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Studies of the Aqueous Chemistry of Fluorine and Hypofluorous Acid[1]

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Abstract: Both F_2 and HOF react with water to produce H_2O_2 concentrations that approach a steady state. The results are consistent with the mechanism

$$F_2 + H_2O \xrightarrow{k_1} HOF + HF \tag{1}$$

$$HOF + H_2O \xrightarrow{k_2} H_2O_2 + HF \tag{2}$$

$$F_2 + H_2O_2 \xrightarrow{k_3} O_2 + 2HF \tag{3}$$

$$HOF + H_2O_2 \xrightarrow{k_4} O_2 + HF + H_2O \tag{4}$$

At 1 °C $k_1/k_3 = 0.24$ M and $k_2/k_4 = 0.86$ M. The O_2 formed in reaction 4 contains a substantial amount of oxygen from HOF. This is a unique observation in the oxidation of H_2O_2, and an oxygen-transfer mechanism has been proposed to account for it. Application of the principles of mass transfer with chemical reaction has led to an estimate of $k_1 = 10^{5.0\pm0.3}$ s^{-1} at 1 °C. Under ordinary conditions the fluorine reacts within a liquid layer about 10^{-5} cm deep.

That fluorine reacts vigorously with water has been known since the time of Moissan.[3] Both the mechanism of the interaction and the actual rate of reaction have, however, remained obscure. The principal products were shown in a classical study by Cady[4] to be HF, O_2, and H_2O_2, along with small amounts of OF_2. It was not until over three decades later, however, that the identification and isolation of HOF[5,6] led to the conclusion that much, though not all, of the behavior of F_2 in water could be attributed to the formation of HOF as an intermediate.[7]

Although the fluorine–water system has not often been employed for synthetic purposes, the results that have been obtained suggest that the system may, in fact, have unique oxidizing and fluorinating capabilities. Thus, for example, fluorination of alkaline bromate solutions is the only practical route to perbromate,[8] while certain boranes are cleanly fluorinated only in aqueous solution,[9] and fluorination of aqueous sulfate solutions produces the unusual fluoroxysulfate ion, O_3SOF^-.[10] A thorough understanding of the fluorine–water interaction could well lead to many further synthetic applications.

In this paper we have undertaken to elucidate a prominent feature of the fluorine–water reaction: the production of H_2O_2 and O_2. Because this process almost certainly involves the intermediate formation of HOF, we have also examined the production and consumption of H_2O_2 in the reaction of HOF with water and the mechanism of the HOF–H_2O_2 reaction. In addition, we have undertaken to obtain at least an order-of-magnitude estimate of the rate of the homogeneous reaction of F_2 with water and have determined the effects of various added substrates.

Experimental Section

Materials. Hypofluorous acid was prepared by the reaction of F_2 with ice at −50 °C in a circulating system.[11] It was collected in a Kel-F U-tube cooled to −183 °C and stored at this or lower temperature until used. Hypofluorous acid enriched in ^{18}O was prepared in the same fashion from ^{18}O-enriched ice.

Fluorine was a commercial product of technical grade (Air Products Corp.). The 97+% material was used for preparation of HOF and for the quantitative studies of absorption kinetics. A 20% v/v mixture in nitrogen was used for the studies of H_2O_2 production and consumption. Carbon dioxide was C.P. Grade, and oxygen was Extra-Dry Grade.

ACS Reagent-Grade H_2O_2 (very lightly stabilized) was used for most experiments, but for one ^{18}O tracer study a highly stabilized material (Du Pont Albone 70DG) was used. Sodium fluorophosphate and selenate were obtained from Alfa Inorganics. All other chemicals were commercial products of analytical reagent grade. Distilled water was redistilled first from alkaline permanganate and then from acid dichromate.

Analytical Methods. Fluorine, HOF, and H_2O_2 were analyzed by reaction with I^- followed by titration of the liberated I_3^- with standardized thiosulfate. The fluorine and HOF were delivered into 1 M KI solutions, the HOF being carried in a stream of nitrogen. The H_2O_2 samples were acidified with H_2SO_4 and mixed with excess 0.2 M KI, after which a small amount of ammonium molybdate was added to catalyze the peroxide–iodide reaction.[12] Hydrogen fluoride was determined by titration with standardized NaOH.

The oxygen content of moderately enriched water was determined mass spectrometrically after conversion to O_2 by the Co(II)-catalyzed reaction with OBr^- in alkaline solution.[13] For the highly enriched (95 atom% ^{18}O) water, the analysis of the supplier (Monsanto Research Corp.) was accepted. Isotopic compositions of O_2 samples were determined with a Consolidated Model 21-620 mass spectrometer.

In the F_2 absorption experiments, pressures were monitored with a Monel Bourdon gauge (Acco Helicoid) that had a full-scale range of 800 torr absolute, an accuracy of $\pm^1/_4$% of full scale, and a resolution of ±1 torr. Composition of gas present at the end of absorption experiments was estimated with a Finnigan 400 quadrupole mass spectrometer, using a Kel-F inlet system.

