This behavior justifies the conclusion that a monomeric $(CH_3)_3Sn^+_{solv}$ is not a stable species in HSO_3F. The low conductance in the early stages of the measurement indicates an incomplete breakdown of the polymeric structure, because the amount of SO_3F^- ions, the main contributor to the electrical conductance for basic solvolysis, is less than expected. This does not rule out the possibility that some $(CH_3)_3Sn^+_{solv}$ may be formed, but it is clearly not the sole tin species as is the case in H_2SO_4.

At higher concentrations, two effects are noticed. Dissociation decreases further and the curve of κ *vs.* molality shows some inflection. In addition further solvolysis of the tin–carbon bond occurs giving rise to dimethyltin(IV) derivatives in solution. The quantitative conversion of $(CH_3)_3SnSO_3F$ into $(CH_3)_2Sn(SO_3F)_2$ has been accomplished at higher solute to solvent ratios and is described together with the detailed solvolysis studies of the latter compound elsewhere.[6b]

Due to limited stability of the incomplete electrolytic dissociation, intended studies such as Raman, nmr, and frozen-solution Mössbauer were found not too meaningful. It must be concluded that weaker protonic solvents may be more suited as solvent systems for organotin cations.

The work presented allows a very good insight into the structure and bonding of the trimethyltin(IV) sulfonates. We hope to verify some of the structural proposals by X-ray diffraction.

Acknowledgments.—We are indebted to the 3M Co. for a generous gift of $Ba(SO_3CF_3)_2$, to Dr. H. A. Carter for the preparation of $(CH_3)_3SnSbF_6$, and also to Mrs. A. Sallos for technical assistance. Financial assistance from the National Research Council of Canada is gratefully acknowledged.

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The Oxidation of Halates to Perhalates by Xenon Difluoride in Aqueous Solution[1]

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Xenon difluoride oxidizes chlorate, bromate, and iodate to the respective perhalates. The maximum yield of perchlorate and periodate is about 93% of the initial XeF_2. The maximum yield of perbromate is only about 12%. In the oxidation of iodate, the maximum yield is obtained at iodate concentrations above 0.001 *M*, while in the oxidation of chlorate and bromate the maximum yield is only approached at halate concentrations in excess of 1 *M*. The oxidation of chlorate and bromate is brought about by an intermediate in the oxidation of water by XeF_2. The same is true of the oxidation of low concentrations of iodate. At high iodate concentrations, however, a direct reaction between XeF_2 and IO_3^- takes place. These reactions have been interpreted in terms of oxidation of the halate to an intermediate that either can go on to form stable perhalate or else can react with water to give back halate. The latter reaction predominates in the case of bromate. Experiments in the chlorine and bromine systems with ^{18}O-enriched water show that during the course of the reaction there is no gross exchange of oxygen between solvent water and halate or perhalate. However, in the bromate case, reversion of the oxidized intermediate to BrO_3^- leads to ^{18}O enrichment of the unreacted bromate. Substantial reduction of periodate by XeF_2 is observed. This reduction can be suppressed, however, if a sufficient excess of iodate is present.

Introduction

The formation of the perhalate ion by chemical oxidation of halate becomes increasingly more difficult as one goes from periodate to perchlorate to perbromate. The only oxidants known to form perbromate from bromate are XeF_2 in acid solution[2] and F_2 in alkaline solution.[3] That this increasing difficulty of oxidation is a kinetic rather than a thermodynamic effect is evident from consideration of the standard electrode potentials of the halate–perhalate couples. For iodate–periodate the potential is 1.64 V,[4] for chlorate–perchlorate it is 1.23 V,[4] and for bromate–perbromate it is 1.74 V.[5]

In this paper we have attempted to shed light on the nature of the activation barrier to the formation of perhalate by examining the reaction between aqueous xenon difluoride and each of the halate ions. We hope in the future to be able to carry out a similar study using molecular F_2 in place of XeF_2.

Xenon difluoride dissolves in water to the extent of about 0.15 *M* at 0°, and the solution appears to contain discrete XeF_2 molecules.[6,7] The standard electrode potential of the reaction

$$Xe(g) + 2HF = XeF_2 + 2H^+ + 2e^-$$

has been calculated to be 2.64 V,[8] making XeF_2 one of the most potent oxidants known in aqueous solution. Aqueous XeF_2 oxidizes water with a half-time of about 27 min at 25°.[9] The reaction is catalyzed by bases and by fluoride acceptors; this fact suggests that the rate-determining step may be hydrolysis to form a xenon oxy compound as an intermediate.[9]

There is good evidence that the reaction between

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XeF_2 and water produces a reducing intermediate—probably H_2O_2.[9] Hence it has been necessary in the course of the present study to determine whether XeF_2 can reduce perhalates as well as oxidize halates.

Experimental Section

Reagents.—XeF_2 was prepared by reaction of fluorine with a *ca.* fivefold excess of xenon at 300° in a Monel reactor.[10] The product was freed from traces of XeF_4 by removal of several equilibrium vapor pressure heads, amounting to *ca.* 5% of the XeF_2.[10] The product was then distilled into a Kel-F tube and water was added. The mixture of solid XeF_2 and saturated aqueous solution was stored at −70 to −80°. It was thawed and kept at 0° during the time portions were being taken for experiments. Tests described elsewhere[9] indicated that there was no more than 0.1 mol % XeO_3 in the XeF_2.

Rubidium chlorate tagged with ^{36}Cl was prepared by a technique described elsewhere.[11] The sample used had about 2% of its ^{36}Cl activity in the form of perchlorate.

Potassium perbromate was prepared in the manner described elsewhere.[3] Sodium perchlorate was made by neutralization of Na_2CO_3 with $HClO_4$ followed by recrystallization of the product. Other chemicals were commercial products of reagent grade.

Distilled water was redistilled through hot copper oxide before use. Water containing 10.8 mol % ^{18}O was obtained from Yeda Research and Development Co., Rehovoth, Israel.

