hydrochloric acid at room temperature.[13] Reaction 7 is much more rapid; in 1.0 M perchloric acid at 25°, k_3 is approximately 37 M^{-1} sec^{-1} and the equilibrium constant, K, is approximately 13.[14] The greater rate of reaction 7 may best be illustrated by comparing the plutonyl(V) half-times in the two reactions; in reaction 6, assuming a representative plutonium(III) concentration of 0.04 M

$$t_{1/2}(PuO_2^+) = \frac{0.693}{0.058 \times 0.04} \simeq 300 \text{ sec}$$

while for reaction 7, assuming a plutonium(IV) concentration of 0.004 M [*i.e.*, only one-tenth of the plutonium(III) has been oxidized to plutonium(IV)]

$$t_{1/2}(PuO_2^+) = \frac{0.693}{37 \times 0.004} \simeq 5 \text{ sec}$$

and the half-time would become progressively shorter as the plutonium(IV) concentration increased. Although the conditions in reactions 6 and 7 differed, this comparison suggests that if reaction occurred by the two-electron-change mechanism, the principal oxidation product should be plutonyl(VI), rather than the plutonium(IV) actually observed. On the other hand, the known chemistry of xenon trioxide suggests that the two-electron-change mechanism would be preferred. This contradiction may be resolved by postulating that the initial plutonium(V) species produced in reaction 5 is not the usual PuO_2^+, but is another species, such as PuO^{3+} or $PuOXeO_2^{3+}$, that reacts with plutonium(III) much more rapidly than it does with plutonium(IV)

$$Pu^{3+} + XeO_3 \longrightarrow PuO^{3+} \quad (\text{or } PuOXeO_2^{3+}) \qquad (8)$$

$$PuO^{3+} + Pu^{3+} \longrightarrow 2Pu^{4+} \quad (\text{relatively rapid}) \qquad (9)$$

$$PuO^{3+} + Pu^{4+} \longrightarrow Pu^{3+} + PuO_2^{2+} \quad (\text{relatively slow}) \qquad (10)$$

Such a mechanism does not seem unreasonable if it is recalled that the formation of oxygenated species such as PuO_2^+ is slow (hence the relatively low rate of most reactions involving the formation or decomposition of such species) and apparently involves more than a single step. It seems plausible that the first step could be the formation of a monoxygenated species, such as PuO^{3+}, or of an intermediate having the same composition as the activated complex, $PuOXeO_2^{3+}$. Either of these postulated intermediates would have a charge of +3 and would therefore experience less electrostatic repulsion in reacting with plutonium(III) than with plutonium(IV), suggesting a preference for reaction 9 compared to reaction 10. On the other hand, reactions 6 and 7 involve a plutonyl(V) ion with only a single charge, and electrostatic effects are therefore less pronounced.

In summary, it appears that the reaction mechanism involves either a one-electron-change to form plutonium(IV) directly or a two-electron-change to form a plutonium(V) species other than the plutonyl(V) ion, which then reacts with plutonium(III). A mechanism involving plutonyl(V) is unlikely since the principal product would be plutonyl(VI) rather than the observed plutonium(IV).

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[13] R. E. Connick, *J. Am. Chem. Soc.*, **71**, 1528 (1949).

[14] S. W. Rabideau and R. J. Kline, *J. Phys. Chem.*, **62**, 617 (1958).

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The Reaction of Xenon Difluoride with Water and with Xenon Trioxide[1]

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In 0.01 M $HClO_4$ xenon difluoride oxidizes water with a first-order rate constant of 4.2×10^{-4} sec^{-1} at 25°, and with $\Delta H^{\ddagger} = 19.6$ kcal/mole and $\Delta S^{\ddagger} = -8.1$ eu. The reaction is catalyzed by bases and by substances with affinity for fluoride ion. Intermediates in the reaction oxidize benzenesulfonic acid and reduce XeO_3. The reduction of XeO_3 has been studied in detail. The number of XeO_3 molecules consumed per molecule of XeF_2 varies from zero to 1, depending on the initial ratio of concentrations. Mechanisms are proposed invoking XeO and XeO_2 as intermediates.

In previous papers[2,3] we have shown that xenon difluoride dissolves in water as molecular XeF_2, which then oxidizes the solvent at a measurable rate, according to the reaction

$$XeF_2 + H_2O \xrightarrow{k_1} Xe + 0.5O_2 + 2HF \qquad (1)$$

We have also observed[4] that xenon trioxide introduced into an XeF_2 solution is consumed in the course of reac-

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2297 (1964).

