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Oxygen Transfer in the Reactions of Hypofluorous Acid with Aqueous Solutions[1]

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Oxygen-18 tracer studies have shown that the reactions of HO*F with H_2O and with aqueous HSO_4^- and $Cr(NH_3)_5N_3^{2+}$ lead to transfer of oxygen with formation of HOO*H, O_3SOO*H^-, and $Cr(NH_3)_5NO*^{2+}$, respectively. Transfer is incomplete in the case of dilute (0.4 M) bisulfate solutions.

Hypofluorous acid is formed as an intermediate in the hydrolysis of F_2:

$$F_2 + H_2O \rightarrow HOF + HF$$

In previous publications, HOF has been shown to act as an oxygenating or hydroxylating agent, converting H_2O to H_2O_2,[3] $Cr(H_2O)_5N_3^{2+}$ to $Cr(H_2O)_5NO^{2+}$,[4] aromatic compounds to phenols,[5] and octaethylporphyrin to its nitroxide.[6] In all of these reactions, HOF may be regarded as a donor of atomic O, or of its conjugate acid, OH^+. It therefore seemed of interest to determine whether HOF does, in fact, directly transfer its oxygen atom to aqueous substrates.

Experimental Section

Reagents. Hypofluorous acid was prepared from the reaction of fluorine with water in a recirculating system.[3] It was purified, stored in a Kel-F U-tube, and delivered into ice-cold aqueous reaction solutions via a nitrogen stream in the manner described elsewhere,[4] a minor modification being the cooling of the HOF reservoir to temperatures between −40 and −50 °C while the reagent was being transferred into the reaction solution. This modification was introduced to prevent the explosions that sometimes took place when the reservoir was permitted to warm to room temperature. The amounts of HOF produced were determined by delivering typical preparations into aqueous KI and titrating with thiosulfate. Hypofluorous acid enriched in ^{18}O was prepared from enriched water.

To prepare sulfate enriched in ^{18}O, enriched water was saturated with SO_2, and an excess of Br_2 was added. The solution was concentrated by distillation first in air and finally under vacuum. The resulting concentrated sulfuric acid was diluted with ice-cold water and neutralized potentiometrically with potassium hydroxide, after which the neutral solution was concentrated by evaporation to obtain crystals of potassium sulfate, which were filtered and dried at 110 °C. Enriched bisulfate solutions were prepared from this material by dissolving it in a stoichiometric quantity of ice-cold perchloric acid and removing the precipitated $KClO_4$ by centrifugation.

Azidopentaamminechromium(III) nitrate was prepared as previously described.[7] This salt was used instead of a $Cr(H_2O)_5N_3^{2+}$ salt because of the ease with which the nitrosylpentaammine product could be precipitated (vide infra).

Potassium peroxymonosulfate, $KHSO_5$, was obtained from Du Pont as "Oxone", a mixture of composition $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$. Other reagents were commercial products of analytical reagent grade. Distilled water was redistilled before use first from alkaline permanganate and then from acidic dichromate.

Isolation and Characterization of $Cr(NH_3)_5NO^{2+}$. The $Cr(NH_3)_5NO^{2+}$ product of the $Cr(NH_3)_5N_3^{2+}$–HOF reaction was precipitated as the bromide salt either directly from the spent reaction mixture (using amounts of NaBr insufficient to precipitate the minor $Cr(NH_3)_5H_2O^{3+}$ product) or after ion-exchange separation on Dowex 50W-X2 resin at 3 °C. In the latter case, trace amounts of $Cr(NH_3)_4(H_2O)NO^{2+}$ were eluted from the column with a solution 0.2 M in NaCl and 0.001 M in NaOH, after which the $Cr(NH_3)_5NO^{2+}$ was eluted with 0.5 M NaCl. The $Cr(NH_3)_5NO^{2+}$ was characterized by its visible absorption spectrum, which was identical to that of an authentic sample prepared according to Mori.[8]

Oxygen Isotope Analyses. The oxygen isotopic composition of hydrogen peroxide was determined by mass spectrometric analysis of the O_2 produced by its reaction with an excess of a solution of ammonium hexakis(nitrato)cerate(IV). The reaction was carried out in a Y-shaped vessel in which the two solutions were outgassed under vacuum and then mixed. The isotopic composition of the terminal peroxy oxygen in HSO_5^- was determined by mass spectrometric analysis of the O_2 evolved in the rapid decomposition of the peroxymonosulfate at a pH of ca. 9.[9] Hydrogen peroxide was first destroyed by reaction with an excess of chlorine, and the excess was removed by flushing with N_2. Then a portion of the acidic peroxymonosulfate solution was placed in one arm of a Y tube, and a Na_2CO_3 solution (containing a little EDTA to complex metallic impurities) was placed in the other. After evacuation and outgassing, the two solutions were mixed and allowed to stand until decomposition of the peroxymonosulfate was essentially complete. An experiment was carried out in which normal peroxymonosulfate was allowed to decompose in this way in water that was sevenfold enriched in ^{18}O. The O_2 obtained was compared with that formed from the same peroxymonosulfate in normal water. A Consolidated Model 12-201 isotope ratio mass spectrometer was used for this comparison.

