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Fluorine–Oxygen Exchange Reactions in IF_5, IF_7, and IF_5O

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When reacted with alkali-metal nitrates, IF_5 readily exchanges two fluorine ligands for a doubly bonded oxygen atom. In all cases MIF_4O salts (M = Li, K, Cs) and FNO_2 are formed as the primary products. The FNO_2 byproduct undergoes a fast secondary reaction with MNO_3 to yield equimolar amounts of N_2O_5 and MF. The N_2O_5 decomposes to N_2O_4 and 0.5 mol of O_2, while the MF, depending on the nature of M, does or does not undergo complexation with the excess of IF_5. Pure MIF_4O salts, free of MF or $MF{\cdot}nIF_5$ byproducts, were prepared from MF, I_2O_5, and IF_5 in either CH_3CN or IF_5 as a solvent. The new compounds $LiIF_4O$, $NaIF_4O$, $RbIF_4O$, and $NOIF_4O$ were characterized by vibrational spectroscopy. It was also shown that, contrary to a previous report, FNO_2 does not form a stable adduct with IF_5 at temperatures as low as −78 °C. An excess of IF_7 reacts with MNO_3 (M = Li, Na) to give MF, FNO_2, IF_5, and 0.5 mol of O_2, but surprisingly no IF_5O. With $CsNO_3$, the reaction products are analogous, except for the CsF reacting with both the IF_5 product and the excess of IF_7 to give $CsIF_6{\cdot}2IF_5$ and $CsIF_8$, respectively. When in the IF_7 reaction an excess of $LiNO_3$, is used, the IF_5 product undergoes further reaction with $LiNO_3$, as described above. The IF_5O molecule was found to be rather unreactive. It does not react with either LiF or CsF at 25 or 60 °C or with $LiNO_3$ or $CsNO_3$ at 25 °C. At 60 °C with $LiNO_3$, it slowly loses oxygen, with the IF_5 product reacting to yield $LiIF_4O$, as described above.

Introduction

Recent work from our laboratory has shown that the nitrate ion is an excellent reagent for replacing two fluorine ligands by one doubly bonded oxygen atom in compounds such as BrF_5,[1,2] XeF_6,[3] and $XeOF_4$.[4] A logical extension of this work was a study of analogous fluorine–oxygen exchange reactions in iodine fluorides.

Although the reaction of KNO_3 with a large excess of IF_5 at its boiling point has previously been reported[5] to yield NO_2 and KIF_6, no mention of any fluorine–oxygen exchange was made. Some evidence for hydrolytic fluorine–oxygen exchange in $CsIF_6$ was observed during its recrystallization from CH_3CN solution. It resulted in the isolation of small amounts of single crystals of $CsIF_4O$, which were used for a crystal structure determination.[6] Attempts to utilize this reaction or the reactions of either MIO_3 or MIO_2F_2 (M = K or Cs) with IF_5 for the preparation of MIF_4O salts, however, resulted only in mixtures of MIF_4O and MIO_2F_2.[7] Finally, pure KIF_4O was prepared from a 5:1 mixture of $KF{:}I_2O_5$ in a large excess of IF_5, and its vibrational spectra have been recorded.[8]

In the case of IF_7, fluorine–oxygen exchange has been achieved by its reaction with either silica at 100 °C,[9] Cab-O-Sil at ambient temperature,[10] or Pyrex,[11,12] I_2O_5,[12] or small amounts of water[11–13] at room temperature with IF_5O being the principal product. Most likely, the reactions with silica or Pyrex also involve the hydrolysis of IF_7, with traces of HF continuously regenerating the required H_2O according to (1) and (2). However, most of these reactions

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O \qquad (1)$$

$$IF_7 + H_2O \rightarrow IF_5O + 2HF \qquad (2)$$

are slow and are difficult to control and scale up. It was, therefore, interesting to examine whether nitrates could be used advantageously to achieve fluorine–oxygen exchange in iodine fluorides and to prepare new iodine oxyfluoride salts.

Experimental Section

Apparatus and Materials. The vacuum lines, handling techniques, and spectrometers used in this study have been described elsewhere.[3] Commercial $LiNO_3$ (J. T. Baker, 99.7%), $NaNO_3$ (J. T. Baker 99.5%) and KNO_3 (J. T. Baker, 99.1%) were dried in vacuo at 120 °C for 1 day prior to their use. The $CsNO_3$ were prepared from Cs_2CO_3 and HNO_3 and dried in the same manner. The heavier alkali-metal fluorides (K, Rb, Cs) were dried by fusion in a platinum crucible and powdered in a drybox prior to use, while the lighter ones (Li, Na) were dried in vacuo at 120 °C. The N_2O_5,[14] FNO_2,[1] FNO,[15] IF_7,[10] and IF_5O,[10] were prepared by literature methods. The IF_5 (Matheson Co.) was treated with ClF_3 (Matheson) at 25 °C until the originally dark brown liquid was colorless. Pure IF_5 was obtained by fractional condenation at −64 °C in a dynamic vacuum. A commercial sample of I_2O_5 (Mallinckrodt), which actually was HI_3O_8, was converted to I_2O_5 by heating to 210 °C in a dynamic vacuum for 12 h. Its purity was verified by Raman spectroscopy.[16] The CH_3CN (Baker, UV grade, <0.001% H_2O) was stored over Linde 3A molecular sieves prior to use.