[3] E. H. Appelman, *Inorg. Chem.*, **6**, 1268 (1967).

[4] E. H. Appelman and J. G. Malm, "Preparative Inorganic Reactions," Vol. 2, W. L. Jolly, Ed., Interscience Publishers, Inc., New York, N. Y., 1965, p 344.

tion 1, although an aqueous solution of XeO_3 is itself stable.[5]

In this paper we report an investigation of reaction 1 and of the interaction of XeO_3 with XeF_2, by which we have hoped to elucidate both the mechanism of reaction 1 and the manner in which XeO_3 acts as an oxidizing agent. To this end we have also examined briefly the reaction of XeF_2 with benzenesulfonic acid.

Experimental Section

Reagents.—Saturated aqueous solutions of xenon difluoride were prepared and stored as described elsewhere.[3] These solutions contained no detectable XeO_3 (less than 0.1 mole %). One sample of XeF_2 was redistilled under vacuum between two Kel-F tubes before being dissolved in water. No difference in behavior was observed between the redistilled XeF_2 and the ordinary preparations.

Solutions of XeO_3 in dilute nitric acid ($[HNO_3] = 0.025 \cdot [XeO_3]$) were also prepared as described elsewhere.[5] A small quantity of XeO_3 was evaporated to dryness, sublimed under vacuum, and redissolved in water to make a high-purity solution.[6] The behavior of the repurified XeO_3 was indistinguishable from that of the ordinary preparations.

Solutions of thorium perchlorate in perchloric acid were made from thorium nitrate by fuming with excess perchloric acid and then diluting. Solutions of benzenesulfonic acid were made by dissolving recrystallized sodium benzenesulfonate (Fluka AG, Buchs SG, Switzerland) in perchloric acid. Ordinary distilled water was redistilled either from alkaline permanganate or through hot copper oxide before use. All other chemicals were commercial products of reagent grade.

Analyses.—Solutions of XeO_3 and of XeF_2 were analyzed iodometrically by adding iodide and acid and titrating the liberated triiodide with thiosulfate.[2,5] To test for XeO_3 present in an XeF_2 solution, a large excess of $Th(ClO_4)_4$ was added. This brought about rapid reduction of the XeF_2 with no loss of XeO_3, and any XeO_3 present could subsequently be determined iodometrically.

Low concentrations of hydrogen peroxide were also determined iodometrically, using ammonium molybdate to catalyze the reaction with iodide.[7] These analyses were carried out in a potassium hydrogen phthalate–sodium hydroxide buffer to minimize the oxidation of iodide by air, and the triiodide formed was determined spectrophotometrically at its 350-mμ absorption peak (ϵ 2.63 × 10^4).[7]

Spectrophotometry.—A Cary 14 spectrophotometer with a thermostated cell compartment was used for all measurements. Fused-quartz cells varied in path length from 0.1 to 10 cm depending on the experiment. The reaction of XeF_2 with water was followed at the 242-mμ XeF_2 absorption peak (ϵ 83),[2] while the reaction of XeO_3 with XeF_2 was followed at 230 mμ, where the XeF_2 absorption goes through a shallow minimum (ϵ 79)[2], while that of XeO_3 is quite high (ϵ 1150).[5] Reactions were generally monitored for at least 3 half-times.

Gas Measurements.—Reactions to be examined by gas measurement were carried out in glass bulbs closed by greaseless valves using Teflon plugs with Viton O-ring packing (Fischer and Porter Co., Warminster, Pa.). When these valves were closed, the materials in the bulbs were exposed only to glass and Teflon.

A typical reaction was carried out in the following way. The solution was frozen and the bulb was evacuated. The solution was then outgassed by successively closing it off, thawing it, refreezing it, and pumping off the evolved gases. Finally, the closed bulb was warmed quickly to 25° and allowed to remain for an interval corresponding to 1–2 half-times of reaction, after which the solution was again frozen, and the evolved gases were measured. A thawing–refreezing cycle removed gases trapped in the solution. The solution was then closed off again, warmed, and allowed to stand until reaction was essentially complete, when once more the evolved gases were measured.

Using a cold trap, the gases were separated into a fraction that could be held in liquid nitrogen (Xe and CO_2) and a fraction that could not (O_2 and N_2). A Toepler pump was used to transfer each fraction into a gas buret, where the quantity was measured, after which its composition was determined mass spectrometrically.