Analytical Methods.—Perbromate was determined in the presence of bromate by the iodometric method described elsewhere.[3] Chlorate was determined by the same method, except that the bromate removal step was omitted. Bromate and iodate were determined by reaction with iodide in acid solution followed by titration with thiosulfate. Molybdate was used to catalyze the reaction of bromate with iodide.[12]

Periodate was determined by reducing it to iodate with iodide in a boric acid–borax buffer.[13] The triiodide liberated was titrated with a standard solution of arsenious oxide. When determining very small amounts of periodate, an excess of arsenite was introduced with the iodide, and the excess was back-titrated potentiometrically with a triiodide solution.[14] The compositions of solutions containing both iodate and periodate were determined by first titrating the periodate with arsenite in the manner just described. Then the solution was acidified to bring about reaction between the iodate and iodide. Finally, the solution was again buffered, and the liberated triiodide was titrated with arsenite.

Xenon difluoride was usually determined by reaction with iodide and titration of the triiodide with thiosulfate.[6] In some cases a boric acid–borax buffer was added to the triiodide and it was titrated with arsenite, or an excess of arsenite was introduced with the buffer, and the excess was back-titrated potentiometrically with I_3^-. The xenon difluoride stock solution was usually analyzed immediately before and after each set of experiments was made up. Because of the gradual oxidation of water by XeF_2 in the stock solution and also because of the tendency for oxygen bubbles to form in the pipets, the XeF_2 analyses had uncertainties of ±1–2%.

Thiosulfate solutions were standardized against primary standard grade potassium iodate, while NBS arsenic trioxide was used as a primary standard. Amylose was used as the titration indicator.

Perchlorate was determined potentiometrically by the "method of successive addition," using a perchlorate ion electrode and a Beckman Research pH meter. A fluoride ion electrode was used as a reference electrode. Acidic solutions were neutralized with $NaHCO_3$, and if fluoride was not already present, a small amount was added. The method was similar to that used by Manahan to determine nitrate.[15] Fluoride and sulfate did not interfere significantly, but chlorate did when $[ClO_3^-]/[ClO_4^-] > 10$. Correction for this interference was made by measuring reference solutions with chlorate and perchlorate concentrations similar to those in the unknown. Potassium perchlorate was used as a primary standard. The perchlorate determinations had uncertainties of ±1–2%.

In a few semiquantitative experiments, the perchlorate formed by oxidation of chlorate was determined radiochemically.[11] The chlorate was tagged with $Rb^{36}ClO_3$, and after reaction the remaining chlorate was destroyed by evaporation to dryness, first with HBr and then with HCl. The perchlorate was then determined by counting the $^{36}ClO_4^-$ in an end-window β proportional counter. If the reaction mixture contained $HClO_4$, this was neutralized before the HBr–HCl treatment to avoid loss of perchlorate.

Traces of bromate in perbromate solutions were determined spectrophotometrically by making the solutions 0.5 *M* in HBr and measuring the Br_3^- absorption at 275 nm.[3] Traces of Cl_2 and lower chlorine oxy compounds in chlorate solutions were determined in the same way. Traces of chlorate in perchlorate solutions were determined similarly, but using 10 *M* HBr. Traces of Br_2 and lower bromine oxy compounds in bromate solutions were also determined similarly, except that the bromide solution was buffered with $H_2PO_4^-$ and HPO_4^{2-} to *ca.* pH 7 to avoid reduction of bromate.

Isotopic analyses were carried out on molecular O_2, using a Consolidated Model 21-620 mass spectrometer. Enriched water was converted to O_2 by reaction with $KBrF_4$, using a method similar to that of Goldberg, *et al.*[16] A 20-μl sample of the water to be analyzed was placed in a small tin capsule, which was then crimped shut. The reaction vessel containing the $KBrF_4$ was filled with a positive pressure of helium and cooled with liquid nitrogen. It was then opened, and the tin capsule was introduced. The vessel was sealed, evacuated, and heated to fluorinate the capsule and its contents. The evolved oxygen was collected in the manner described by Goldberg, *et al.*[16]

Procedures.—Kinetic measurements were carried out at 25.0° in silica cells using a Cary 14 spectrophotometer equipped with a thermostated cell compartment. In iodate systems the growth of the periodate absorption at *ca.* 222 nm was monitored.[17] In all other systems the decrease of the XeF_2 absorption at 240–255 nm was measured.[6] Reactions were followed for at least 6 half-times. In all but iodate systems the optical density *vs.* time data were fitted by a least-squares method to a three-parameter first-order equation

$$\text{density} = P_1e^{-P_2t} + P_3$$

where P_2 is the first-order rate constant k_a. In the iodate systems a more complex three-parameter equation was used that included both a unimolecular and bimolecular term (*vide infra*). In every case the equation used could be made to fit the data to within their experimental scatter.

For experiments in which the stoichiometries of reactions were being determined, the reaction mixtures were allowed to stand overnight in a 25.0° water bath. In a few experiments, solutions were outgassed and mixed in evacuated vessels, and the gases evolved were analyzed by mass spectrometry.

Halates and perhalates were introduced as the sodium salts in all except the isotopic exchange experiments and a few experiments using $KBrO_4$.

The ^{18}O isotopic exchange experiments were carried out in Kel-F vessels by dissolving solid $KClO_3$ or $KBrO_3$ in a saturated solution of XeF_2 in water containing 10.8 mol % ^{18}O. Isotopic analyses were carried out after 4 hr to minimize slow-exchange effects. Analyses of portions of the solutions for halate and perhalate content were carried out after at least 24 hr.

To determine the isotopic composition of the oxygen in the halate and perhalate together, a portion of the solution was placed in a glass tube, one end of which was closed with a break-seal. The open end was attached to a high-vacuum line, and the solution was evaporated to dryness. The residue was baked for 10 min at 150°, after which the tube was sealed and ignited at 480° to evolve O_2 from the solid. The isotopic composition of this oxygen was then determined by mass spectrometry.

To determine the isotopic composition of the perchlorate oxygen alone, the chlorate was reduced by 4 *M* HBr prior to evaporation. To determine the isotopic composition of the perbromate oxygen alone, the bromate was reduced by 6 *M* HCl prior to evaporation.

Blanks were run on chlorate–perchlorate and bromate–per-

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bromate mixtures in enriched water containing HF but no XeF_2. Some of the blanks showed substantial ^{18}O enrichment. This enrichment was not time dependent, however, and probably came about during the separation and analysis.