Caution! ClF_3 is a powerful oxidizer and contact with organic materials must be avoided.

Reaction of $LiNO_3$ with an Excess of IF_7. A 30-mL stainless-steel cylinder was loaded in the drybox with $LiNO_3$ (4.32 mmol). On the vacuum line, IF_7 (12.94 mmol) was added at −196 °C. The cylinder was allowed to warm to room temperature slowly and was kept at this temperature for 3 days. It was recooled to −196 °C, and the noncondensible gas (2.16 mmol of O_2 based on *PVT* measurements and the weight change of the cylinder) was pumped off. The material volatile at 30 °C was separated by fractional condensation through a series of traps at −95, −126, and −196 °C. These traps contained the following materials: −196 °C, 4.26 mmol of FNO_2; −126 °C, 8.6 mmol of IF_7; −95 °C, 4.3 mmol of IF_5. In its Raman spectrum, the white solid residue (120 mg; weight calculated for 4.32 mmol of LiF = 112 mg) showed no evidence for the presence of unreacted $LiNO_3$.

Reaction of $NaNO_3$ with an Excess of IF_7. The reaction was carried out in the same manner as described for $LiNO_3$. After 15 h at 25 °C, no noticeable reaction had occurred, but after 60 h at 60 °C, IF_5, NaF, FNO_2, and 0.5 mol of oxygen were formed in quantitative yield.

Reaction of $CsNO_3$ with an Excess of IF_7. A 75-mL stainless steel cylinder was loaded in the drybox with $CsNO_3$ (2.47 mmol). On the vacuum line, IF_7 (12.48 mmol) was added at −196 °C. The cylinder was kept for 3 days at 25 °C and then recooled to −196 °C. It contained 0.44 mmol of a gas (O_2) noncondensible at −196 °C. The material volatile at 25 °C was separated by fractional condensation through a series of traps kept at −45, −95, −126, and −196 °C while the cylinder was allowed

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to warm from −196 to 25 °C. The −45 °C trap was empty, the −95 and −126 °C traps contained IF_7 (11.07 mmol), and the −196 °C trap had FNO_2 (0.86 mmol). The white solid residue (764 mg; weight calculated for 0.54 mmol of $CsIF_8$, 1.61 mmol of $CsNO_3$, 0.27 mmol of $CsIF_6{\cdot}2IF_5$, and 0.04 mmol of $CsIF_6$ = 770 mg) was shown by vibrational spectroscopy to consist of $CsNO_3$, $CsIF_8$,[17] $CsIF_6{\cdot}2IF_5$,[18] and a small amount of $CsIF_6$.[18]

Reaction of an Excess of $LiNO_3$ with IF_7. A 30-mL stainless-steel cylinder was loaded with $LiNO_3$ (8.62 mmol) and IF_7 (1.90 mmol) at −196 °C. The cylinder was allowed to slowly warm to ambient temperature and was kept at this temperature for 3 days. It was recooled to −196 °C and the noncondensible gas (2.71 mmol of O_2) was pumped off. The material volatile at 30 °C consisted of N_2O_4 (3.47 mmol) and IF_5 (0.30 mmol). The white solid residue (601 mg; weight calculated for a mixture of 1.62 mmol of $LiNO_3$, 1.60 mmol of $LiIF_4O$, and 5.40 mmol of LiF = 613 mg) was shown by its infrared and Raman spectra to contain LiF_4O and unreacted $LiNO_3$.

Reaction of $LiNO_3$ with an Excess of IF_5. A 30-mL stainless-steel cylinder containing $LiNO_3$ (5.55 mmol) was cooled to −196 °C, and IF_5 (62.94 mmol) was added. The cylinder was kept for 15 h on a shaker at ambient temperature. After the cylinder was recooled to −196 °C, noncondensible material (0.51 mmol of O_2) was pumped off. The material volatile at 35 °C consisted of FNO_2 (0.34 mmol), N_2O_4 (1.03 mmol), and IF_5 (61.5 mmol). The white solid residue (589 mg; weight calculated for a mixture of 3.15 mmol of $LiNO_3$, 1.37 mmol of $LiIF_4O$, and 1.03 mmol of LiF = 553 mg) was shown by vibrational spectroscopy to contain $LiIF_4O$ and unreacted $LiNO_3$.

