reactions 1 and 2 are both extremely rapid. Hence, any substrate must compete favorably with a large excess of water if it is to be oxidized. It is not evident at the present time just what factors make a reducing substrate an effective competitor in reacting with aqueous F_2 and HOF.

If fluorine is to react directly with a Cr(III) species as suggested in reaction 10, it in effect has to add an F^+ to one of the ligands attached to the chromium, thereby forming the intermediate $CrXF^{3+}$. Presumably the azide ion, with its 16-electron system, will be more readily capable of forming such an intermediate than will a simple ligand like Cl^- or Br^-, which will have a substantial part of its electron density drawn into the Cr–X bond. Addition of the strongly electrophilic fluorine can be expected to weaken the Cr–X bond in all cases, but the extra electrons should make the effect less for azide than for chloride or bromide. Hence, we might expect the intermediate CrN_3F^{3+} to be longer-lived than the analogous $CrBrF^{3+}$ or $CrClF^{3+}$ and therefore to have more of an opportunity to transfer fluorine to the chromium before dissociating. In this way we can rationalize the high reactivity of CrN_3^{2+} with fluorine as well as the formation of CrF^{2+} as the major reaction product.

To form $CrNO^{2+}$ from CrN_3^{2+}, it is necessary for the nitrogen bound to the chromium to add what is formally a neutral oxygen atom

$$CrN_3^{2+} + [O] \rightarrow CrNO^{2+} + N_2$$

The process is formally similar to the addition of an oxygen atom to water to form hydrogen peroxide. NMR studies of HOF suggest that the molecule may have a charge distribution approximating $^{1/2+}H\cdots O\cdots F^{1/2-}$.[16] Hence, its oxygen atom is already neutral, whereas the oxygen atom in OF_2 is probably positive, and the oxygen atoms in HNO_2 and HOCl are almost certainly negative. Furthermore, microwave spectroscopy has shown the H–O–F bond angle to be an unusually acute 97°,[17] which gives the molecule a geometric configuration that should be especially favorable to the transfer of an oxygen atom with formation of HF. The corresponding bond angles in OF_2 and HOCl are both around 103°.[18,19] Finally, the large bond energy of HF makes the reaction

$$HOF \rightarrow HF + O$$

much less endoergic than the analogous reactions of HOCl and OF_2, and should make it much easier for HOF to transfer an oxygen atom. All three of these factors probably contribute to making hypofluorous acid a remarkably effective oxygen atom donor, and they can account for the ease with which HOF transfers O to H_2O to form H_2O_2 and to CrN_3^{2+} to form $CrNO^{2+}$.

It is interesting that reactions 8 and 9 become competitive with reactions 2 and 1, respectively, at about the same concentration of CrN_3^{2+}. This means that the *relative* reactivities of CrN_3^{2+} and H_2O are about the same toward F_2 as they are toward HOF.

We see from Table I that Rh^{3+}, like Cr^{3+}, is unreactive toward F_2 and HOF. Experiments with RhN_3^{2+} similar to those with CrN_3^{2+} reported here might prove interesting, although the synthesis of the rhodium azido complex has never been reported.

All in all, the work that we have reported provides a fairly consistent picture of the interaction of fluorine and HOF with aqueous solutions. Much of the chemistry that takes place when fluorine is introduced into an aqueous solution probably can be attributed to HOF. However, many reducing agents are able to react directly with F_2, and in favorable cases the direct reaction can lead to a product that may be distinguished from the product of the reaction with HOF.

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Registry No. F_2, 16984-48-8; HOF, 14034-79-8; $(H_2O)_5CrClO_3^{2+}$, 54566-83-5; $(H_2O)_5CrNO^{2+}$, 14951-34-9; $(H_2O)_5CrCl^{2+}$, 14404-08-1; $(H_2O)_5CrBr^{2+}$, 26025-60-5; $(H_2O)_5CrN_3^{2+}$, 18517-09-4; OF_2, 7783-41-7; HOCl, 7790-92-3; H_2SO_5, 7722-86-3.

References and Notes

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Contribution from the Department of Chemistry,
Florida State University, Tallahassee, Florida 32306

Nuclear Magnetic Resonance Study of the Structure in Solution of Lanthanide Complexes with Benzene-1,2-dioxydiacetate

L. KULLBERG and G. R. CHOPPIN*

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The induced shifts of ^1H and ^{13}C nuclei in the ligand benzene-1,2-dioxydiacetate complexed by Pr^{3+}, Eu^{3+}, and Yb^{3+} have been measured. From the ratios of the shifts, the relative extent of contact and dipolar contributions to the shifts has been estimated. The dipolar shifts were used with the McConnell–Robertson equation to calculate the internuclear distances and angles of 1:1 and 1:2 complexes.

Introduction

The application of lanthanide chelates as shift reagents in the NMR spectra of organic molecules is well established as a useful tool for investigating structural features of complex molecules.[1-4] Providing the observed shifts are dipolar the lanthanide shift data have the potential for quantitative structure determination. Unfortunately, the observed shifts are often composed of a mixture of dipolar and contact shifts, but by using more than one lanthanide ion, the contact contribution can be estimated.[5-7] Pr(III), Eu(III), and Yb(III) provide a satisfactory trio of paramagnetic ions as (a) they span the lanthanide series, (b) they induce relatively little line broadening (because of a combination of short electron-spin relaxation times and moderate magnetic anisotropies), (c) they give rise to shifts with different relative amounts of contact contribution, and (d) Pr(III) causes shifts in the opposite