Exchange Measurements.—For the xenon exchange experiments, xenon gas containing a mixture of radioactive isotopes was obtained from Oak Ridge National Laboratory. It was diluted with inactive xenon and used to synthesize radioactive XeF_2. Solutions containing various other reagents were made up *ca.* 0.03 *M* in this XeF_2 and in inactive XeO_3. After the XeF_2 had all reacted with the water, argon was bubbled in to flush out the xenon gas, and the remaining solutions were counted in a well-type sodium iodide scintillation counter. The XeO_3 content of the solutions was then determined iodometrically.

Fluoride Measurements.—In one experiment the progress of reaction 1 was followed by monitoring the HF produced. A Beckman Research pH meter was used in conjunction with a fluoride-sensitive electrode (Orion Research, Inc., Cambridge, Mass.) and a calomel reference electrode. Samples of the reaction mixture were withdrawn at periodic intervals, and their emf's were measured with this electrode system.

General Conditions.—Except as otherwise indicated, all reactions were carried out at 24.95 ± 0.1°. Unless otherwise specified, all solutions contained sufficient $HClO_4$ to make the initial H^+ concentration 0.01 *M*. (In some cases HNO_3 from the XeO_3 stock made an appreciable contribution to the acidity.)

Computations and Conventions

Throughout this paper the symbols $[X]_0$ and $[X]_\infty$ refer, respectively, to the concentration of species X at the beginning and end of a reaction. All concentrations are expressed in units of moles per liter.

Measurements of the kinetics of first-order reactions were fitted to the equation $D(t) = D(\infty) + Ae^{-kt}$, where $D(t)$ is the measured optical density, titer, HF concentration, or quantity of gas evolved at time t, and k is the first-order rate constant. Gas evolution data were fitted by inspection, but in all other cases a weighted least-squares program was used on an IBM 1620 computer, with k, A, and $D(\infty)$ introduced as adjustable parameters. In the case of iodometric titrations at high XeF_2 concentrations, $D(\infty)$ was fixed at zero. First-order rate constants are all given in units of reciprocal seconds.

When reaction kinetics were monitored by fluoride evolution, the HF concentrations were calculated from the measured emf values, $E(t)$, by means of the relation

$$[\mathrm{HF}] = \left[1 + \frac{KC(e^{-aE(t)} - e^{-aE(0)})}{([\mathrm{H}^+]_0 + 2[\mathrm{XeF}_2]_0)^2}\right]Ce^{-aE(t)}$$

where

$$C = \frac{2[\mathrm{XeF}_2]_0}{e^{-aE(\infty)} - e^{-aE(0)}}$$

a is the reciprocal of the Nernst constant, RT/F, and K is the acid dissociation constant of HF, taken to be 7 × 10^{-4}. The factor in brackets is an approximate correction for changes in acidity during the reaction.

Spectrophotometric data for kinetic systems that did not have analytical solutions (Table IV) were fitted

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[5] E. H. Appelman and J. G. Malm, *J. Am. Chem. Soc.*, **86**, 2141 (1964).

[6] The repurified XeO_3 solution was prepared by Dr. John Huston of Loyola University, Chicago, Ill.

[7] E. J. Hart, *J. Am. Chem. Soc.*, **73**, 68 (1951).

with the help of an analog computer. Extinction coefficients and starting concentrations were introduced, and rate constants were varied to fit the experimental curves of optical density *vs.* time. Intermediates were assumed to make negligible contribution to the total optical density.

Solutions to the transcendental eq 6 for the stoichiometry of the XeF_2–XeO_3 reaction were obtained on the IBM 1620 computer.

Results

Reaction of XeF_2 with Water.—The reduction of XeF_2 by water in dilute acid was found to be first order in XeF_2 over at least 90% of the reaction and over a 1000-fold range of initial concentrations. Essentially the same rate constant was obtained by spectrophotometry, by iodometric titration, and by measurements of HF production and gas evolution. Typical results appear in Table I. From the observed temperature dependence we can calculate $\Delta H^{\ddagger}_{298} = 19.6 \pm 0.3$ kcal/mole and $\Delta S^{\ddagger}_{298} = -8.1 \pm 0.9$ eu.

TABLE I

OXIDATION OF WATER BY XeF_2[a]

$10^3[XeF_2]_0$, M	Special conditions	10^4k_1, sec^{-1}
150	By iodometric titration	4.33
15		4.24
14	By gas evolution	4.5
3.2	By HF production	4.4
2.2		4.23
0.1		4.00
2.2	34.95°	12.7
2.2	14.87°	1.27
1.2	0.001 M $HClO_4$	5.06
2.2	1.98 M $HClO_4$	8.2
0.5	0.0068 M NaOH	505
1	0.0094 M $Th(ClO_4)_4$	230[b]

[a] Spectrophotometric measurements unless otherwise specified.
[b] Based on initial rate. The apparent rate constant decreased as reaction proceeded.