General Procedures. To monitor the production and consumption of H_2O_2 in the reaction of F_2 with aqueous solutions, F_2(20% v/v in N_2) was bubbled through ca. 200 mL of aqueous solution in a 250-mL Teflon bottle immersed in a water bath. A Teflon delivery tube with a ca. 1-mm orifice was used, and the solution was stirred with a magnetic stirrer and a Teflon-coated stirring bar. Under these conditions ca. 70% of the fluorine reacted with the solution and the remainder escaped. (Retention was determined by collecting the effluent gas in 1 M KI and titrating with thiosulfate.)

Reactions of HOF with aqueous H_2O_2 were carried out by delivering the HOF in a stream of nitrogen into 1–10 mL of the desired solution in a Kel-F tube immersed in an ice bath. The HOF was held in a Kel-F

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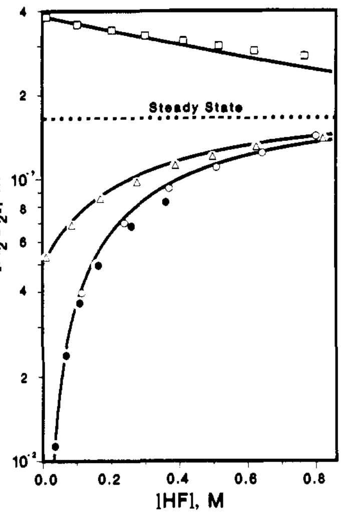

Figure 1. Approach of H_2O_2 concentration to steady state in reaction of F_2 with aqueous solutions at 1 °C. Absorption of F_2 is ca. 3×10^{-5} M/s except for (●), where it is 1×10^{-5} M/s. Initial $[H_2O_2]$: (● and ○) none; (△) 0.053 M; (□) 0.381 M. All solutions initially 0.01 M in HF. Smooth curves calculated for $k_1/k_3 = 0.243$ M and $k_2/k_4 = 0.86$ M.

U-tube at −40 to −50 °C through which the nitrogen stream was passed. A Kel-F bubbler with a ca. 1-mm orifice was used.

To determine the isotopic composition of the O_2 formed in the reaction between HOF and H_2O_2, a plug of 9 M H_2O_2 was drawn into an evacuated Kel-F U-tube containing frozen HOF in such a way that no significant amount of air was introduced. The mixture was allowed to warm up and react, and the evolved O_2 was analyzed by mass spectrometry. In one experiment the unreacted H_2O_2 that remained after the reaction was transferred to a two-legged glass mixing tube, reevacuated, and oxidized with excess Ce(IV) to yield O_2 for further mass spectrometric analysis.

Experiments on the kinetics of absorption of fluorine into aqueous solution were carried out in a stirred reactor that consisted of a cylindrical Pyrex vessel 16 cm long by 65 mm i.d. (see Figure 2). The bottom of the vessel was sealed flat, while the top was tapered to a neck 12.5 mm o.d. × 9 mm i.d. × 45 mm long. The vessel had a volume of 546 cm^3 and contained a Teflon-coated magnetic stirring bar 27 mm long × 8 mm o.d. For use it was charged with aqueous solution (usually 100 cm^3) and connected by its neck to a Monel vacuum line of ca. 470 cm^3 volume, by means of a Monel bellows valve and a $^1/_2$-in. Swagelok fitting with a Teflon ferrule. A second valve permitted isolation of the portion of the vacuum line directly adjacent to the Pyrex vessel from the rest of the line. This portion had a total volume of ca. 45 cm^3 and contained the Monel Bourdon gauge used to monitor pressure. The aqueous solution was frozen, and the vessel was evacuated. The solution was thawed, and residual gas was removed by pumping off several 470-cm^3 vapor "heads". The valve between the reaction vessel and the vacuum line was closed, and the line was filled with F_2 (97+%) to a pressure about double that desired for the reaction. The valve to the reaction vessel was quickly opened and the isolation valve was closed. This left the reaction vessel connected only to the 45-cm^3 portion of the vacuum line that contained the pressure gauge. The decrease in pressure with time was monitored. If stirring was employed, it was usually carried out at about 600 rpm. This created a small vortex but did not substantially increase the surface area of the solution. In some cases, after reaction was complete, the residual gas was removed by pumping off vapor heads, and a second charge of F_2 was added.

In a few experiments that were carried out to test the effect of water initially absorbed on surfaces, no water was placed directly into the reaction vessel, but instead a small amount of water was contained in a tube of 6-mm i.d. which was inserted into the vessel.

In one experiment a Teflon valve (Fluoroware, Inc.) was used to isolate the glass reaction vessel from the metal vacuum line. During the reaction this valve was opened briefly about once every minute to permit measurement of the pressure.

Results

Production and Consumption of H_2O_2 in the Reactions of F_2 and HOF with Aqueous Solutions. The steady-state concentrations of H_2O_2 formed in the reactions of F_2 and HOF were established by identifying initial H_2O_2 concentrations that were only slightly increased or decreased by the addition of reagent. The results of these experiments are given in Tables I and II. Figure 1 shows the buildup or consumption of H_2O_2 during the addition of F_2 to solutions containing initial H_2O_2 concentrations that were far from the steady-state values. The derivation of the calculated curves will be given in the Discussion. In most cases, if no other pH-controlling substrate was present, the solutions were initially made 0.01 M in HF to minimize pH changes in the early part of the reactions.