Results

General Information.—None of the reactions appeared sensitive to normal room illumination. The stoichiometry of the reactions is expressed in terms of "yield," which we define as moles of perhalate formed per mole of XeF_2 initially present. All concentrations are expressed as moles per liter (M). Initial concentrations are indicated by a subscript zero as in $[XeF_2]_0$.

The Oxidation of Chlorate by XeF_2.—At low chlorate concentration the yield of perchlorate is enhanced if the reaction is carried out in Pyrex vessels. The effect is especially pronounced if an excess of HF is present. Silica, Kel-F, and Teflon vessels do not produce such enhancement, and to avoid the problem most experiments were carried out in Kel-F or Teflon vessels.

Table I shows the dependence of the yield of perchlorate on chlorate and XeF_2 concentrations. The calculated values were obtained from the equation

TABLE I

THE OXIDATION OF CHLORATE BY XeF_2[a]

$[NaClO_3]_0$	$[XeF_2]_0$	Yield Calcd	Yield Exptl
0.00355	0.024	0.0142	0.0154[b]
0.00497	0.023	0.0199	0.0210[b]
0.0071	0.022	0.0282	0.0299[b]
0.00994	0.022	0.0390	0.0414[b]
0.0142	0.022	0.0548	0.0585[b]
0.0199	0.045	0.0720	0.0776[b]
0.0199	0.022	0.0752	0.0767
0.0199	0.011	0.0767	0.0745
0.0278	0.024	0.102	0.103
0.0398	0.022	0.140	0.141
0.0568	0.022	0.188	0.190
0.0795	0.023	0.244	0.243
0.114	0.022	0.314	0.314
0.171	0.066	0.393	0.393
0.169	0.032	0.400	0.396
0.169	0.016	0.404	0.397
0.169	0.0065	0.407	0.410
0.331	0.066	0.552	0.551
0.418	0.080	0.602	0.607
0.663	0.128	0.692	0.671
1.32	0.101	0.799	0.797
1.99	0.077	0.841	0.856
4.00	0.127	0.886	0.882

[a] In Kel-F or Teflon vessel. [b] Not used for least-squares fitting because of HF catalysis (see text).

$$[\text{yield}]^{-1} = 1.070 + 0.2327[ClO_3^-]^{-1} \quad (1)$$

where $[ClO_3^-]$ is a mean chlorate concentration, *i.e.*, $[ClO_3^-] = [ClO_3^-]_0 - 0.5[ClO_4^-]_{final}$. The constants in eq 1 were obtained by a weighted least-squares fit to the data of Table I, assuming a 2% uncertainty in the yields. The first six experiments in the table were not used for this fit because their yields are catalytically enhanced by the HF formed from the XeF_2 (see Table II and Discussion).

The effects of HF and glass on the yield of perchlorate are shown in Table II; the effect of H_2SO_4 is shown in Table III. A few semiquantitative experiments with $Rb^{36}ClO_3$ indicated that $HClO_4$ had essentially the same effect as H_2SO_4.

TABLE II

EFFECTS OF HF AND GLASS ON THE OXIDATION OF CHLORATE BY XeF_2[a]

$[HF]_0$	Yield	$[HF]_0$	Yield	$[HF]_0$	Yield
		$[NaClO_3]_0 = 0.0036\ M$			
...	0.0154	...	0.0190[b]	0.19	0.027
		$[NaClO_3]_0 = 0.010\ M$			
...	0.041	0.23	0.064	0.24	0.118[b]
...	0.044[b]	0.23	0.064[c]		
		$[NaClO_3]_0 = 0.17\ M$			
...	0.40	0.18	0.39	0.46	0.38
...	0.38[b]	0.18	0.38[b]		

[a] Unless otherwise specified, reactions were carried out in Kel-F or Teflon vessels. Experiments with 0.17 M $NaClO_3$ had $[XeF_2]_0$ = 0.032–0.034 M; other experiments had $[XeF_2]_0$ = 0.022–0.024 M. [b] In Pyrex vessels. [c] In vitreous silica vessels.

TABLE III

EFFECT OF H_2SO_4 ON THE OXIDATION OF CHLORATE BY XeF_2[a]

$[H_2SO_4]$	Yield	$[H_2SO_4]$	Yield	$[H_2SO_4]$	Yield
		$[NaClO_3]_0 = 0.0050\ M$			
...	0.021	0.029	0.042		
		$[NaClO_3]_0 = 0.0142\ M$			
...	0.059	0.029	0.091	0.51	0.057
0.0072	0.071	0.143	0.081	1.29	0.042
		$[NaClO_3]_0 = 0.114\ M$			
...	0.31	0.029	0.32	0.71	0.141
0.0072	0.32	0.143	0.27		

[a] In Kel-F or Teflon vessels with $[XeF_2]_0$ = 0.022–0.024 M.

The effect of base was determined using $Rb^{36}ClO_3$ in a mixture 0.4 M in NaOH, with $[NaClO_3]_0$ = 0.123 M and $[XeF_2]_0$ = 0.082 M. A yield of 0.023 was obtained.

Table IV shows the effect of $NaClO_3$ on the rate of consumption of XeF_2 and compares it with the effect of comparable amounts of $NaClO_4$. The calculated rate constants are explained in the Discussion.

TABLE IV

RATE OF DISAPPEARANCE OF XeF_2 FROM CHLORATE AND PERCHLORATE SOLUTIONS[a]

$[NaClO_3]_0$	$[NaClO_4]_0$	10^4k_a, sec^{-1} Calcd	10^4k_a, sec^{-1} Exptl	$[NaClO_3]_0$	$[NaClO_4]_0$	10^4k_a, sec^{-1} Calcd	10^4k_a, sec^{-1} Exptl
...	...	...	4.38	0.80	...	2.37	2.87
0.10	...	3.67	3.68	...	0.40	...	4.03
0.20	...	3.28	3.45	...	0.80	...	3.75
0.40	...	2.83	3.15				

[a] $[HClO_4]$ = 0.010 M;[18] $[XeF_2]_0$ = 0.0024 M.

The oxygen isotopic exchange that accompanies the oxidation of chlorate by XeF_2 is shown in the first half of Table V.

No evidence was found for significant reduction of chlorate or perchlorate by XeF_2.