After the XeF_2 had been consumed, a residual oxidizing species was found in the solutions. This species, unlike XeF_2 itself, oxidized iodide very slowly in dilute acid. The reaction was markedly catalyzed by ammonium molybdate, and the species was thereby identified as hydrogen peroxide. The concentration of the peroxide residue was independent of the initial XeF_2 concentration, at least over the 10^{-4}–10^{-3} M interval, but it was not reproducible, varying from 6×10^{-7} to 3×10^{-6} M.

Reaction of XeF_2 with Benzenesulfonic Acid.—Experiments were carried out in deaerated solutions at XeF_2 concentrations of 6×10^{-4} and 3×10^{-3} M, with benzenesulfonic acid concentrations of 8×10^{-4} and 4×10^{-3} M, respectively. The reactions were followed by gas evolution. In neither experiment was any significant quantity of oxygen evolved. At the lower concentration 66.7% of the xenon was evolved in 51 min. At the higher concentration 67.2% of the xenon was evolved in 48 min. If the rates were first order in XeF_2 and independent of the benzenesulfonic acid, the respective constants would be 3.6 and 3.9×10^{-4} sec^{-1}. The solutions remaining at the end of these reactions were distinctly yellow.

Reaction of XeF_2 with XeO_3.—This reaction may be represented

$$XeF_2 + nXeO_3 + H_2O \longrightarrow (1 + n)Xe + \left(\frac{1 + 3n}{2}\right)O_2 + 2HF$$

The stoichiometry number, n, was observed to vary from zero to 1. It was found to depend primarily on the *ratio* of the initial concentrations, $[XeF_2]_0/[XeO_3]_0$, and only weakly on the concentrations themselves. The results appear in Figures 1 and 2. The two figures display the same data, but in Figure 2, the stoichiometry is expressed in terms of the fraction of the initial XeO_3 remaining at the end of the reaction: $[XeO_3]_\infty/[XeO_3]_0$. This is related to n by the equation

$$n = \frac{[XeO_3]_0}{[XeF_2]_0}\left[1 - \frac{[XeO_3]_\infty}{[XeO_3]_0}\right] \qquad (2)$$

The stoichiometry was found to be unaffected by light and to be the same whether the reactions were carried out in glass or Kel-F vessels. Table II shows the effect of changes in medium on the stoichiometry.

The kinetic and stoichiometric data have been analyzed in terms of the reaction scheme

$$XeF_2 \xrightarrow{k_2} A \qquad (3)$$

$$A + XeF_2 \xrightarrow{k_3} \text{products} \qquad (4)$$

$$A + XeO_3 \xrightarrow{k_4} \text{products} \qquad (5)$$

If a steady state is assumed in A, these equations can be solved to give an expression for the stoichiometry[8]

$$\frac{[XeO_3]_\infty}{[XeO_3]_0} = \left[1 - \frac{[XeF_2]_0}{[XeO_3]_0}\alpha\right]^{1/\alpha} \qquad (6)$$

where $\alpha = 1 - (2k_3/k_4)$. Equations 2 and 6 have been used to calculate the lines in Figures 1 and 2, and the k_3/k_4 values in Table II.

The differential equations corresponding to reactions 3–5 cannot be solved explicitly as a function of time, except for the limiting cases in which $[XeF_2]_0/[XeO_3]_0$ approaches zero or infinity. In the former limit n approaches unity and we have

$$[XeO_3] - [XeO_3]_\infty = ([XeO_3]_0 - [XeO_3]_\infty)e^{-k_2t} \qquad (7)$$

and

$$[XeF_2] = [XeF_2]_0e^{-k_2t} \qquad (8)$$

In the latter limit n approaches zero, leaving us with reaction 1 and the expression

$$[XeF_2] = [XeF_2]_0e^{-2k_2t} = [XeF_2]_0e^{-k_1t} \qquad (9)$$

Thus we predict that $k_1 = 2k_2$.

The kinetic results are summarized in Tables III and IV. When limiting conditions applied, k_2 was evaluated from the appropriate ones of eq 7–9. Otherwise k_2 and k_3/k_4 were determined with an analog computer. The computed values of k_3/k_4 are compared in

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(8) This expression was derived by Dr. Robert Buchal of the Argonne Applied Mathematics Division. In the special case of $\alpha = 0$, the equation reduces to $[XeO_3]_\infty/[XeO_3]_0 = e^{-[XeF_2]_0/[XeO_3]_0}$.