Table I. Steady-State $[H_2O_2]$ from Reaction of F_2 with Aqueous Solutions[a]

substrate	F_2 absorbed,[b] M	$[H_2O_2]$, M initial	$[H_2O_2]$, M final	$[H_2O_2]$, M steady-state
0.01 M HF	0.05	0.1789	0.1756	0.16_3
	0.05	0.1472	0.1495	
0.01 M HF[c]	0.04	0.1630	0.1621	0.15_2
	0.05	0.1391	0.1419	
0.01 M HF[d]	0.016	0.1535	0.1517	
	0.016	0.1180	0.1186	0.136
	0.026	0.1364	0.1364	
H_2O	0.05	0.1984	0.1924	
	0.05	0.1607	0.1619	0.165
	0.05	0.1714	0.1669	
H_2O[a]	0.08	0.1763	0.1880	
	0.09	0.2226	0.2272	0.25
	0.08	0.2584	0.2569	
0.1 M NaF +	0.055	0.1310	0.1291	
0.01 M HF	0.05	0.1131	0.1112	0.106
	0.06	0.1001	0.1024	
0.5 M $NaHCO_3$	0.07	0.3945	0.3921	
	0.08	0.2669	0.2748	0.31
	0.10	0.3382	0.3335	
1 M $HClO_4$	0.05	0.1658	0.1607	
	0.05	0.1511	0.1480	0.142
	0.08	0.1341	0.1357	

[a] Unless otherwise specified, at 1 °C with a flow of 0.4–0.5 mmol F_2/min into 200 cm^3 of solution. [b] Based on HF produced except for $NaHCO_3$ and $HClO_4$ solutions, for which it is based on gross F_2 flow and independently measured retention. [c] Volume of solution only 40 cm^3. [d] F_2 flow ca. 0.06 mmol/min. [e] At 23 °C.

Table II. Steady-State $[H_2O_2]$ from Reaction of HOF with Aqueous Solutions[a]

substrate	volume, cm^3	$[H_2O_2]$, M initial	$[H_2O_2]$, M final	$[H_2O_2]$, M steady state
0.01 M HF	1[b]	8.97	6.21	
	9	0.450	0.519	0.86
	4.5	0.987	0.904	
	5.2	0.784	0.830	
0.5 M $NaHCO_3$	9.5	0.657	0.703	1.1
		1.075	1.078	

[a] At 1 °C. Unless otherwise noted, ca. 1.5 mmol of HOF delivered. [b] Ca. 3 mmol of HOF delivered.

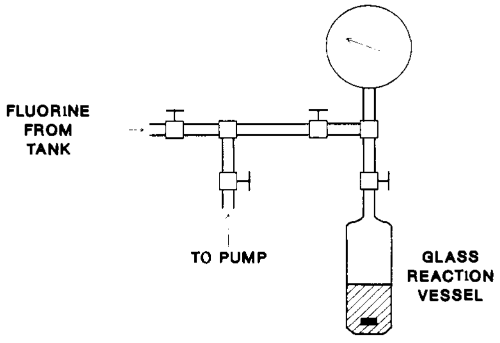

Figure 2. Apparatus for measuring the rate of reaction between fluorine and aqueous solutions.

Table III shows the results of ^{18}O isotopic tracer experiments designed to determine the source of the O_2 formed from the reaction of HOF with H_2O_2. The results indicate that a sub-

Table III. ^{18}O Tracer Studies of the $HOF-H_2O_2$ Reaction[a]

atom % ^{18}O in HOF[b]	$^{34}O_2/^{32}O_2$	n[c]
1.566	0.0088	0.40
1.566	0.0147	0.90
1.566	0.0100	0.50
1.566[d]	0.0104	0.54
94.9	0.466[e]	0.33
94.9	0.595[f]	0.39
0.205[g]	0.00468	0.028[h]

[a] Reaction of ca. 0.2 mmol of HOF with 0.9 mL of 9 M H_2O_2. [b] Atom % $^{18}O = 100[^{18}O]/([^{16}O] + [^{17}O] + [^{18}O])$. Normal abundance of ^{18}O taken to be 0.205 atom %. [c] $n = [R(1 - N)^2 - 2N]/[x(1 - N) - 2N - NR + R(1 - N)(x + y)]$, where n = number of O atoms from HOF per O_2, x = atom fraction of ^{18}O in enriched HOF, y = atom fraction of ^{17}O in enriched HOF, N = normal atom fraction of $^{18}O = 0.00205$, and R = measured ratio $^{34}O_2/^{32}O_2$. [d] Using highly stabilized H_2O_2. [e] $^{36}O_2/^{32}O_2 = 0.0128$. [f] $^{36}O_2/^{32}O_2 = 0.0191$. Generation of O_2 from residual H_2O_2 by reaction with Ce(IV) yielded $^{34}O_2/^{32}O_2 = 0.00717$, $^{36}O_2/^{32}O_2 < 8 \times 10^{-5}$. [g] Using 9 M H_2O_2 in water whose oxygen was 2.51 atom % ^{18}O. [h] Number of O atoms from H_2O found in each O_2. The equation given in *c* applies if x and y are taken to refer to the composition of the enriched water.