The gases evolved from a mixture 0.1 M in XeF_2 and 4.0 M in $NaClO_3$ were found by mass spectrometry to consist of oxygen and xenon in the ratio 0.063:1. If the remainder of the XeF_2 oxidizing power is assumed to have gone into production of perchlorate, the perchlorate yield of this experiment is 0.874, in fairly good agreement with eq 1.

The Oxidation of Bromate by XeF_2.—This reaction was found to give the same yields in Pyrex vessels as in Kel-F ones. The dependence of the yield of perbromate on the concentration of XeF_2 is shown in Table VI. The dependence on bromate and acid

TABLE V
^{18}O EXCHANGE IN THE OXIDATION OF CHLORATE AND BROMATE BY XeF_2[a]

	Chlorate		Bromate	
Initial XeF_2, M	0.156	0.163	0.156	0.164
Initial halate, M	0.160	0.160	0.160	0.160
Final perhalate, M	0.053	0.059	0.010	0.012
^{18}O in final halate + perhalate, %	1.58	1.72	3.4	4.0
Blank, %[b]	0.70	0.70	2.5	2.5
Net ^{18}O enrichment of halate + perhalate, %	0.88	1.02	0.9	1.5
^{18}O in final perhalate, %	2.41	2.47	2.84	2.96
Blank, %[b]	0.23	0.23	0.36	0.36
Net ^{18}O enrichment of perhalate, %	2.18	2.24	2.48	2.60
Net ^{18}O enrichment of halate, %	−0.05	+0.06	0.8	1.4
Apparent ^{18}O content of O atom added to halate to give perhalate, %[b]	8.9	9.2	8.9[c]	8.5[c]

[a] In water containing 10.8 mol % ^{18}O. All ^{18}O percentages are mole per cents. [b] Including natural abundance of ^{18}O. [c] Assuming that the average ^{18}O enrichment of the bromate oxidized to perbromate is half the final bromate enrichment.

TABLE VI
EFFECT OF XeF_2 CONCENTRATION ON THE OXIDATION OF BROMATE BY XeF_2

$[XeF_2]_0$	Yield × 100	$[XeF_2]_0$	Yield × 100	$[XeF_2]_0$	Yield × 100
		$[NaBrO_3]_0 = 0.044\ M$			
0.0167	3.9	0.066	3.6	0.135	3.2
0.033	3.8				
		$[NaBrO_3]_0 = 0.22\ M$			
0.0081	8.8	0.034	8.7	0.137	8.1
0.0153	8.7	0.068	8.4		

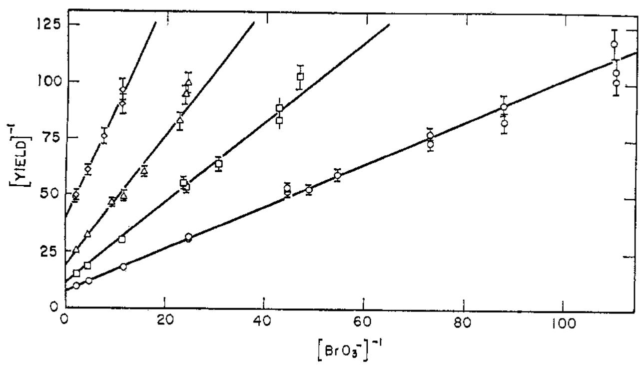

Figure 1.—The oxidation of bromate by XeF_2; $[XeF_2]_0$ = 0.063–0.073 M. Bromate was introduced as $NaBrO_3$, and $NaClO_4$ was added to make $[Na^+]$ = 0.41–0.46 M. Where error bars are not shown, uncertainties were taken to be ±2%. O, no added acid; □, 0.167 M $HClO_4$; Δ, 0.408 M $HClO_4$; ◇, 0.85 M $HClO_4$.

concentration is shown in Figure 1. The abscissa in the figure is a mean bromate concentration, *i.e.*, $[BrO_3^-] = [BrO_3^-]_0 - 0.5[BrO_4^-]_{final}$. The experiments shown in Figure 1 all contained enough $NaClO_4$ to maintain the Na^+ concentration at 0.41–0.46 M. The straight lines drawn in the figure are weighted least-squares fits to the equation

$$[\text{yield}]^{-1} = K_1 + K_2[BrO_3^-]^{-1}$$

The values obtained for K_1 and K_2 are listed in Table VII. The other entries in Table VII will be explained in the Discussion. Not shown in Figure 1 is an experiment with $[NaBrO_3]_0$ = 1.0 M, $[XeF_2]_0$ = 0.080 M, and no added acid that gave a yield of 0.110. Despite

TABLE VII
PARAMETERS FOR THE OXIDATION OF BROMATE BY XeF_2

$[HClO_4]$	K_1	K_2	k_6/k_7	k_5/k_4
0	8.1	0.93	0.283	9.8
0.167	11.4	1.77	0.192	7.0
0.408	18.6	2.85	0.114	6.9
0.85	38.8	4.91	0.053	8.1

its higher Na^+ concentration this experiment would fall on the "no acid" line of Figure 1.

Table VIII shows the effects of base, $NaClO_4$, HF,

TABLE VIII
EFFECTS OF VARIOUS ADDITIVES ON THE OXIDATION OF BROMATE BY XeF_2[a]

$[NaBrO_3]_0$	Additive	Yield × 100	$[NaBrO_3]_0$	Additive	Yield × 100
0.0113	...	0.98	0.044	0.34 M HF	3.1
0.0113	0.22 M HF	0.80	0.20	...	8.1
0.0113	0.032 M $HClO_4$	0.82	0.21	0.21 M $NaClO_4$	8.0
0.044	...	3.6	0.20	0.34 M HF	7.4
0.041	0.41 M $NaClO_4$	3.2	0.20[b]	0.30 M NaOH	0.59

[a] Except as otherwise noted, $[XeF_2]_0$ = 0.06–0.08 M. [b] $[XeF_2]_0$ = 0.10 M.

and low concentrations of $HClO_4$ on the yield of perbromate.

Measurements were made of the rate of consumption of XeF_2 in mixtures 0.007 M in $HClO_4$ and with $[XeF_2]_0$ = 0.014 M.[18] In the absence of other reagents the unimolecular rate constant is $k_a = 4.5 \times 10^{-4}$ sec^{-1}. Both in 0.36 M $NaBrO_3$ and in 0.36 M $NaClO_4$ $k_a = 4.2 \times 10^{-4}$ sec^{-1}.