Reaction of KNO_3 with an Excess of IF_5. A 30-mL stainless-steel cylinder containing KNO_3 (3.17 mmol) and IF_5 (42.45 mmol) was shaken for 12 h at 25 °C and then kept in an oven at 50 °C for 5 days. The cylinder was cooled to −196 °C and noncondensible material (0.75 mmol of O_2) was pumped off. The material volatile at 35 °C consisted of N_2O_4 (1.6 mmol), IF_5 (39.2 mmol) and a small amount of $IONO_2$ (see Results and Discussion). The white solid residue (850 mg; weight calculated for a mixture of 1.58 mmol of KIF_4O and 1.58 mmol of KIF_6 = 847 mg) contained according to its vibrational spectra KIF_4O,[8] KIF_6,[18] and a small amount of unreacted KNO_3.

Reaction of $CsNO_3$ with an Excess of IF_5. When $CsNO_3$ was reacted with a 5-fold excess of IF_5 at 25 °C for 40 h, the main reaction products were N_2O_4, O_2, $CsIF_4O$, and $CsIF_6{\cdot}2IF_5$[18] in addition to unreacted IF_5 and $CsNO_3$, and a smaller amount of FNO_2. Harsher reaction conditions (70 °C for 6 days, 20-fold excess of IF_5, and vacuum pyrolysis of the solid product at 100 °C) resulted in complete conversion of $CsNO_3$ to $CsIF_4O$ and $CsIF_6$.

Synthesis of $LiIF_4O$. A prepassivated 30-mL stainless-steel cylinder was loaded in the glovebox with LiF (4.85 mmol) and I_2O_5 (0.97 mmol). On the vacuum line IF_5 (31.84 mmol) was added at −196 °C. The cylinder was shaken for 20 h at ambient temperature and then kept at 50 °C for 3 days with occasional agitation. The material volatile at 25 °C was pumped off and consisted of IF_5 (29 mmol). The white solid residue (1030 mg; weight calculated for 4.85 mmol of $LiIF_4O$ = 1095 mg) consisted of a mixture of mainly $LiIF_4O$, LiF, and IF_3O and a small amount of IO_2F. The IF_3O and IO_2F were concentrated in the material found in the bottom of the reactor, whereas essentially pure $LiIF_4O$ was obtained from the upper walls of the reactor.

Synthesis of $NOIF_4O$. A 30-mL stainless-steel cylinder was loaded in the drybox with I_2O_5 (1.43 mmol). On the vacuum line, IF_5 (154.8 mmol) and FNO (12.66 mmol) were added at −196 °C. The cylinder was placed on a shaker at ambient temperature for 2 days and then reconnected to the vacuum line. The volatile material was removed in a dynamic vacuum at 20 °C. After several hours of pumping, the weight of the residue (1.80 g) approached that predicted for 7.15 mmol of $NOIF_4O$ (1.78 g), but after an additional 14 h of pumping further decreased to 886 mg, indicating that the complex was not completely stable at ambient temperature. Inspection of the residue in the reactor revealed in its bottom a white, sticky solid and on its upper walls a white, dry solid. More of the white, dry solid had also sublimed to a −196 °C cold trap used to collect the volatile material during the final stages of the pumping. Its Raman and infrared spectra were in good agreement with a predominantly ionic $NO^+IF_4O^-$ salt, whereas the sticky white solid exhibited, in addition to the $NOIF_4O$ absorptions, broad bands in the range characteristic for iodine oxyfluorides and/or their polyanions.

Syntheses of MIF_4O (M = Li, Na, Rb) in CH_3CN Solution. All reactions were carried out in a similar manner by loading within the drybox a mixture of MF (5 mmol) and I_2O_5 (1 mmol), followed by about 20 mL of dry CH_3CN into a 12 in. long, $^3/_4$ in. o.d. Teflon FEP ampule, equipped with a stainless-steel valve and a Teflon-coated magnetic stirring bar. On the vacuum line, IF_5 (3 mmol) was added at −196 °C, and the mixture was stirred at 25 °C for 20 h. All volatile material was removed in a dynamic vacuum at room temperature, leaving behind the desired MIF_4O salts in almost quantitative yield. The color of the solid products was sometimes off-white causing a strong fluorescence background when their laser Raman spectra were recorded.