The oxygen isotopic compositions of normal and enriched water samples were determined by mass spectrometric analysis either as O_2 or as CO_2. Conversion to O_2 was accomplished by dissolving 15 μL of Br_2 and 25 mg of freshly cut sodium in 250 μL of the water to make a hypobromite solution, which was placed in one arm of a Y tube. Three to five milligrams of anhydrous $CoCl_2$ was placed in the other arm, and after evacuation and outgassing, the two were mixed. Catalytic decomposition of the OBr^- produced the desired O_2.[10] Conversion of water oxygen to CO_2 was effected by reaction with $Hg(CN)_2$ in a sealed tube.[11] Fractionation of isotopes in these reactions was neglected. Conversion of water to CO_2 was used in the experiments with the chromium complexes. Conversion to O_2 was used in all other cases, except that the supplier's analysis was accepted for the water used to prepare the highly enriched HOF. (This water was supplied by Monsanto Research Corp., Mound Laboratories, Miamisburg, OH.)

The isotopic composition of the oxygen in HOF was determined by allowing a sample to decompose and analyzing the O_2 that was formed. The ^{18}O content determined in this way was 1.3% higher than that found by the Co^{II}–OBr^- method for the water from which

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Table I. Transfer of Oxygen during Oxidations by HOF[a]

substrate		atom % ^{18}O[b]			product		
species	molarity	HOF[c]	substrate	solvent	species	atom % ^{18}O[b]	n[d]
$HClO_4$	0.12	1.54_4	0.2	0.19_3	H_2O_2	0.88_9	1.03
						0.90[e]	1.05[e]
$HClO_4$	0.12	0.19_3	0.2	1.53_6	H_2O_2	0.86_2	1.00
		89.5[f]		0.19	H_2O_2	44.8[g]	1.00
HSO_4^-	0.40	0.19_3	1.33	0.19_3	HSO_5^-	0.20_1[h]	
HSO_4^-	0.40	1.54_4	0.20	0.19_3	HSO_5^-	1.30_9[h]	0.84[i]
HSO_4^-	0.40	0.19_3	0.20	1.56_9	HSO_5^-	0.38_4[h]	0.86[i]
HSO_4^-	1.60	0.19_3	0.20	1.56_9	HSO_5^-	0.24_9[h]	0.96[i]
					H_2O_2	0.87	1.02
RN_3^{2+}[j]	0.0185	1.49_7		0.20_4	RNO^{2+}[k]	1.35_6	0.89
RN_3^{2+}[j]	0.0185	0.20_4		1.49	RNO^{2+}[k]	0.20_6	1.00
RN_3^{2+}[j]	0.0229	0.528		0.204	RNO^{2+}[l]	0.454	0.77

[a] One to three millimoles of HOF, contaminated with an approximately equal amount of HF, was delivered into 5–20 mL of aqueous solution at 0 °C. Substrate was present in substantial excess except in the case of the chromium complex, which was totally consumed. [b] Atom % $^{18}O = 100[^{18}O]/([^{16}O] + [^{17}O] + [^{18}O])$. [c] ^{18}O content of HOF assumed to be the same as that of the water from which it was prepared. [d] n = number of atoms of oxygen from HOF found in each molecule of product. [e] Duplicate experiment. [f] Analysis of water by supplier (Monsanto Research Corp., Mound Laboratories, Miamisburg, OH) (atom %): 7.08, ^{16}O; 3.37, ^{17}O; 89.55, ^{18}O. [g] Actual analysis (mol %): 7.48, $^{32}O_2$; 3.23, $^{33}O_2$; 88.95, $^{34}O_2$; 0.05, $^{35}O_2$; 0.29, $^{36}O_2$. [h] Isotopic composition of the oxygen obtained by decomposition of the peroxymonosulfate in a carbonate buffer at a pH of ca. 9. [i] On the assumption that decomposition of the peroxymonosulfate product produces O_2 of which 98.5% comes from oxygen added in the course of the reaction with HOF, 0.7% from one of the original bisulfate oxygens, and 0.8% from solvent during the decomposition. In the two experiments that used enriched solvent, the solution in which the peroxymonosulfate decomposed was approximately 1.0 atom % in ^{18}O. [j] $R = Cr(NH_3)_5$; $[HClO_4] = 0.10$ M. [k] Product purified by ion exchange before precipitation. [l] Product precipitated directly without prior purification.

the HOF had been made. This difference is barely significant and may reflect isotopic fractionation in the water analysis, in the formation of HOF, or both. For simplicity, we have assumed that HOF always has the isotopic composition of the water from which it was prepared.