The oxygen isotopic exchange that accompanies the oxidation of bromate by XeF_2 is shown in the second half of Table V.

A very small amount of reduction of perbromate by XeF_2 was observed. After standing overnight a solution initially 0.175 M in $KBrO_4$, 9×10^{-5} M in $KBrO_3$, and 0.15 M in XeF_2 was found to be 3×10^{-4} M in bromate. No evidence was found for reduction of bromate to lower states by XeF_2, and within an experimental uncertainty of about 0.5% the sum of the final bromate and perbromate concentrations was always equal to the initial bromate concentration.

The Oxidation of Iodate by XeF_2.—The yields of this reaction were about the same in Pyrex as in silica, Kel-F, or Teflon vessels, but the results in Pyrex vessels seemed somewhat less reproducible for experiments at very low concentrations. Kel-F or Teflon vessels were therefore used for such experiments.

Table IX shows the dependence of the reaction yield and rate on the initial concentrations of XeF_2 and $NaIO_3$. The kinetic data were treated by assuming parallel unimolecular and bimolecular reaction paths, and they were fitted by a least-squares technique to the equation

$$\text{optical density} = \frac{P_1 e^{P_2 t} - P_1}{e^{P_2 t} - k_b B/(k_a + k_b A)} + P_3$$

where the P's are the fitted parameters, $A = [IO_3^-]_0$, $B = [IO_4^-]_{final} = [XeF_2]_0(\text{yield})$, and k_a and k_b are, respectively, the unimolecular and bimolecular rate constants, expressed in terms of $d[XeF_2]/dt$. P_2 is related to k_a and k_b by the expression $P_2 = k_a + k_b \cdot$

(18) All kinetic experiments were carried out in 0.007–0.01 M $HClO_4$ to make the results comparable to those of our previous study.[9] Under the conditions of these experiments, this small amount of acid does not appear to have had a significant effect on the yield of perhalate.

TABLE IX

THE OXIDATION OF IODATE BY XeF_2[a]

$10^3[NaIO_3]_0$	$10^3[XeF_2]_0$	Yield	10^4P_2, sec^{-1}	10^4k_a, sec^{-1}	k_b, $M^{-1} sec^{-1}$
0.0117	0.022	0.080			
0.0160	0.025	0.088			
0.236	0.022	0.140			
0.444	0.022	0.278			
0.100[b]	0.022	0.555	3.11	3.17	...
0.200	0.043	0.711	3.12	2.83	0.17
0.400	0.049	0.822	3.23	2.58	0.18
0.399	0.132[c]	0.776	3.45	2.67	0.26
0.99	0.24	0.868	3.76	2.48	0.162
1.00	0.40	0.807			
1.99	0.20	0.914	5.12	2.38	0.150
2.00	0.40	0.899			
3.95	0.38	0.916	7.19	2.37	0.133
9.8	1.6	0.913	13.9	2.38	0.137
10.0	4.0	0.876			
10.0	8.0	0.778			
19.4	2.0	0.926	24.0	2.35	0.124
38.4	2.6	0.923	50.3	2.37	0.133
38	4.8	0.935			
38	10.0	0.927			
38	20	0.840			
38	30	0.765			
121	9.3	0.935			
121	23	0.917			
121	46	0.878			
121	93	0.778			
365	0.89	0.857			
360	3.6	0.926			
360	15.0	0.908			

[a] In 0.010 M $HClO_4$. [b] In the kinetic experiment $[NaIO_3]_0 = 9.7 \times 10^{-5}$ M. [c] In the kinetic experiment $[XeF_2]_0 = 1.22 \times 10^{-4}$ M.

$(A - B)$. On the basis of the rate constants in Table III in the absence of added salts, k_a was represented by the expression

$$k_a = 2.19 \times 10^{-4}(2 - \text{yield}) \text{ sec}^{-1}$$

which will be justified in the Discussion. The term $k_bB/(k_a + k_bA)$ is relatively small in our experiments, and a value of k_b that was sufficiently accurate to use in it was obtained by successive approximation. A final value of k_b was calculated from P_2.

Table X shows the effect of the initial presence of periodate on the yield of the XeF_2–iodate reaction, and Table XI shows the effects of acid and base.

TABLE X

EFFECT OF PERIODATE ON THE OXIDATION OF IODATE BY XeF_2[a]

$10^3[NaIO_3]_0$	$10^3[XeF_2]_0$	$10^3[NaIO_4]_0$	Yield: With $NaIO_4$	Yield: Without $NaIO_4$
0.0117	0.019[b]	0.0012	0.032	0.080
0.0236	0.019[b]	0.0025	0.035	0.140
0.0444	0.019[b]	0.0062	0.238	0.278
0.100	0.019[b]	0.012	0.539	0.555
6.3	2.4	2.2	0.785	0.878
38	2.5[c]	2.2	0.932	0.923
38	18.5	16	0.724	0.840
274	21	19	0.914	0.935

[a] In 0.010 M $HClO_4$. [b] Experiments without $NaIO_4$ had $[XeF_2]_0 = 2.2 \times 10^{-5}$ M. [c] Experiment without $NaIO_4$ had $[XeF_2]_0 = 2.6 \times 10^{-3}$ M.

XeF_2 can bring about substantial reduction of periodate to iodate, as is shown in Table XII. However, after reaction of XeF_2 with either iodate or periodate, the sum of the final iodate and periodate concentrations was closely equal to the initial iodate or periodate concentration. This indicated the absence of a significant reduction of iodate by XeF_2.