The FNO_2–IF_5 System. A mixture of IF_5 (4.42 mmol) and FNO_2 (6.9 mmol) was kept in a 30-mL stainless-steel cylinder at 25 °C for 24 h. Then, the cylinder was cooled to −78 °C, and the volatile material (FNO_2, 6.7 mmol) was collected in a −196 °C trap. Therefore, FNO_2 does not form a stable adduct with IF_5 at temperatures as low as −78 °C. The slight discrepancy in the observed FNO_2 material balance is attributed to FNO_2 trapped in the solid IF_5.

Results and Discussion

Fluorine–Oxygen Exchange in IF_7. An excess of IF_7 reacted quantitatively with either $LiNO_3$ at ambient temperature or $NaNO_3$ at 60 °C according to (3). In the case of $CsNO_3$ for

$$\begin{gathered} MNO_3 + IF_7 \rightarrow MF + FNO_2 + IF_5 + 0.5O_2 \\ M = Li,\ Na \end{gathered} \tag{3}$$

3 days at 25 °C, reaction 3 proceeded with a yield of about 35%. However, the CsF formed in (3) underwent the secondary reactions (4)–(6), thus resulting in a mixture of $CsIF_8$,[17] $CsIF_6{\cdot}2IF_5$,[18]

$$CsF + IF_7 \rightarrow CsIF_8 \tag{4}$$

$$CsF + 3IF_5 \rightarrow CsIF_6{\cdot}2IF_5 \tag{5}$$

$$CsF + IF_5 \rightarrow CsIF_6 \tag{6}$$

$CsIF_6$,[18] and unreacted $CsNO_3$ as the solid products. The fact that reaction 3 produced exclusively IF_5 and O_2 and no IF_5O was surprising in view of the previously observed ease of fluorine–oxygen exchange in BrF_5,[1,2] XeF_6,[3] and $XeOF_4$[4] and the ready formation of IF_5O from IF_7 by controlled hydrolysis.[9–13]

One possible explanation for the lack of IF_5O observation in (3) could be that IF_5O is formed initially, but one of the starting materials or byproducts catalyzes its decomposition to IF_5 and O_2. To test this hypothesis, we have examined the stability of IF_5O in the presence of $LiNO_3$, $CsNO_3$, LiF, CsF, FNO_2, or $LiNO_3$ + FNO_2. There was no reaction of IF_5O with either LiF or CsF at 25 °C and LiF at 60 °C. Furthermore, neither $LiNO_3$ nor $CsNO_3$ reacted with a large excess of IF_5O at 25 °C. A temperature of 60 °C was required to achieve the very slow reaction (7). The formation of MIF_4O in (7) and the absence of any

$$\begin{gathered} 2MNO_3 + IF_5O \rightarrow MIF_4O + MF + N_2O_4 + O_2 \\ M = Li\ or\ Cs \end{gathered} \tag{7}$$

MIF_4O_2[19] in the products suggest that IF_5O does not undergo a fluorine–oxygen exchange with MNO_3, but decomposes first to O_2 and IF_5, which then reacts with MNO_3 (see below). For M in (7) being Cs, the secondary reaction 5, i.e. the formation of $CsIF_6{\cdot}2IF_5$, was also observed. Since in the $LiNO_3$–IF_7 system IF_5 and O_2 are being rapidly generated at 25 °C, the slow decomposition of IF_5O at 60 °C in the presence of MNO_3 does not provide a satisfactory explanation for (3).

This conclusion was further supported by a ^{19}F NMR study of the $LiNO_3$–IF_7 system between −20 and +25 °C. Besides a very broad signal at ϕ of about 170 due to IF_7, the only other signals observed were those of IF_5 (quintet at $\phi = 65$ and doublet at $\phi = 11$),[20] which grew with increasing temperature and time.

The effect of FNO_2 on the decomposition of IF_5O was also studied, but again no O_2 evolution was observed at 25 °C. Finally, the effect of FNO_2 in the presence of $LiNO_3$ at 25 °C was investigated. Since $LiNO_3$ is known[14] to react with FNO_2 (eq 8), and the formed N_2O_5 slowly decomposes at 25 °C to N_2O_4 and O_2 (eq 9), a sequence such as (8)–(10) might explain the formation of IF_5 and O_2, as shown by the overall equation (11). Although

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$$LiNO_3 + FNO_2 \rightarrow LiF + N_2O_5 \tag{8}$$

$$2N_2O_5 \rightarrow 2N_2O_4 + O_2 \tag{9}$$

$$N_2O_4 + IF_5O \rightarrow N_2O_5 + IF_5 \tag{10}$$

$$\text{net:}\quad LiNO_3 + FNO_2 + IF_5O \rightarrow LiF + N_2O_4 + IF_5 + O_2 \tag{11}$$

an experiment at 25 °C using a mole ratio of FNO_2:$LiNO_3$:IF_5O = 1:1.2:3.4 resulted in IF_5, N_2O_4, and O_2 formation, the rate was very slow and even after 5 days only about half of the excess of IF_5O used had decomposed to IF_5 and O_2. This finding together with the above described NMR experiment, which showed no detectable IF_5O signal, mitigates against (11) being the cause for the rapid IF_5 formation in the $LiNO_3$–IF_7 system.