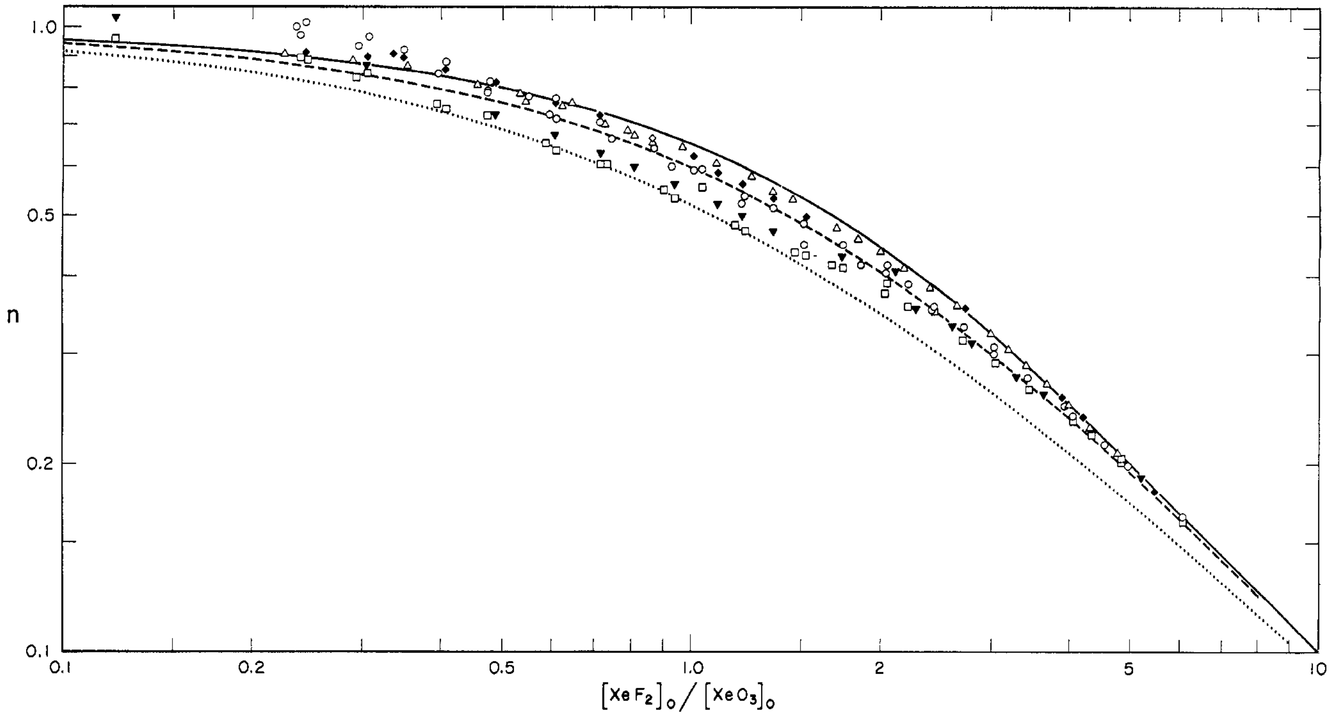

Figure 1.—Stoichiometry of reaction of XeO_3 with XeF_2: □, $[XeF_2]_0 = 1.5 \times 10^{-3}$ *M*; ▼, $[XeF_2]_0 = 5 \times 10^{-3}$ *M*; ○, $[XeF_2]_0 = 0.015$ *M*; ◆, $[XeF_2]_0 = 0.05$ *M*, $[H^+]_0 = 0.008$ *M*; △, $[XeF_2]_0 = 0.13$ *M*, no added $HClO_4$; ———, $k_3/k_4 = 0.45$; – – – –, $k_3/k_4 = 0.6$; · · · · ·, $k_3/k_4 = 0.9$. The two points at the far left were obtained from gas evolution data. The others came from analysis of the XeO_3 remaining at the end of the reactions.