Table IV. Kinetics of Absorption of F_2 into Aqueous Solutions[a]

medium	P,[b] torr initial	final	$10^3\kappa$,[c] s^{-1}	10^5D, cm^2/s	10^3S, M/atm	$10^{-5}k'$, s^{-1}
0.01 M HF	60	14	7.7	1.42	3.21	1.75
0.01 M HF	107	22	5.1	1.42	3.21	0.77
0.01 M HF	207	49	4.6	1.42	3.21	0.63
0.01 M HF[d]	115	40	5.4	1.42	3.21	0.86
0.01 M HF[e]	115	26	5.6	1.42	3.21	0.93
0.01 M HF[f]	107	28	5.1	1.42	3.21	0.97
0.01 M HF[g]	113	37	8.8	2.52	2.00	2.9
1 M $HClO_4$	112	22	4.6	1.21	2.82	0.95
1 M $NaClO_4$	120	30	6.4	1.38	2.49	2.1
1 M KF + 0.16 M HF	108	42	8.0	1.31	2.37	3.8
1 M $KHSO_4$	110	14	9.6	1.30	2.56	4.7
1 M Cs_2SO_4	112	17	18	1.33	2.10	24
1 M Na_2SeO_4[h]	100	16	9.8	1.07	1.66_5	14
1 M Na_2PO_3F[h]	110	37	16	1.07	1.66_5	37
0.2 M NaOH	60	22	56	1.38	2.92	115
1 M NaOH	56	22	71	1.24	2.04	420
0.2 M KI	58	5	3600[i]	1.46	3.09	
1 M KI	60	5	3500[i]	1.56	2.64	
1 M KI	120	8	4100[i]	1.56	2.64	

[a] Reaction of 491 cm^3 of gas with 100 cm^3 of solution at 1 °C with stirring at 600 rpm, unless otherwise specified. [b] Includes vapor pressure of water. [c] $\kappa = -d \ln P_{F_2}/dt$. [d] No stirring. [e] Reaction vessel isolated from metal line with Teflon valve and opened intermittently for pressure measurement. [f] 551 cm^3 gas, 40 cm^3 solution, stirring at 400 rpm. [g] At 22 °C. [h] Effects on solubility and solution viscosity taken to be the same as those of Na_2SO_4. [i] Zero-order rate constant $\kappa = -10^3 dP_{F_2}/dt$, torr/s.

Table V. Kinetics of Absorption of CO_2 into Aqueous NaOH[a]

[NaOH], M	Initial P,[b] torr	$10^3\kappa$,[c] s^{-1}	10^5D, cm^2/s	S, M/atm	$10^{-3}k_{bm}$, $M^{-1}\,s^{-1}$
1.0	240	17	1.50	0.0266	10.1
1.0	130	17	1.50	0.0266	10.1
1.0[d]	130	9	1.50	0.0266	2.8
0.2	125	9	1.73	0.0345	7.3

[a] Reaction of 491 cm^3 of gas with 100 cm^3 of solution at 22 °C with stirring, unless otherwise specified. [b] Includes water vapor; final P = 15–19 torr. [c] $\kappa = -d \ln P_{CO_2}/dt$. [d] No stirring.

stantial, though not very reproducible, portion of the O_2 oxygen derives from the HOF.

Kinetics of Absorption of Fluorine into Aqueous Solutions. Table IV summarizes the results of studies of the kinetics of absorption of F_2 into aqueous solutions. The kinetics were measured as the rate of decrease of the pressure over the solutions. With the exception of those for the iodide solutions, the data gave fairly good fits over at least 2 half-times to the first-order relation

$$P - P_\infty = P_0 e^{-\kappa t}$$

The slow reactions sometimes showed an initial rapid decrease in pressure before the expected exponential decay set in. This effect was most severe for the slow reactions with an initial F_2 pressure around 50 torr and for reactions carried out at room temperature. Essentially the same effect was observed when water was contained in a small tube placed inside the reaction vessel. In this latter case the reaction became extremely slow after the pressure had decreased by 10–20%. We attribute this initial rapid pressure drop to the reaction of F_2 with water initially adsorbed on surfaces above the bulk liquid.

The gas left above the solution at the end of the reaction consisted primarily of O_2, along with smaller quantities of OF_2. The ratio O_2/OF_2 ranged from 2 to 4 after the NaOH reactions and from 9 to 16 after the others. As can be seen from Table IV, very little gas remained after the iodide reactions.

To test the reliability of our absorption measurements, we also measured the rate of the reaction between CO_2 and aqueous NaOH solutions, which has been very well characterized.[14,15] The results of these measurements are detailed in Table V.