Finally, one might argue that in the $LiNO_3$ + IF_7 reaction the IF_7 acts simply as a fluorinating agent (eq 12), similar to the

$$MNO_3 + IF_7 \rightarrow MF + FONO_2 + IF_5 \tag{12}$$

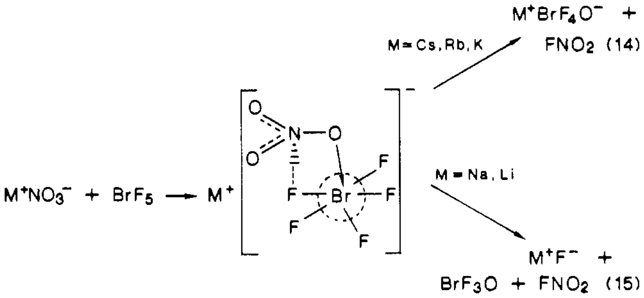
known reaction of F_2 with alkali-metal nitrates.[21,22] The $FONO_2$ could then undergo decomposition to FNO_2 and O_2 (eq 13). The

$$FONO_2 \rightarrow FNO_2 + 0.5O_2 \tag{13}$$

summation of (12) and (13) is identical with the observed reaction 3. Arguments against this reaction path are that (13) is extremely slow at 25 °C,[23] that the above NMR experiment showed no signal due to $FONO_2$,[24] and that the stronger fluorinating agents ClF_5[25] and BrF_5[1,2] undergo fluorine–oxygen exchange with MNO_3 and not O_2 elimination.

Since IF_5O by itself is a stable molecule[10] and there is no evidence for its catalytic decomposition at 25 °C (see above), the lack of IF_5O formation cannot be attributed to instability of the final product. This conclusion is further supported by the case of BrF_3O, which in spite of its well-known instability[26,27] is formed in high yield from BrF_5 and $LiNO_3$.[1]

Possible explanations for the different behavior of IF_7 and BrF_5 include (i) the difference in stability of their oxo anions, IF_6O^- and BrF_4O^-. Whereas BrF_4O^- can form stable salts,[1,26,27] there is no evidence for the formation of IF_6O^- salts (see above). If these anions are crucial intermediates, required for the formation of IF_5O and BrF_3O, respectively, then the nonexistence of IF_6O^- could explain the lack of IF_5O formation. Another explanation is that (ii) the mechanism, previously proposed[1] for the formation of BrF_3O from BrF_5, involves an ionic intermediate formed by the attack of BrF_5 on the nitrate anion (eq 14 and 15).



A crucial part of this mechanism is the existence of a free valence electron pair on the bromine atom that can easily be shifted to open up a required coordination site for the approach of an oxygen atom. If, however, the halogen central atom of the halogen fluoride does not possess a free valence electron pair, as is the case in IF_7 or IF_5O, then the mechanism in (14) and (15) becomes more difficult and O_2 elimination (eq 3) might take place.

When IF_7 was reacted with a large excess of $LiNO_3$, reaction 3, i.e. formation of LiF, FNO_2, IF_5, and 0.5 mol of O_2, occurred in quantitative yield. However, the products FNO_2 and IF_5 underwent further high-yield reactions (eq 16–18) with $LiNO_3$,

$$LiNO_3 + IF_5 \rightarrow LiIF_4O + FNO_2 \tag{16}$$

$$LiNO_3 + FNO_2 \rightarrow LiF + N_2O_5 \tag{17}$$

$$N_2O_5 \rightarrow N_2O_4 + 0.5O_2 \tag{18}$$

resulting in (19) as the overall reaction. Reaction 17 has previously

$$4LiNO_3 + IF_7 \rightarrow LiIF_4O + 3LiF + 2N_2O_4 + 1.5O_2 \tag{19}$$

been demonstrated,[14] and the decomposition of N_2O_5 to N_2O_4 and O_2 (eq 18) is well-known.