TABLE XI

EFFECT OF ACID AND BASE ON THE OXIDATION OF IODATE BY XeF_2

$10^3[NaIO_3]_0$	$10^3[XeF_2]_0$	$[HClO_4]$	$[NaOH]_0$	Yield
0.40	0.13	0.010	...	0.776
0.40	0.13	...	0.010	0.664
0.99	0.25	0.010	...	0.868
0.97	0.24	1.0	...	0.53
0.99	0.40	0.010	...	0.807
0.98	0.37	...	...	0.820
33	13	...	...	0.890
31	12	...	0.077	0.863
33	7.3	...	...	0.920
33	7.2	0.012	...	0.926
33	7.2	0.10	...	0.878
31	6.7	0.9	...	0.685
310	6.7	0.9	...	0.707

TABLE XII

REDUCTION OF PERIODATE BY XeF_2

$10^3[NaIO_4]_0$	$10^3[XeF_2]_0$	$[HClO_4]$	Periodate remaining, %
0.0138	0.050	0.010	15
0.0285	0.048	0.010	36.3
0.0685	0.050	0.010	69.0
0.184	0.131	0.010	78.2
0.180	0.261	0.010	76.4
0.199	0.155	...	73.4
5.6	4.4	...	86.5
62	48	...	85.3
60	47	0.038	89.3
56	44	1.2	98.2
49	38	...	100.2[a]
78	27	...	98.2[b]
99	38	...	91.5
114	8.0	...	94.8
120	4.2	...	96.8
123	2.1	...	97.9

[a] $[NaOH]_0 = 0.20$ M. [b] $[NaIO_3]_0 = 0.0129$ M.

Because of the reduction of IO_4^- by XeF_2, it was not possible to obtain quantitative oxidation of iodate by excess XeF_2 in weakly acidic solution. Thus, a solution 0.08 M in XeF_2 and 0.0200 M in $NaIO_3$ yielded only 0.0182 M periodate.

A solution 0.025 M in XeF_2 and 0.33 M in $NaIO_3$ yielded oxygen and xenon in the ratio 0.03:1. This corresponds to about a 94% yield of periodate, which is within experimental uncertainty of the maximum yields shown in Table IX.

Discussion

The Oxidation of Chlorate and Bromate by XeF_2.—The yields of perchlorate and perbromate are not appreciably dependent on the XeF_2 concentration,[19] but they do depend on the concentration of halate. The halate dependence is of the form

$$[\text{yield}]^{-1} = K_1 + K_2[ZO_3^-]^{-1} \tag{2}$$

in which Z is either Cl or Br. This relation is typical of systems in which the stoichiometry is determined by the balance of two competing reactions. We may therefore interpret this dependence to indicate that halate and water are competing for the oxidant. If the reaction of oxidant with halate leads directly to perhalate, the intercept K_1 should be unity, corresponding to a limiting 1:1 stoichiometry at high halate con-

(19) The significant decrease in yield of perbromate at $[XeF_2]_0 = 0.13$–0.14 M (see Table VI) is probably caused at least in part by the relatively high HF concentration.

centration. In the chlorate case K_1 is 1.07, slightly but significantly greater than unity, while in the bromate case the intercept is 8.1. The fact that the intercepts exceed unity suggests that the halate is being oxidized to an intermediate that can either go on to stable perhalate or else decompose (or react with water) to give back halate.

So far we have deliberately left ambiguous the identity of the oxidant. If the oxidant is XeF_2 itself, then high halate concentration should markedly increase the rate of disappearance of XeF_2 from solution. The kinetic measurements show that this is not the case. In fact, chlorate significantly *decreases* the rate of disappearance of XeF_2, even when compared to sodium perchlorate solutions of the same concentration. Hence, it is evident that the halate is being oxidized not by XeF_2, but by an intermediate produced in the reaction of XeF_2 with water.

In a previous paper[9] we have shown that the reaction of XeF_2 with water is slowed down by the presence of XeO_3, which is partially reduced at the same time. In that paper we concluded that the reaction of XeF_2 with water produces an intermediate capable of attacking a second molecule of XeF_2. We proposed that the rate-determining step is a hydrolysis of the XeF_2, *e.g.*

$$XeF_2 + H_2O \longrightarrow XeO + 2HF$$

and we suggested two alternate mechanisms to complete the reaction

$$XeO + XeF_2 \longrightarrow XeOF_2 + Xe$$

$$XeOF_2 + H_2O \longrightarrow Xe + O_2 + 2HF$$

or

$$XeO + H_2O \longrightarrow Xe + H_2O_2$$

$$H_2O_2 + XeF_2 \longrightarrow Xe + O_2 + 2HF$$

Although these mechanisms are kinetically equivalent, the second one is supported by the detection of a residue of H_2O_2 after the XeF_2 has all reacted.[9] In the following discussions we shall make use of the second mechanism in preference to the first.

The fact that chlorate *decreases* the rate of disappearance of XeF_2 means that the halate must be oxidized before the second molecule of XeF_2 is involved. We shall assume that the oxidizing agent is the hydrolyzed xenon oxy compound, and we can then postulate a mechanism

$$XeF_2 + H_2O \xrightarrow{k_3} XeO + 2HF \tag{3}$$

$$XeO + H_2O \xrightarrow{k_4} Xe + H_2O_2 \tag{4}$$

$$XeO + ZO_3^- \xrightarrow{k_5} Xe + ZO_4^{-*} \tag{5}$$

$$ZO_4^{-*} \xrightarrow{k_6} ZO_4^- \tag{6}$$

$$ZO_4^{-*} + H_2O \xrightarrow{k_7} ZO_3^- + H_2O_2 \tag{7}$$

$$H_2O_2 + XeF_2 \xrightarrow{k_8} Xe + O_2 + 2HF \tag{8}$$

If we assume a steady state in XeO, ZO_4^{-*}, and H_2O_2, we may obtain a value for $d[XeF_2]/d[ZO_4^-]$ that is only a function of $[ZO_3^-]$. In our experiments the relative change in halate concentration is fairly small, and we may take the mean $[ZO_3^-]$ to be approximately a constant over the course of the reaction. Then

$$[\text{yield}]^{-1} = 1 + \frac{2k_7}{k_6} + \frac{2k_4(k_6 + k_7)}{k_5k_6}[ZO_3^-]^{-1}$$

Comparing this to eq 2, we conclude that

$$\frac{k_6}{k_7} = \frac{2}{K_1 - 1}$$

and

$$\frac{k_5}{k_4} = \frac{K_1 + 1}{K_2}$$

In the chlorate system, $k_6/k_7 = 29 \pm 5$ and $k_5/k_4 = 8.9 \pm 0.1$. In the bromate system (without added acid) $k_6/k_7 = 0.28 \pm 0.01$ and $k_5/k_4 = 9.8 \pm 0.1$. The values for the two systems are not quite comparable, inasmuch as the bromate mixtures contained added $NaClO_4$, while the chlorate ones did not. The salt effects do not appear to be important, however.