The isotopic composition of the oxygen in $[Cr(NH_3)_5NO]Br_2$ was determined mass spectrometrically after conversion to CO_2 by reaction with $Hg(CN)_2$ in a sealed tube.[11]

The isotopic composition of the oxygen in enriched potassium sulfate was determined by conversion to barium sulfate, ignition with graphite, and mass spectrometric analysis of the resulting CO_2.[12]

Except for the experiment on the decomposition of peroxymonosulfate in enriched water referred to above, all O_2 isotopic analyses were carried out with a Consolidated Model 21-620 mass spectrometer. All CO_2 isotopic analyses were carried out with either a Nuclide RMS-6 or a Consolidated Model 21-201 isotope ratio mass spectrometer.

Determination of H_2O_2, HSO_5^-, and $S_2O_8^{2-}$. Solutions thought to contain these species were first titrated potentiometrically with Ce(IV) to determine the content of H_2O_2. An aliquot of the solution resulting from this titration was made 0.2 M in KI, and the liberated iodine was immediately titrated with thiosulfate to give the HSO_5^- content. The sum of HSO_5^- and $S_2O_8^{2-}$ was determined on another aliquot of the solution from the Ce(IV) titration by making it 1 M in KI, flushing with N_2 to prevent air oxidation, allowing the solution to stand for 15 min, and again titrating the liberated iodine with thiosulfate. In some cases the sum of H_2O_2 and HSO_5^- was determined by making an aliquot of the original reaction mixture 0.2 M in KI, adding a few milligrams of ammonium molybdate, and titrating the liberated iodine immediately with thiosulfate.

Results

General Observations. The reaction of HOF with aqueous $KHSO_4$ produces a mixture of HSO_5^- and H_2O_2. In a typical experiment, approximately 2.8 mmol of HOF was passed into 25 mL of 0.40 M $KHSO_4$ at 0 °C to produce 2.2 mmol of H_2O_2 and 0.56 mmol of HSO_5^-. In another experiment, approximately 1.3 mmol of HOF was passed into 10 mL of 1.6 M $KHSO_4$ at 0 °C to yield 0.65 mmol of H_2O_2 and 0.58 mmol of HSO_5^-. In neither experiment was any $S_2O_8^{2-}$ detected (limit of detection 1–2% of the HSO_5^-).

The reaction of HOF with $Cr(NH_3)_5N_3^{2+}$ produced primarily $Cr(NH_3)_5NO^{2+}$, along with a small amount of $Cr(NH_3)_5H_2O^{3+}$. Traces of $Cr(NH_3)_4(H_2O)NO^{2+}$ were also formed but were not usually distinguished from the $Cr(NH_3)_5NO^{2+}$. In a typical experiment, ca. 1.2 mmol of HOF was added at 0 °C to 25 mL of a solution 0.1 M in $HClO_4$ and 0.002 81 M in $Cr(NH_3)_5N_3(NO_3)_2$ to produce 0.063 mmol of $Cr(NH_3)_5NO^{2+}$ and 0.0072 mmol of $Cr(NH_3)_5H_2O^{3+}$.

Oxygen-Transfer Experiments. Table I gives the results of oxygen-transfer experiments in which either the HOF, the reacting substrate, or the solvent water was enriched in oxygen-18. The oxygen-transfer results are expressed in terms of the parameter "n", which we define as the number of oxygen atoms transferred from HOF to each molecule of product formed. In the table, the $Cr(NH_3)_5$ group is designated as "R".

Decomposition of HSO_5^- in Enriched Water. The decomposition of unenriched 0.1 M peroxymonosulfate at a pH around 9 in water that contained 1.46 atom % ^{18}O produced O_2 with an ^{18}O content that was 5.3% greater than the natural abundance. This corresponds to an 0.83% incorporation of solvent oxygen into the O_2.

Discussion

The results in Table I establish that in the cases that we have studied, HOF reacts predominantly via the direct transfer of an oxygen atom to a substrate molecule and that this transfer must proceed substantially faster than the exchange of oxygen between HOF and water. The transfer of an oxygen atom from HOF to water to produce hydrogen peroxide appears to be essentially quantitative, although we cannot account for the value of n slightly greater than unity that we observe with HOF containing 1.5% ^{18}O. This effect appears to be reproducible and persists even when allowance is made for the 1.3% enrichment of ^{18}O in the HOF relative to the water from which it was made (see Experimental Section).