Fluorine–Oxygen Exchange in IF_5. In the case of IF_5, which contains a free valence electron pair on iodine, fluorine–oxygen exchange was observed in high yield with $LiNO_3$, KNO_3 and $CsNO_3$ (eq 20). Reaction 20 was always accompanied by the

$$MNO_3 + IF_5 \rightarrow MIF_4O + FNO_2 \qquad M = Li, K, Cs \tag{20}$$

secondary reactions (21) and (18). The fact that the secondary

$$MNO_3 + FNO_2 \rightarrow MF + N_2O_5 \tag{21}$$

reaction (21) always consumed as much MNO_3 as (20) did, strongly indicates that (21) must be considerably faster than (20). Furthermore, if the MF byproduct, formed in (21), can complex with the excess of IF_5, reaction 22 or 23 ensues. These sequences

$$MF + IF_5 \rightarrow MIF_6 \qquad M = K \tag{22}$$

$$MF + 3IF_5 \rightarrow MIF_6{\cdot}2IF_5 \qquad M = Cs \tag{23}$$

explain the observed overall reactions (24)–(26). These results

$$2LiNO_3 + IF_5 \rightarrow LiIF_4O + LiF + N_2O_4 + 0.5O_2 \tag{24}$$

$$2KNO_3 + 2IF_5 \rightarrow KIF_4O + KIF_6 + N_2O_4 + 0.5O_2 \tag{25}$$

$$2CsNO_3 + 4IF_5 \rightarrow CsIF_4O + CsIF_6{\cdot}2IF_5 + N_2O_4 + 0.5O_2 \tag{26}$$

are in excellent agreement with our expectations based on the known reaction chemistry of BrF_5[1] and deviate from the previous report[5] that KNO_3 reacts with a large excess of IF_5 to give KIF_6 and NO_2. Furthermore, the previous claim[28] that FNO_2 and IF_5 produce a white, solid $NO_2^+IF_6^-$ adduct of marginal stability at room temperature could not be verified. In our study it was shown that at temperatures as low as −78 °C, IF_5 does not form a stable adduct with FNO_2.

It should be noted that in one of the fractions of the volatile products from the KNO_3–IF_5 reactions a small amount of material was observed that, on the basis of its gas-phase infrared spectrum, is attributed to iodine mononitrate, $IONO_2$. It exhibited very strong absorption bands at 1686, 1271, and 795 cm^{-1}, that are assigned to the antisymmetric NO_2 stretch, the symmetric NO_2 stretch, and the NO_2 scissoring modes, respectively. The observed frequency trends are in excellent agreement with those predicted from the known series $FONO_2$, $ClONO_2$, and $BrONO_2$.[2]

Alternate Syntheses of IF_4O^- Salts. The only previously known IF_4O^- salts had been $CsIF_4O$[6,7] and KIF_4O.[7,8] The successful synthesis of a stable $LiIF_4O$ salt in this study and the fact that the stability of this type of salt generally decreases with decreasing cation size suggested that all alkali metals and probably also NO^+ should be capable of forming stable IF_4O^- salts. Since the above reactions of alkali-metal nitrates with IF_5 always yielded other solid byproducts in addition to MIF_4O, the synthesis (eq 27)

$$5MF + I_2O_5 + 3IF_5 \xrightarrow{\text{solvent}} 5MIF_4O \tag{27}$$

previously demonstrated[8] for KIF_4O was used for the preparation of essentially pure IF_4O^- salts of Li, Na, Rb, and NO. With CH_3CN used as a solvent, the new compounds $LiIF_4O$, $NaIF_4O$, and $RbIF_4O$ were prepared. Alternatively, an excess of IF_5 can be used as a solvent in (27). In this manner KIF_4O had previously

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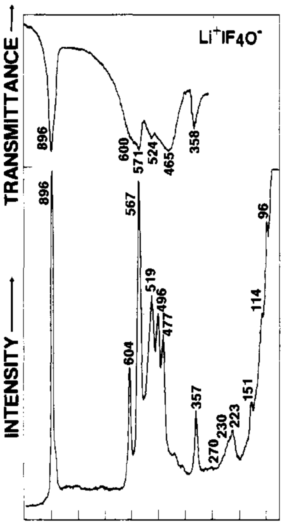
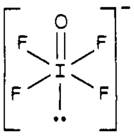


Figure 1. Vibrational spectra of solid $LiIF_4O$.

been prepared,[8] and $LiIF_4O$ and $NOIF_4O$ were synthesized in this study. On the basis of the vibrational spectra, the products prepared in CH_3CN solution appeared to be of better purity than those from IF_5 solution, which, in the case of $LiIF_4O$, showed some IF_3O and IO_2F as impurities. In the case of CH_3CN, however, the products sometimes were off-white, and trace residues of organic materials caused a strong fluorescence background when the laser Raman spectra were recorded. All of the alkali-metal IF_4O^- salts are white solids, stable at room temperature, while the $NO^+IF_4O^-$ salt slowly dissociates at room temperature.

^{19}F NMR Spectra. The IF_4O^- salts were of low solubility in IF_5, but were quite soluble in CH_3CN. The IF_4O^- anion in CH_3CN showed in the ^{19}F NMR spectrum a singlet at ϕ = 3–9 ppm depending on the nature of the cation. The observation of a singlet confirms the presence of a pseudooctahedral IF_4O^- anion with four equivalent equatorial fluorine atoms.