Our mechanism would predict that XeF_2 should be consumed with a first-order rate constant

$$k_a = k_3(2 - \text{yield}) \tag{9}$$

Hence 0.36 M $NaBrO_3$ should decrease the rate of disappearance of XeF_2 by about 5%. In actuality, the rate is the same in 0.36 M $NaBrO_3$ as in 0.36 M $NaClO_4$. The expected 5% decrease may be lost in medium effects, or else a small amount of direct interaction between XeF_2 and BrO_3^- may compensate for the decrease.

Chlorate does indeed decrease the rate of disappearance of XeF_2, as is shown in Table IV. To obtain the calculated rate constants in the table, we have assumed that the general salt effect on k_3 is the same in $NaClO_3$ solutions as in $NaClO_4$ solutions and may be represented approximately by the equation

$$\log k_3(x) = \log k_3^0 + 0.085x$$

where $k_3(x)$ is the value of k_3 at total $[Na^+] = x$. Values of k_a are then calculated by combining this equation with eq 9 and using yields computed from eq 1.

We see that the calculated values of k_a are considerably smaller than the experimental ones. We may note, however, that sodium perchlorate itself reduces the rate substantially, and it may be that the salt effect of $NaClO_3$ is significantly different from that of $NaClO_4$. Alternatively, as we have suggested for the bromate case, a small contribution from a direct reaction between XeF_2 and chlorate may partially cancel out the rate decrease.

Yields of perchlorate and perbromate become negligible in alkaline solution, and they are also reduced by high concentrations of strong acids. The effect of acid appears to be most pronounced in the bromate system. The yield of perbromate is also slightly inhibited by high HF concentration. The yield of perchlorate at low chlorate concentration is actually enhanced by HF or small amounts of strong acid.

The effect of strong acids on the oxidation of bromate is shown in Figure 1 and analyzed in Table VII. While there is some effect of acid on k_5/k_4, the principal effect is on k_6/k_7. This effect may consist of an acid catalysis of reaction 7.

The positive effect of acids on the formation of perchlorate from low concentrations of chlorate is a little surprising. We may explain it in terms of a protonation equilibrium: $XeO + H^+ = XeOH^+$. Although this equilibrium may lie to the left, if $XeOH^+$ reacts very efficiently with ClO_3^- a catalysis of perchlorate formation by H^+ may appear at low $[ClO_3^-]$. The HF may then be acting simply as a source of H^+. Actually the HF produced from the XeF_2 should cause the perchlorate yields in Table I to deviate more from the calculated values at low $[ClO_3^-]$ than they do, and some compensating effect may be involved.

An unsatisfying aspect of this explanation is that there is no obvious reason why H^+ should not also enhance the yields of perbromate at low bromate concentrations. Although the bromate concentrations at which such an effect should be noticeable are near the low end of our experimental range, it would appear from Table VIII that there is in fact no enhancement.

The effect of HF on the yield of perchlorate is markedly increased in Pyrex vessels. This probably results from leaching of some substance, such as boron, from the glass. However, it does not seem worthwhile at this time to speculate in detail on the nature of the effect.

The isotopic exchange experiments indicate that the formation of perchlorate and perbromate does not involve exchange of the perhalate oxygens with the solvent. The apparent ^{18}O content of the oxygen added to the halate to give perhalate is significantly less than the ^{18}O content of the solvent. Part of this difference may be due to a kinetic isotope effect, and part may result from a small amount of exchange between ZO_3^- and ZO_4^{-*} or ZO_4^-. In the chlorine case, such exchange cannot account for more than about half of the discrepancy, because a larger effect would have to show up as significant ^{18}O enrichment of the unoxidized chlorate.

Although the unoxidized chlorate is not significantly enriched in ^{18}O, the unoxidized bromate is. The high blank correction, however, makes quantitative interpretation of the bromate enrichment difficult. The enrichment can largely be accounted for if we assume that BrO_4^{-*} has all four oxygen atoms equivalent. Then reaction 7 will produce enriched BrO_3^-, *i.e.*

$$Br^{16}O_3{}^{18}O^{-*} + H_2O \xrightarrow{k_7} Br^{16}O_2{}^{18}O^- + H_2O_2$$

In the case of ClO_4^{-*}, k_6/k_7 is large, and there is no significant enrichment of the chlorate.

The Oxidation of Iodate by XeF_2.—This reaction is complicated by direct interaction between XeF_2 and iodate and by the reduction of periodate by XeF_2. The latter should not be unexpected, inasmuch as periodate is rapidly reduced by H_2O_2. The reduction of periodate does not appear to be important if the iodate concentration is *ca.* 10^{-4} *M* or more and if the periodate in the system never exceeds about one-third of the iodate concentration. We may draw this conclusion from the fact that the addition of significant amounts of periodate to mixtures that satisfy these conditions does not affect the yield (Table X). This conclusion is also supported by the observation that the yields are little if at all affected by varying the ratio of XeF_2 to iodate, so long as the periodate formed does not exceed one-third of the iodate.[20] In particular we must conclude that the limiting yield of 92–93% is not a consequence of reduction of periodate by XeF_2.

The data of Table IX indicate that the iodate is oxidized both by a direct attack on XeF_2 and by reaction with an intermediate in the oxidation of water by XeF_2. The direct reaction predominates at iodate concentrations in excess of 0.002 *M* and has a fixed yield of 92–93%. The indirect reaction must have a maximum yield of about the same value, inasmuch as there is no marked increase in yield above 0.002 *M* iodate. Below this iodate concentration the yield of the indirect reaction begins to drop substantially.