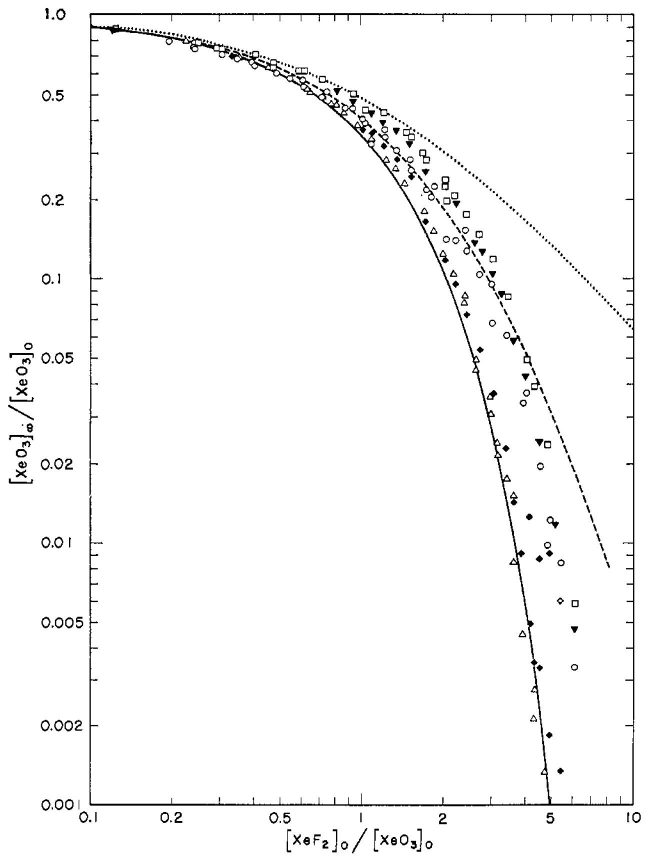

Figure 2.—XeO_3 remaining after reaction with XeF_2. The data are the same as in Figure 1, and the same key applies.

Table IV with those calculated by means of eq 6 from the stoichiometry data at comparable concentrations.

Each of the spectrophotometric runs of Table IV could be fitted to within the experimental uncertainties of the measurements. However, the variation of k_3/k_4 among the runs is seen to reflect that in the stoichiometric data. In an attempt to explain this variation, the analog computer was used to consider the effects of three other reactions

TABLE II

EFFECT OF MEDIUM ON THE STOICHIOMETRY OF THE REACTION BETWEEN XeF_2 AND XeO_3[a]

Medium	$[XeO_3]_\infty/[XeO_3]_0$	k_3/k_4
H_2O	0.192	0.62
0.01 *M* $HClO_4$	0.175	0.58
0.12 *M* $HClO_4$	0.232	0.71
1.2 *M* $HClO_4$	0.455	1.56
0.3 *M* HF	0.238	0.73
0.2 *M* NaOH	0.919	29
$[Th(ClO_4)_4] = [HClO_4] = 0.45$ *M* $[XeF_2]_0 = 0.1$, $[XeO_3]_0 = 0.001$ *M*	1.00	∞

[a] Except as otherwise noted, $[XeF_2]_0 = 0.015$ *M* and $[XeO_3]_0 = 0.0074$ *M*.

TABLE III

KINETICS OF REACTION OF XeF_2 WITH XeO_3 (GAS EVOLUTION MEASUREMENTS)

$10^3[XeF_2]_0$, *M*	$10^3[XeO_3]_0$, *M*	10^4k_2,[a] sec^{-1}	$[Xe]/[O_2]$[b]
14	. . .	2.2	2.04
0.3	2.5	2.6	1.00
1.5	12.5	2.7	1.01
7	58	3.0	0.99
7	235	4.2	0.98
29[c]	1520	11	1.00

[a] First value from eq 9; others from eq 7 and 8. [b] Ratio of gases evolved in entire reaction. [c] No added $HClO_4$; $[H^+]_0 = 0.04$ *M*.

$$\mathrm{A} \longrightarrow \text{products}$$

$$2\mathrm{A} \longrightarrow \text{products}$$

$$XeF_2 + XeO_3 \longrightarrow \text{products}$$

These equations were introduced one by one with various values for their rate constants, and $[XeO_3]_\infty/[XeO_3]_0$ *vs.* $[XeF_2]_0/[XeO_3]_0$ was calculated and compared with the data of Figures 1 and 2. A significant contribution by any of these reactions was found to be inconsistent with the experimental results. In a similar manner, we also found that breakdown of the steady-state approximation would lead to results quite different from those observed.

Isotopic Exchange between XeO_3 and XeF_2.—Exchange was sought in each of the following media: 0.1 *M* $HClO_4$, 0.6 *M* $Th(ClO_4)_4$ + 0.6 *M* $HClO_4$, 0.7 *M* Na_2HPO_4 + 0.9 *M* NaH_2PO_4, 0.25 *M* $K_2B_4O_7$ + 0.1 *M* H_3BO_3, 0.6 *M* K_2CO_3 + 0.8 *M* $KHCO_3$, and 0.4 *M* NaOH. In no case was exchange observed to exceed 0.15%.