For comparison, the ^{19}F NMR spectrum of IF_3O in CH_3CN was also recorded and showed a broad singlet at ϕ = 14.

Vibrational Spectra. The infrared and Raman spectra of solid $LiIF_4O$, $NaIF_4O$, KIF_4O, $RbIF_4O$, $CsIF_4O$, and $NOIF_4O$ are shown in Figures 1–6, and the observed frequencies and their assignments are summarized in Table I. As in the case of the closely related BrF_4O^- anion,[1,8] the number of observed Raman bands strongly depends on the cation and indicates strong interaction between anions and cations in the crystal lattice. As expected, this interaction is stronger for the smaller cations.

The assignments given in Table I are in very good agreement with those previously made for KIF_4O.[8] The only correction proposed with respect to the previous work is the location of the band center for the antisymmetric IF_4 stretching vibration ν_7(E). The frequency of this band is difficult to determine from the infrared spectra because of the broadness of the bands in the 450–600-cm^{-1} region. Since in $LiIF_4O$ and $NaIF_4O$ one of the degenerate components of this mode is also observable in the Raman spectra, which exhibit much narrower line widths, its frequency can be located more precisely. An averaged value of about 560 cm^{-1} appears much more plausible for ν_7(E) than the previously proposed[8] value of 482 cm^{-1}. This revised frequency for ν_7(E) of IF_4O^- is in much better agreement with the value of 608 cm^{-1} found for isoelectronic $XeOF_4$[29,30] and should alleviate

Table I. Vibrational Spectra of $M^+IF_4O^-$ Salts (M = NO, Li, Na, K, Rb, Cs) Compared to Those of $XeOF_4$

assigns for IF_4O^- in point group C_{4v}				obsd freq, cm^{-1} (rel intens)													
				$NO^+IF_4O^-$		$LiIF_4O$		$NaIF_4O$		KIF_4O		$RbIF_4O$		$CsIF_4O$		$XeOF_4$[b] gas	
				IR	RA	IR	RA	IR	RA	IR	RA	IR	RA	IR	RA	IR	RA
A_1	ν_1	ν_{IO}		868 vs	864 (100)	896 vs	896 (100)	895 vs	896 (100)	885 vs	883 (100)	895 vs	898 (100)	888 vs	889 (90)	926 s	926 m
	ν_2	ν_{sym}	IF_4 in phase	540–460	530 (20) 508 (2)	524 w	567 (90) 519 (55)		541 (85)		540 (98)		531 (80)		528 (100)	576 m	577 vs
	ν_3	δ_{sym}	IF_4 out of plane		286 (1)		270 sh		284 (2)	279 ms[a]	278 sh				270 sh	294 s	286 mw
B_1	ν_4	ν_{sym}	IF_4 out of phase	540–460	484 (17) 460 sh	465 vs	496 (50) 477 (43)	455 vs	513 (30) 457 (30)	500 vs 460 s	492 (30) 465 sh	570–440 vs, br	478 (60)	475 vs	475 (64)		543 m
	ν_5	δ_{asym}	IF_4 out of plane				230 sh										
B_2	ν_6	δ_{sym}	IF_4 in plane		225 (10)		223 (10)		230 (6)		224 (5)[a]				220 sh		225 mw
E	ν_7	ν_{asym}	IF_4	540–460 vs, br	540 sh	600 sh 571 vs	604 (35)	580 sh 540 vs	584 (20)	580 sh 550 vs		570–440 vs, br		530 vs		608 vs	
	ν_8	δ	OIF_4	391 m 350 m	393 (17) 351 (5)	358 m	357 (19)	350 ms	354 (20)	380 m 366 sh[a]	366 (20)	365 m	370 (20)	360 ms	360 (25)	361 s	360 mw
	ν_9	δ_{asym}	IF_4 in plane		159 (3)		151 (4)		150 sh		140 (2)[a]						161 vw

[a] Values from ref 8. [b] Values from ref 29 and 30.

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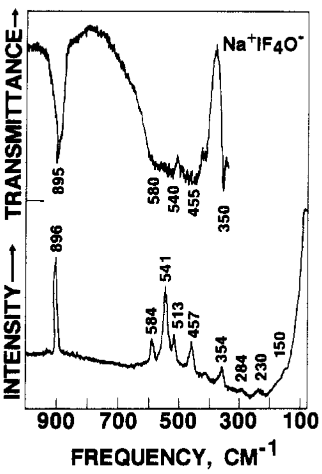

Figure 2. Vibrational spectra of solid $NaIF_4O$.