The reaction of normal HOF with bisulfate enriched in ^{18}O and subsequent decomposition of the resulting HSO_5^- produces O_2 in which less than 1% of the atoms come from the bisulfate. This is generally consistent with the double-tagging experiments in which Koubek et al.[13] have shown that most of the O_2 produced in the decomposition of peroxymonosulfate contains one atom from each of two different peroxymonosulfate ions. Koubek et al. explain their observations in terms of a bimolecular decomposition mechanism that involves combination of two terminal peroxy oxygen atoms:

$$O_3SO{*}O{*}H^- + OOSO_3^{2-} \rightarrow O_3SO{*}^{2-} + HO{*}OOSO_3^-$$

$$HO{*}OOSO_3^- \rightarrow O{*}O + H^+ + SO_4^{2-}$$

They found, however, that about 9% of their O_2 contained two atoms from the same peroxymonosulfate ion. In our experiment, this would translate to 4.5% incorporation of bisulfate oxygen into the O_2, which is far more than we observe. We have no explanation for this discrepancy. Nevertheless, our results do imply that HOF contributes the terminal peroxy oxygen atom to the HSO_5^- and that two of these terminal atoms combine to form the O_2.

The results of our experiments in which either the HOF or the water was enriched indicate that when HOF reacts with 1.6 M $KHSO_4$, each HSO_5^- ion formed contains 0.96 of an O atom from the HOF and 0.04 from the solvent. In a more dilute bisulfate solution, considerably more of the HSO_5^- oxygen comes from the solvent. In fact, the extent of incorporation of solvent oxygen into the peroxymonosulfate product appears to be inversely proportional to the bisulfate concentration. We cannot account for this effect by invoking exchange of oxygen between HOF and solvent, since such exchange should lead to low values of *n* for the reaction of HOF with water to produce H_2O_2. This is not consistent with our observations. A possible explanation is that HOF does not react directly with bisulfate, but reacts with water to form an unsymmetrical peroxy intermediate that can either react with bisulfate, scramble its oxygens and then react with bisulfate, or rearrange to ordinary hydrogen peroxide. For example:

$$H_2O + HO^*F \rightarrow H_2OO^* + HF$$

$$H_2OO^* + O_3SOH^- \rightarrow H_2O + O_3SOO^*H^-$$

$$H_2OO^* \rightleftarrows H_2O^*O$$

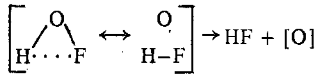
$$H_2O^*O + O_3SOH^- \rightarrow H_2O^* + O_3SOOH^-$$

$$H_2OO^* \rightarrow HOO^*H$$

The reaction of $Cr(NH_3)_5N_3^{2+}$ with HOF in enriched water indicates that the oxygen introduced into the $Cr(NH_3)_5NO^{2+}$ product comes entirely from the HOF. The low transfer values from enriched HOF to $Cr(NH_3)_5N_3^{2+}$ in normal water may result from exchange during the purification process, or from inclusion of $Cr(NH_3)_4(H_2O)(NO)^{2+}$ with the $[Cr(NH_3)_5NO]Br_2$ precipitate when the purification was omitted.

Although we have considered the relation between the isotopic composition of HOF and that of the water from which it was prepared, there are other potential fractionation effects which we have not taken into account. It seems highly unlikely, however, that any of these would be large enough to alter our conclusions significantly.

The readiness with which HOF transfers an oxygen atom to reducing substrates is consistent with NMR studies that indicate the HOF molecule to be polarized in the sense $^{\delta+}HO\text{-}F^{\delta-}$.[14] The oxygen transfer may then be regarded as a virtual ionization to OH^+ and F^-. Alternatively, the transfer may be interpreted in terms of the great affinity between the proton and the fluorine atom in HOF. This affinity should make it relatively easy for HOF to transfer an oxygen atom to a suitable acceptor and leave behind the very stable HF molecule:



The facile production of HO*OH by either the HOF–H_2O^* or the HO*F–H_2O reaction provides a method of preparing what is to the best of our knowledge a uniquely labeled molecule that has not previously been described. Rather pure samples of HO*OH can be obtained by this technique, and nearly pure O*–O can readily be made by oxidation of the HO*OH, as we have shown in the third experiment in Table I. In addition, the reaction of HOF with various organic and inorganic oxyacids may serve as a means of synthesizing a variety of "end-labeled" peroxyacids.

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Registry No. HOF, 14034-79-8; $HClO_4$, 7601-90-3; HSO_4^-, 14996-02-2; $Cr(NH_3)_5N_3^{2+}$, 22317-10-8; H_2O_2, 7722-84-1; HSO_5^-, 12188-01-1; $Cr(NH_3)_5NO^{2+}$, 14951-33-8.

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