Discussion

Production and Consumption of H_2O_2. The results shown in Tables I and II and in Figure 1 clearly indicate that the reactions of F_2 and HOF with water and with aqueous solutions of hydrogen peroxide will lead to steady-state concentrations of H_2O_2 if they are allowed to proceed for a long enough time. The simplest mechanism that can account for this observation is the following:

$$F_2 + H_2O \xrightarrow{k_1} HOF + HF \tag{1}$$

$$HOF + H_2O \xrightarrow{k_2} H_2O_2 + HF \tag{2}$$

$$F_2 + H_2O_2 \xrightarrow{k_3} 2HF + O_2 \tag{3}$$

$$HOF + H_2O_2 \xrightarrow{k_4} HF + H_2O + O_2 \tag{4}$$

If we make the usual steady-state assumption for HOF (but not for H_2O_2), we may integrate this set of equations to interrelate the concentrations of H_2O_2 and HF as the reaction proceeds:

$$[HF] - [HF]_0 = 2C_1 \ln \frac{([H_2O_2] + C_3)([H_2O_2]_0 + C_2)}{([H_2O_2] + C_2)([H_2O_2]_0 + C_3)} - 2([H_2O_2] - [H_2O_2]_0) \tag{5}$$

where

$$C_1 = 2k_1k_2/k_3k_4Q$$

$$C_2 = (k_2k_3 + k_1k_4 - k_3k_4Q)/2k_3k_4$$

$$C_3 = (k_2k_3 + k_1k_4 + k_3k_4Q)/2k_3k_4$$

and

$$Q = \sqrt{\left(\frac{k_2k_3 + k_1k_4}{k_3k_4}\right)^2 + \frac{4k_1k_2}{k_3k_4}}$$

From eq 2 and 4, we may conclude that the reaction of HOF with water should lead to a steady-state H_2O_2 concentration equal simply to k_2/k_4, which is seen from Table II to be 0.86 M.

Establishment of a steady-state H_2O_2 concentration in the reaction of F_2 with water requires that in eq 5 as [HF] becomes large $[H_2O_2] \rightarrow [H_2O_2]_{lim} = -C_2$, from which we may derive

$$\frac{k_1}{k_3} = \frac{[H_2O_2]_{lim}(k_2/k_4) + [H_2O_2]_{lim}^2}{k_2/k_4 - [H_2O_2]_{lim}}$$

From Table I we conclude that $[H_2O_2]_{lim} = 0.165$ M and therefore

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$k_1/k_3 = 0.243$ M. These ratios of constants allow the construction of the calculated curves in Figure 1. They provide a moderately good fit to the experimental data, although the deviations are real and suggest that our simple reaction scheme does not give a complete picture. In particular, the data obtained with a high initial H_2O_2 concentration tend toward a higher steady-state concentration. In addition, the data in Table I suggest that a significantly lower steady-state H_2O_2 concentration is reached at very low F_2 flow rates. However, the data shown in Figure 1 do indicate that, at least during the early stages of the reaction, the overall stoichiometry is that implied by eq 1–4.

One obvious limitation of our scheme is its failure to account for the production of OF_2, which must entail some further reaction such as

$$F_2 + HOF \rightarrow OF_2 + HF$$

The results in Table I show only small variations in the H_2O_2 steady state over the pH range 0–7. The increase observed in bicarbonate solutions, where we can calculate $k_1/k_3 = 0.55$ M, could arise from the contribution of either a direct reaction between F_2 and HCO_3^- or a hydroxide-assisted reaction between F_2 and H_2O. The very small variation with pH observed for the ratio k_2/k_4 suggests that the pK of HOF is probably greater than 7.

We may compare our value of k_1/k_3 (0.243 M at 1 °C and somewhat larger at 23 °C) with the corresponding ratio of 0.10 M for chlorine at 20 °C.[16,17] A reasonable mechanism for reaction 3 is

$$F_2 + H_2O_2 \rightarrow HOOF + HF$$

$$HOOF \rightarrow O_2 + HF$$

The homologous species HOOCl has been proposed as an intermediate in the reaction of chlorine with H_2O_2.[17,18]

Methanism of Reaction between HOF and H_2O_2. The ^{18}O tracer results in Table III shows that a substantial amount of the O_2 produced in this reaction comes from the HOF. To the best of our knowledge, this is the first example of an oxidation of H_2O_2 in which an appreciable portion of the oxygen comes from a source other than the H_2O_2 itself. Because of the highly inhomogeneous manner in which the reactions were carried out, we undertook to determine the extent to which possible side reactions might contribute to O_2 production. In particular, we have considered the bimolecular decomposition of HOF

$$2HOF \rightarrow 2HF + O_2 \qquad (6)$$

and the reaction of a localized excess of HOF with water from the H_2O_2 solution

$$HOF + H_2O^* \rightarrow HF + HOO^*H \qquad (7)$$

$$HOO^*H + HOF \rightarrow H_2O + HF + OO^* \qquad (8)$$

Reaction 6 would lead to the formation of $^{36}O_2$ from highly enriched HOF, while reactions 7 and 8 would lead to the formation of $^{34}O_2$ from the reaction of normal HOF with enriched H_2O. From the results in Table III, we conclude that reaction 6 contributes no more than 1% of the O_2, while reactions 7 and 8 contribute no more than 3%.