If we assume the indirect reaction to proceed by the mechanism of eq 3–8, the fact that its limiting yield is about the same as that of the direct reaction implies that the latter produces the same or a very similar intermediate. We may then represent the direct reaction as

$$XeF_2 + IO_3^- + H_2O \longrightarrow Xe + 2HF + IO_4^{-*} \quad (10)$$

The intermediate IO_4^{-*} may then undergo reactions 6 and 7, with a ratio k_6/k_7 of about 25. For the indirect reaction we may estimate $k_5/k_4 \cong 3 \times 10^4$. We may thus express the disappearance of XeF_2 in terms of a bimolecular process, with rate constant k_b, and a unimolecular process, with rate constant k_a. In our experiments the yield is nearly constant throughout the reaction. Hence the rate constants for formation of periodate by the direct and indirect paths are, respectively, k_b(yield) and k_a(yield). Values of k_a may be calculated from eq 9, if we evaluate k_3 as *half* the rate of disappearance of XeF_2 from 0.01 *M* $HClO_4$ in the absence of other solutes. From the data of Table IV we have set $k_3 = 2.19 \times 10^{-4}$ sec^{-1}. This allows us to calculate the values of k_b shown in Table IX. Their constancy is generally within experimental uncertainty, except for the very high value at 0.0004 *M* IO_3^- and 0.00013 *M* XeF_2, which seems to constitute a real and unexplained discrepancy.

We can only conjecture as to the detailed nature of reaction 10. We may imagine the formation of an iodate ester of Xe(II)

$$XeF_2 + IO_3^- \xrightarrow{k_b} FXeOIO_2 + F^-$$

This ester may then hydrolyze rapidly

$$FXeOIO_2 + H_2O \longrightarrow Xe + HF + H^+ + IO_4^{-*}$$

At iodate concentrations below 10^{-4} *M* the initial presence of periodate does alter the yield, and we may conclude that reduction of periodate is playing a significant role. At relatively high iodate concentrations, there is a drop-off in yield as $[XeF_2]_0$ becomes comparable to $[IO_3^-]_0$, *i.e.*, as the periodate formed becomes comparable in concentration to the iodate. This effect cannot be attributed simply to a decrease in average iodate concentration, and the fact that under these conditions the yield is decreased by the initial presence of periodate (see Table X) suggests that reduction of periodate may also be involved here. If the reduction of periodate takes place only by reaction with the H_2O_2 intermediate, the drop-off in yield should become less as the iodate concentration increases. Examination of Table IX reveals that this is not the case over the range 0.01–0.12 *M* iodate, and to explain our results we must postulate a direct attack

(20) The relatively low yield of the experiment in Table IX with 0.365 *M* iodate and 8.9×10^{-2} *M* XeF_2 may be caused by reducing impurities in the iodate.

of periodate on XeF_2. Again ester formation is a possibility, *e.g.*

$$IO_4^- + 2H_2O = H_4IO_6^-$$

$$XeF_2 + H_4IO_6^- \longrightarrow FXeOIO_5H_4 + F^-$$

$$FXeOIO_5H_4 \longrightarrow Xe + HF + IO_3^- + O_2 + H^+ + H_2O$$

The formation of periodate is unaffected by low concentrations of acid but is decreased at high acid concentration. As in the bromine and chlorine systems, we may attribute this to an acid catalysis of reaction 7. Surprisingly, however, the yield of periodate is changed rather little in alkaline solution. This is markedly different from the behavior of the bromine and chlorine systems, and it suggests that in alkaline solution the oxidation of iodate must proceed by a mechanism that is not available to the other halates. The oxidation of water by XeF_2 proceeds very rapidly in alkaline solution, but little is known about the mechanism, and we have no basis for meaningful speculation on the manner of oxidation of iodate in such media.

The reduction of periodate by XeF_2 is inhibited both by acid and by base. The effect of acid may result from protonation of the IO_4^- to H_5IO_6,[21] while the effect of base may result either from the formation of $H_3IO_6^{2-}$ [21] or from a change in the mechanism of oxidation of water by XeF_2. We may note that the reduction of XeO_3 by XeF_2 is also markedly inhibited by base.[9]

Schneer-Erdey and Kozmutza[22] were able to analyze iodide by oxidizing it to periodate with excess XeF_2 in sulfuric acid solution and then titrating the periodate formed. Our results show that the accuracy of this method must depend on the acidity being kept high enough to suppress the reduction of periodate by XeF_2.

General Conclusions.—Although the mechanisms we have postulated for the oxidation of the halates by XeF_2 are by no means unique representations of our results, nonetheless they do permit an intercomparison of the three systems. In Table XIII are listed

TABLE XIII

PARAMETERS FOR THE OXIDATION OF HALATES BY XeF_2

Halate	$E°$, V	k_6/k_7	k_5/k_4, M^{-1}
Chlorate	1.23	29	8.9
Bromate	1.74	0.28	9.8
Iodate	1.64	25	3×10^4

values of $E°$ and of k_5/k_4 and k_6/k_7 for each of the systems. The first ratio represents the efficiency with which the halate competes with water for the oxidizing intermediate. The second ratio represents the relative tendency of the oxidized halate intermediate to go on to stable perhalate instead of reverting to halate.

We may see from the table that the efficiency with which the halate is oxidized is a function not of the electrode potential of the halate–perhalate couple but rather of its lability. Thus, for the fairly labile iodine system this ratio is much greater than for the relatively inert chlorine and bromine systems.

The value of k_6/k_7 does not show a clear-cut relationship either to lability or to electrode potential. Only in the bromate–perbromate system is this ratio particularly small. This probably indicates that oxidation of bromate to perbromate requires the formation of an intermediate of unusually high energy, and this energy is dissipated more readily by reversion to bromate than by formation of stable perbromate. The need to form such an energetic intermediate may explain why perbromates have been so difficult to synthesize.

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The Reaction of Lithium Aluminum Hydride with Secondary Amines in Diethyl Ether

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The reaction of $LiAlH_4$ with secondary amines has been studied in detail. The following compounds are formed at various stages of the reaction: Li_3AlH_6, $LiAl_2H_6NR_2$, $(R_2N)_2AlH$, $LiAlH(NR_2)_3$, and $LiAl(NR_2)_4$. The compound $LiAl_2H_6N(C_2H_5)_2$ was characterized by elemental analysis, infrared spectroscopy, and molecular association studies. A new crystalline modification of Li_3AlH_6 has been observed, and the infrared spectrum of Li_3AlH_6, prepared by the reaction of *n*-butyllithium with $LiAlH_4$, was found to be different from that previously reported.

Introduction

In their characterization of $LiAlH_4$, Schlesinger's group reported in 1947 that secondary amines react with $LiAlH_4$ to produce $LiAl(NR_2)_4$.[2] The reaction products were deduced from gas evolution studies of reaction mixtures. In 1948, in a study using $LiAlH_4$ for the measurement of active hydrogen from a series

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