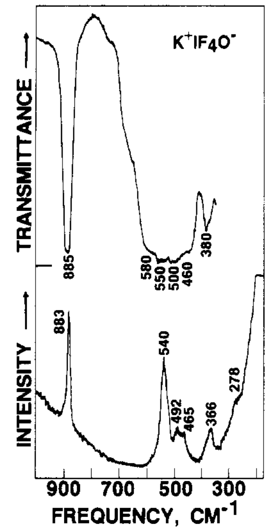

Figure 3. Vibrational spectra of solid KIF_4O.

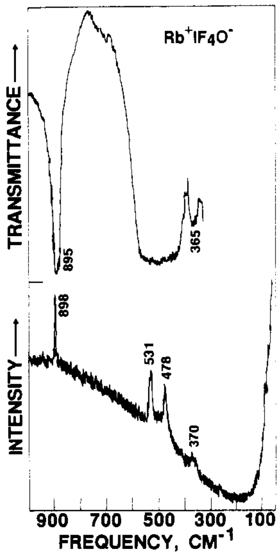

Figure 4. Vibrational spectra of solid $RbIF_4O$.

the anomaly found for $f_{rr'}$ in the normal-coordinate analysis of IF_4O^-.[8]

The vibrational spectra of the solid product obtained from the reaction of FNO with I_2O_5 and IF_5 demonstrate that the compound has the predominantly ionic composition $NO^+IF_4O^-$. The infrared and Raman spectra show an intense band at about 2302 cm^{-1}, which is characteristic for NO^+,[31] in addition to bands that are quite similar to those of the alkali-metal IF_4O^- salts. The slight frequency shifts are attributed to weak covalent contributions to the bonding.

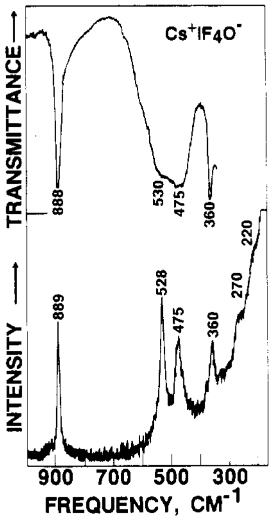

Figure 5. Vibrational spectra of solid $CsIF_4O$.

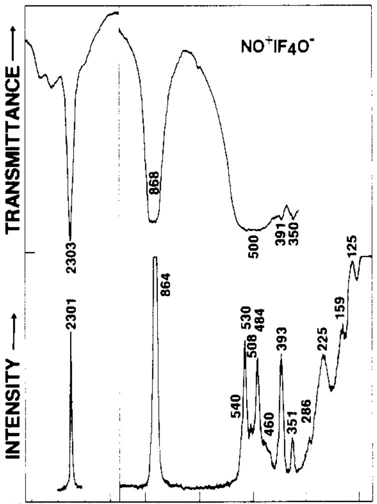

Figure 6. Vibrational spectra of solid $NOIF_4O$.

Conclusions. The nitrate ion is a useful reagent for fluorine-oxygen exchange in IF_5. The resulting IF_4O^- anion is capable of forming stable salts, even with cations as small as Li^+. It also forms a marginally stable, highly ionic NO^+ salt. With IF_7, the NO_3^- anion does not undergo a fluorine–oxygen exchange but causes a surprising reductive deoxygenation, which is attributed to the absence of a free valence electron pair on the iodine central atom of IF_7. With IF_5O, again no fluorine–oxygen exchange was observed. At elevated temperatures, oxygen loss occurred first, followed by the reaction of the resulting IF_5 with NO_3^- to give IF_4O^- salts.

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Registry No. $LiNO_3$, 7790-69-4; $NaNO_3$, 7631-99-4; KNO_3, 7757-79-1; $CsNO_3$, 7789-18-6; FNO_2, 10022-50-1; FNO, 7789-25-5; IF_7, 16921-96-3; IF_5O, 16056-61-4; I_2O_5, 12029-98-0; O_2, 7782-44-7; IF_5, 7783-66-6; NaF, 7681-49-4; $CsIF_8$, 54988-13-5; $CsIF_6{\cdot}2IF_5$, 36949-61-8; $CsIF_6$, 20115-52-0; N_2O_4, 10544-72-6; $LiIF_4O$, 118867-55-3; $IONO_2$, 14696-81-2; KIF_4O, 59654-71-6; KIF_6, 20916-97-6; $CsIF_4O$, 36374-06-8; LiF, 7789-24-4; IF_3O, 19058-78-7; IO_2F, 28633-62-7; $NOIF_4O$, 118867-56-4; $NaIF_4O$, 118831-04-2; $RbIF_4O$, 118831-05-3; RbF, 13446-74-7.

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