Dilution of the O_2 by normal oxygen from catalytic decomposition of the excess H_2O_2 also appears not to be an important factor, since results were essentially unaltered when highly stabilized H_2O_2 was used.

Since we have previously established HOF to be an excellent oxygen atom donor,[19] we might plausibly write for its reaction with H_2O_2 the scheme

$$HOF + H_2O_2 \rightarrow H_2O_3 + HF \qquad (9)$$

$$H_2O_3 \rightarrow H_2O + O_2 \qquad (10)$$

The molecule H_2O_3 is known to exist in aqueous solution and to decompose via reaction 10.[20] If the H_2O_3 oxygen were completely scrambled, this scheme would lead to the inclusion of 0.67 atom of HOF oxygen per molecule of O_2. The observed inclusion ranges from 0.33 to 0.90. It is clear that extensive oxygen transfer occurs, but the lack of reproducibility suggests contribution from a chain reaction under the extremely heterogeneous condition and high H_2O_2 concentrations that prevail in our tracer experiments. One possibility is

$$HO^*F + H_2O_2 \rightarrow HF + O^*H + HO_2$$

$$HO_2 + HO^*F \rightarrow O_2 + HF + O^*H$$

$$H_2O_2 + O^*H \rightarrow HO_2 + H_2O^*$$

The absence of detectable $^{36}O_2$ after Ce(IV) oxidation of the residual H_2O_2 from reaction with highly enriched HOF implies that recombination of O*H is unimportant, except perhaps as a chain termination step.

Kinetics of Reaction of Fluorine with Aqueous Solution. Although it is taken for granted that the reaction of F_2 with water is rapid, no one has heretofore determined just how rapid it might be. In a previous paper[7] we have shown that reaction 1 is slow enough that even relatively low concentrations of reactive substrates can compete with water for the F_2.

The reaction of F_2 with water can be treated as a particular case of the problem of interaction between a gas and a solution with which it reacts. This problem has been studied by chemical engineers as a subset of a somewhat more general situation designated mass transfer with chemical reaction.[21,22] The interaction is controlled by the rates of a number of processes in addition to that of the homogeneous chemical reaction, and an overall description of the system can be quite complex. However several regimes have been recognized[21] in which treatment of the interaction becomes relatively straightforward. They are (a) the kinetic regime, in which the rate of homogeneous reaction controls the overall interaction, and the solution remains virtually saturated with the gas; (b) the diffusional regime, in which migration of dissolved gas through the solution controls the interaction; (c) the fast-reaction regime, in which reaction is complete within a very short distance of the surface; and (d) the instantaneous-reaction regime, in which the overall interaction is usually limited by the rate of migration of substrate to the surface. Some authors have also considered an instantaneous regime at low pressures in which overall reaction is limited by transfer of gas across the surface interface.[23] In addition, if a gaseous product is formed, or if an inert diluent gas is present, diffusion of reactant gas to the surface can be limiting.

Only in regimes a and c is it possible to obtain explicit information about the kinetics of the homogeneous reaction between substrate and dissolved gas, and we shall see that the regime of principal concern to us is c—the fast-reaction regime. In this regime, if the homogeneous reaction is first order in gaseous reactant G, consumption of G may be expressed by the relation[21,23]

$$-\mathrm{d} \ln P_G/\mathrm{d}t = \kappa = RTS(Dk')^{1/2}(A/V_G) \qquad (11)$$

where P_G is the partial pressure of G, A the area of the gas–liquid interface, V_G the gas volume, D the diffusivity of G in the solution, k' the homogeneous first- or pseudo-first-order rate constant, S the solubility of G, R the gas constant, and T the absolute temperature.

Our approach to a kinetic study of the reaction of F_2 with aqueous solutions is based on a method used for a different system by Richardson et al.,[23] the most significant difference being that we monitored only the total pressure and that we provided for stirring of the solution in the reaction vessel. We have "calibrated" the system by using it to measure the rate of reaction of CO_2 with

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aqueous NaOH. In order to derive pseudo-first-order rate constants for this reaction from eq 11, we have estimated the solubility of CO_2 in the reaction media from its solubility in water,[24] correcting for salt effects by the method of van Krevelen and Hoftijzer,[25] and we have used the values of Nijsing et al.[15] for its diffusivity in the reaction media. The resulting bimolecular rate constants $k_{bm} = k'/[OH^-]$ are shown in the last column of Table V. The values obtained with stirring are in good agreement with those reported in the literature for the same temperature and ionic strength.[14,15] Our results do, however, show a dependence on stirring that should not be observed if the system is truly in the fast-reaction regime.[21] It is probable that without stirring our system is intermediate between the fast- and instantaneous-reaction regimes and that stirring accelerates the transport of NaOH sufficiently to bring the system into the fast-reaction regime.