TABLE IV

KINETICS OF REACTION OF XeF_2 WITH XeO_3 (SPECTROPHOTOMETRIC MEASUREMENTS)

$10^3[XeF_2]_0$, *M*	$10^3[XeO_3]_0$, *M*	10^4k_2,[a] sec^{-1}	k_3/k_4	
			Kinetics[a]	Stoichiometry[b]
1.04	14.9	2.4[c]	...	
3.04	15.1	2.5	0.45	0.45
7.07	15.3	2.5	0.85	0.75
15.2	14.4	2.4	0.7	0.6
0.63	7.3	2.3[c]	...	
1.73	7.3	2.6	0.7	0.5
6.0	7.3	2.3	0.7	0.8
15.1	6.8	2.6	0.7	0.6
0.282	2.72	2.4[c]	...	
0.94	2.58	2.4	0.85	0.8
2.48	2.63	2.2	0.75	0.85
6.85	2.62	2.45	0.7	0.65
15.9	2.45	2.25	0.6	0.5
0.147	1.38	2.3[c]	...	
0.464	1.34	2.2	0.75	
1.42	1.34	2.3	0.85	0.9
5.09	1.34	2.3	0.65	0.6
8.25	1.08	2.4	0.65	0.5
15.4	0.62	2.45	0.8	
0.071	0.695	2.4[c]	...	
0.229	0.684	2.1	0.85	
0.732	0.685	2.3	0.95	0.9
2.53	0.682	2.1	0.65	0.6
4.28	0.493	2.2	0.6	0.5
6.91	0.385	2.45	0.85	
0.0287	0.279	2.4[c]	...	
0.093	0.275	2.3	0.85	
0.275	0.271	2.35	0.9	
0.93	0.272	2.25	0.65	0.65
1.61	0.226	2.25	0.65	0.5
2.72	0.136	2.15	0.7	
0.0136	0.139	2.2[c]	...	
0.0445	0.139	2.1	1.0	
0.1515	0.137	2.25	0.9	
0.478	0.138	2.15	0.65	
0.784	0.113	2.15	0.65	0.5
1.33	0.0745	2.25	0.8	

[a] Constants evaluated with analog computer unless otherwise indicated. [b] From data of Figures 1 and 2, using eq 6. [c] From eq 7.

Discussion

The data in Table I substantiate our previous observation that the oxidation of water by XeF_2 is markedly catalyzed by bases and by substances with strong affinity for fluoride, such as ZrO_2 and Th^{4+}.[2] This suggests that the rate-determining step in reaction 1 is a bimolecular hydrolytic process consisting of either a nucleophilic attack on the xenon by H_2O or OH^-, or else an electrophilic attack on the fluorines by such species as Th^{4+}. The hydrolyzed Xe(II) species, whether an oxide or an ion, must then react rapidly with the solvent.

Our results show that XeF_2 reacts with benzenesulfonic acid at the same rate at which it reacts with water. Hence the rather inert benzenesulfonic acid must be reacting with a powerful oxidant formed as an intermediate in the reaction of XeF_2 with water. On the other hand, the reaction with XeO_3 indicates that an intermediate with reducing properties must also be formed.

Equations 2–4 clearly do not provide a perfect description of the reaction between XeF_2 and XeO_3. Figures 1 and 2 and Table IV show a definite dependence of k_3/k_4 on concentration and on the $[XeF_2]_0/[XeO_3]_0$ ratio, while Table III shows k_2 to increase at the highest XeO_3 concentrations. The variation in k_3/k_4, however, generally does not exceed a factor of 2 over a range of 10^4 in concentration and 10^2 in $[XeF_2]_0/[XeO_3]_0$. (An exception is the set of high points at the left side of Figure 1, but in that region k_3/k_4 is extremely sensitive to small changes in $[XeO_3]_\infty$.) The value of k_2 is nearly constant below 0.05 *M* XeO_3 and is approximately equal to $k_1/2$. The increase at higher XeO_3 concentrations may be due to catalysis either by XeO_3 itself or by impurities in the XeO_3 stock. (The repurified XeO_3 was not used for these high concentration experiments.) In view of all of these considerations it seems probable that eq 2–4 do represent the major processes involved in the interaction of XeF_2 with XeO_3, though they almost certainly do not tell the entire story.