To interpret our kinetic measurements of the reaction of F_2 with water by means of eq 11 we must know the solubility of F_2 in water. This solubility obviously cannot be measured directly, but it can be estimated by application of the scaled particle theory of fluids,[26] through which the energy of solution of a gas may be estimated as the sum of a solvent–solute interaction energy plus the energy required to form cavities in the solvent large enough to contain the solute molecules. For a nonpolar solute in water, the interaction energy is dependent on the polarizability of the solute and on the Lennard-Jones size and energy parameters σ and ϵ for solute and solvent, whereas the energy of cavity formation is dependent only on the size parameters. When literature values for the polarizability of F_2[27] and for the Lennard-Jones parameters for F_2[28] and water[26] are used, we may calculate that F_2 should be approximately 50% more soluble in water than O_2, with an uncertainty that may be as great as ±40%. The differences in solubility among the gases N_2, O_2, and F_2 derive largely from differences in the energy of cavity formation, and the principal source of uncertainty appears to lie in evaluation of the size parameters.

We have taken the solubility of F_2 in water to be 1.5 times that of O_2 both at 1 °C and at 22 °C, and we have further assumed that the dependence of the fluorine solubility on salt concentrations closely parallels that of O_2.[24] The latter assumption probably does not introduce an error larger than ±15% in the *relative* solubilities of fluorine in various media.

We have related the diffusivity of fluorine in water to that of O_2[29] by assuming a –0.6 power dependence on the molar volume of the solute *as a liquid* at its normal boiling point.[30] These volumes are, respectively, 28 cm^3 for O_2 and 25.1 cm^3 for F_2,[31] from which we conclude that the diffusivity of F_2 is about 7% greater than that of O_2 at the same temperature, with an uncertainty of about ±10%. The effect of dissolved salt on the diffusivity has been taken to be proportional to the –0.64 power of the viscosity of the resulting solution.[32,33] The *relative* diffusivities of fluorine in various media obtained through the use of this assumption should not be in error by more than about ±12%.

The first-order rate constants derived from our measurements of the reaction of F_2 with aqueous solutions are given in the last column of Table IV. In the absence of reactive substrates these should approximate k_1, since the buildup of H_2O_2 is relatively low. Therefore, subject to the uncertainty in the solubility of F_2, we have set $k_1 = 10^{5.0\pm0.3}$ s^{-1} at 1 °C. Reaction 1 is thus very considerably faster than the analogous reactions of the heavier halogens, which have rate constants between 3 and 110 at 20 °C.[16] The concentration of F_2 will decay exponentially with depth of penetration into the liquid phase, the mean reaction depth being $(D/k')^{1/2} \simeq 10^{-5}$ cm.[21]

The data in Table IV indicate the reaction of F_2 with water to be independent of stirring, as would be expected in the fast-reaction regime. This would also be the expectation if the system were in the kinetic regime. In the kinetic regime, however, the overall reaction rate should be proportional to the ratio of liquid volume to gas volume. That this is not the case can be seen from the experiment in Table IV in which only 40 cm^3 of liquid was used.

The ability to measure a first-order rate constant of 10^5 s^{-1} by conventional means might seem at first glance to be quite remarkable. That such a measurement is possible in the present instance may be attributed to the fact that the overall reaction rate is proportional to the rather low solubility of fluorine and only to the square root of the homogeneous first-order rate constant.

The fluorine–water reaction differs from most other gas–solution interactions in that the solvent itself is a reactant. We must therefore consider the possibility that reaction may take place homogeneously in the gas phase or on surfaces other than the gas–liquid interface. Slabey and Fletcher[34] have studied the reaction of F_2 with water vapor. They found the homogeneous reaction to be negligibly slow, while in glass vessels at 35 °C the surface-catalyzed reaction obeyed the rate law

$$-d[F_2]/dt = (3 \times 10^{-4})[F_2][H_2O]A$$

where A is the total surface area and the rate constant is in cm^{-2} s^{-1}. This is much too slow to account for our results. Our observations, however, do indicate a rapid initial reaction that is independent of the area of the gas–liquid interface. It presumably results from reaction of F_2 with water initially adsorbed on surfaces and decreases as this water is consumed. This effect is most severe at higher temperature and at low F_2 pressures, and it probably explains the apparent increase in k_1 at low pressure. Slabey and Fletcher[34] found that the surface-catalyzed reaction between F_2 and H_2O produced HF and O_2, without significant formation of H_2O_2. The residual O_2 pressure left at the end of our reactions is greater than would be expected from the amount of H_2O_2 that should be produced. Reaction on extraneous surfaces may account for a portion of this excess O_2. Another cause of the excess may be the fact that the H_2O_2 concentration is greater at the interface than in the bulk of the solution. This possibility is supported by the increase in residual O_2 when the solution is not stirred, although the expected increase in rate is not evident. The lack of effect of initially added O_2 indicates that even with substantial O_2 production, diffusion of F_2 to the liquid surface is not becoming a rate-limiting process, at least in the slower reactions.

A variety of substrates increase the overall reaction rate. In some cases, the residual O_2 pressure is also increased. The increase in rate becomes even more marked when we calculate k_1. In the case of the oxy salts, formation of more or less stable fluoroxy compounds could account for this increase in rate.[10] The increased rate in NaF solutions, however, is rather surprising.