What, then, is the nature of the reducing intermediate "A"? Hydrogen peroxide is an attractive choice, since it is found as a residue from the oxidation of water by XeF_2. We could then write the reaction scheme

$$XeF_2 + H_2O \xrightarrow{k_2} XeO + 2HF \quad \text{(rate determining)} \qquad (10)$$

$$XeO + H_2O \longrightarrow Xe + H_2O_2 \quad \text{(fast)} \qquad (11)$$

$$H_2O_2 + XeF_2 \xrightarrow{k_3} Xe + O_2 + 2HF \qquad (12)$$

$$H_2O_2 + XeO_3 \xrightarrow{k_4} XeO_2 + O_2 + H_2O \qquad (13)$$

$$XeO_2 \longrightarrow Xe + O_2 \quad \text{(fast)} \qquad (14)$$

The powerful oxidant that reacts with benzenesulfonic acid could be XeO, or it could be OH formed as an intermediate in reaction 11. In either case, a product of the oxidation has to react with XeF_2 in order that the rate of the xenon difluoride–benzenesulfonic acid reaction remain the same as that of the XeF_2–H_2O reaction.

This mechanism could be tested by examining the reactions of XeF_2 and XeO_3 with H_2O_2. Detailed studies of these reactions are now underway and will be published separately. Preliminary results, however, are not quantitatively consistent with the identification of intermediate A as hydrogen peroxide.

An alternate possibility is that A is the hydrolyzed divalent xenon species, to which we must then attribute reducing properties. In that case, after formation of the hydrolyzed species by rate-determining reaction 10, we may write

$$\mathrm{XeO} + \mathrm{XeF_2} \xrightarrow{k_3} \mathrm{Xe} + \mathrm{XeOF_2} \tag{15}$$

$$\mathrm{XeO} + \mathrm{XeO_3} \xrightarrow{k_4} 2\mathrm{XeO_2} \tag{16}$$

$$\mathrm{XeOF_2} + \mathrm{H_2O} \longrightarrow \mathrm{XeO_2} + 2\mathrm{HF} \quad \text{(fast)} \tag{17}$$

followed by reaction 14. The lack of xenon exchange between XeF_2 and XeO_3 rules out reversibility of reaction 16. The H_2O_2 remaining after reaction of XeF_2 with water could arise from a side reaction of XeO or XeO_2 with the solvent, while benzenesulfonic acid could be oxidized by either the XeO or the XeO_2.

These reaction schemes can hardly be considered unique, but a tetravalent xenon species appears to be an essential intermediate in any satisfactory mechanism, while a hydrolyzed divalent species, though not essential, seems highly probable.

At this time we can say little about the effect of changes in the medium on the stoichiometry of the XeF_2–XeO_3 reaction (Table II). In all cases the consumption of XeO_3 is decreased, indicating a change in the nature of the reducing intermediate or in its reactivity or both. The lack of a strong H^+ dependence is consistent with either of our proposed mechanisms, but in alkaline solution the situation is complicated by the oxidation of XeO_3 to perxenate by the XeF_2.[2] It is worthy of note that when the oxidation of water by XeF_2 is catalyzed by Th^{4+}, no XeO_3 is consumed. At the time it is being reduced, the divalent xenon may be coordinated to the thorium through a fluoride bridge and therefore may be unable to attack an XeO_3 molecule.

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Alkyl- and Arylaluminum Complexes. I. The Reaction of Trialkyl- and Triarylaluminum with Bidentate Ligands

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A series of dialkyl- and diarylaluminum complexes have been prepared through the reactions of trialkyl- and triarylaluminum compounds with bidentate ligands featuring hydroxyl and amino functional groups. The dimeric nature of these compounds is explained on the basis of stereochemical considerations and nmr and infrared spectroscopy, upon which evidence it is concluded that, in all but one case, bridging occurs through the terminal oxygen *and* nitrogen atoms of the bidentate ligands. The exception is diethylaluminum 3-aminopropoxide, in which bridging occurs through the oxygen bonded to the metal ion.

Introduction

While there have been extensive investigations pertaining to the reactions of triaryl- and trialkylaluminum compounds with alcohols[1] and amines,[2] relatively few studies have been reported concerning the interaction of such aluminum compounds with chelating agents containing both of these functional groups. In fact, whereas there have been recent reports of the preparation of dialkylaluminum complexes of bis-oxygen bidentate ions such as acetylacetonate[3] or diphenylphosphinate,[4] the only well-documented example of aluminum, featuring oxygen and nitrogen bonding, is aluminum tris-8-quinolinate.[5] Several types of aluminum complexes with nitrogen- and oxygen-containing bidentate ligands are reported herein together with the structural elucidation of these compounds.

Results and Discussion

In the interests of comparing stabilities, characteristics, and stereochemistry, we have prepared a series of dialkyl- and diarylaluminum complexes with bidentate ligands featuring hydroxyl and amino functional groups. The empirical formula of the series is R_2Al-

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