The reaction of fluorine is greatly accelerated in alkali and in iodide solutions. The results in alkali suggest a bimolecular rate constant of ca. 5 × 10^7 M^{-1} s^{-1} at 1 °C, while the iodide reaction appears to be in the instantaneous reaction regime, for which our observed zero-order kinetics are predicted.[21] The iodide reaction rate does not, however, show the expected first-order dependence on the concentration of KI,[21] and this suggests that some process

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other than migration of iodide is limiting the reaction. We shall only set a lower limit of ca. 10^8 M^{-1} s^{-1} for the bimolecular rate constant of the iodide reaction. It is quite possible that the observed rate constant for the reaction with base is also a lower limit.

Conclusions

In this study we have examined the relative reactivities of H_2O and H_2O_2 toward F_2 and HOF and have obtained support for a simple mechanism for the fluorine–water interaction. We have obtained for the first time an order-of-magnitude estimate for the rate of reaction of dissolved fluorine with water. This rate is considerably greater than the analogous rates for the heavier halogens. This aspect of our present results should be regarded as preliminary in nature. Refinement of the technique should make possible the evaluation of a variety of rate constants for reaction of fluorine with aqueous substrates, at least on a relative basis.

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Registry No. H_2O, 7732-18-5; F_2, 7782-41-4; HOF, 14034-79-8; H_2O_2, 7722-84-1; O_2, 7782-44-7.

ESR of Intermediate Radicals in Thermolysis Mechanisms: Peroxidic Perfluoro Polyethers

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Abstract: The photothermolysis between 100 and 250 °C of polymers with perfluorooxymethylene, oxyethylene, and oxypropylene structures and containing perioxidic units as photoactive initiators has been studied by ESR and the INDO MO method. Following the initial homolysis of peroxidic bonds and the β scission of resulting alkoxy radicals, alkoxyfluoroalkyl radicals are formed which, above 100 °C, undergo thermal decomposition by β scission, initiating a chain depolymerization with formation of carbonyl compounds and C_2F_4 and C_3F_6 monomers; the latter add to $RCF_2\cdot$ species yielding C_n ($n \geq 3$) units. By extension of these results, it is inferred that this mechanism is of major importance in the high-temperature pyrolysis of this class of compounds. Among the intermediates of the C2P and C3P photothermolysis, of special interest are some novel primary alkoxyfluoroalkyl radicals with strongly bent structures at the radical centers and showing unusually large long-range interactions with γ- and δ-fluorine atoms, which are actually being investigated by MO methods.

ESR has a great potentiality as a method for elucidating the thermolysis mechanism;[1] however, its applications to this field is severely hindered by difficulties inherent to the high temperature and pressure that must be attained within the sample cavity. Furthermore, at high temperature, the lifetime of the radicals is shorter so that most of the species do not attain the limit of detection. We have tried to avoid these difficulties, in polymer thermolysis studies, by taking advantage of the fact that the radical reactions in the propagation stage have a much lower activation energy as compared to the initiation stage; as a consequence they can occur at a lower temperature provided initiation is obtained in a nonthermal way. Several methods for nonthermal initiation can be proposed, such as ionizing radiations (radiation-assisted thermolysis) or UV radiations; in the latter case photoactive groups must be inserted within the polymer chains. We have attempted to apply the latter method to investigate the major features of the mechanism of thermolysis of perfluoro polyethers[2] containing structural units of formula

$$-(OCF_2CF_2)_m-(OCF_2)_n- \quad n/m \sim 1 \quad \mathrm{C2P}$$

$$-(OCF_2CF(CF_3))_x-(OCF_2)_y \quad x/y \sim 10 \quad \mathrm{C3P}$$

When obtained by photooxidation of C_2F_4 and C_3F_6, C2P and C3P contain about 1% of peroxidic units of formula

$$\begin{array}{ll} \mathrm{a} & -OCF_2CF_2OOCF_2CF_2O- \\ \mathrm{b} & -OCF_2CF_2OOCF_2O- \\ \mathrm{c} & -OCF_2OOCF_2O- \end{array} \Bigg\} \quad \mathrm{C2P}$$

$$\begin{array}{ll} \mathrm{d} & -OCF_2CF(CF_3)OOCF_2CF(CF_3)O- \\ \mathrm{e} & -OCF_2CF(CF_3)OOCF(CF_3)CF_2O- \end{array} \Big\} \quad \mathrm{C3P}$$

which are suitable as photoactive initiators of the thermolysis. In addition to the mechanism of thermal degradation, a major interest of this investigation is the characterization of the expected intermediates alkoxyfluoroalkyl radicals; only few examples belonging to this important class of radicals are reported in literature,[3c,4,5] and no information pertaining to their stability and reaction at relatively high temperature are available.

Experimental Section

Peroxidic C2P and C3P were prepared by photooxidation at low temperature of perfluoroethylene and perfluoropropylene according to the methods described in ref 2. For the ESR measurements, samples of C2P and C3P were sealed in quartz tubes under high vacuum and submitted to UV irradiations from a 100-W high-pressure mercury lamp within the cavity of an E-109 ESR Spectrometer equipped with an authomatic temperature-control device. Photothermolysis experiments were performed in the range 60–250 °C.

MO Calculations. The INDO method has become the standard technique for studying the geometry and electronic structure of organic

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