Registry No. 1-C_2H_5-2,4-$C_2B_5H_6$, 118319-03-2; 3-C_2H_5-2,4-$C_2B_5H_6$, 118319-04-3; 5-C_2H_5-2,4-$C_2B_5H_6$, 93243-43-7; 1,3-$(C_2H_5)_2$-2,4-$C_2B_5H_5$, 118319-05-4; 1,5-$(C_2H_5)_2$-2,4-$C_2B_5H_5$, 118319-06-5; 1,7-$(C_2H_5)_2$-2,4-$C_2B_5H_5$, 118319-07-6; 3,5-$(C_2H_5)_2$-2,4-$C_2B_5H_5$, 105930-51-6; 5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_5$, 93243-42-6; 1-Cl-3,5-$(C_2H_5)_2$-2,4-$C_2B_5H_4$, 118319-08-7; 1-Cl-3,7-$(C_2H_5)_2$-2,4-$C_2B_5H_4$, 118319-09-8; 1-Cl-5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_4$, 118319-10-1; 1-Cl-5,7-$(C_2H_5)_2$-2,4-$C_2B_5H_4$, 118319-11-2; 3-Cl-1,5-$(C_2H_5)_2$-2,4-$C_2B_5H_4$, 118319-12-3; 3-Cl-1,7-$(C_2H_5)_2$-2,4-$C_2B_5H_4$, 118319-13-4; 3-Cl-5,6-$(C_2H_5)_2$-2,4-$C_2B_5H_4$, 105930-50-5; 5-Cl-1,3-$(C_2H_5)_2$-2,4-$C_2B_5H_4$, 118319-14-5; 5-Cl-1,6-$(C_2H_5)_2$-2,4-$C_2B_5H_4$, 118319-15-6; 5-Cl-1,7-$(C_2H_5)_2$-2,4-$C_2B_5H_4$, 118319-16-7; 5-Cl-3,6-$(C_2H_5)_2$-2,4-$C_2B_5H_4$, 118319-17-8; 3-Cl-5-C_2H_5-2,4-$C_2B_5H_5$, 118334-42-2; 3-Cl-2,4-$C_2B_5H_6$, 28347-93-5; $C_2B_5H_7$, 20693-69-0; C_2H_5Cl, 75-00-3.

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Canoga Park, California 91303

Reactions of Chlorine Fluorides and Oxyfluorides with the Nitrate Anion and Alkali-Metal Fluoride Catalyzed Decomposition of ClF_5

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The binary chlorine fluorides ClF_5, ClF_3, and ClF, when used in an excess, all undergo facile fluorine–oxygen exchange reactions with the nitrate anion, forming $FClO_2$, unstable FClO, and $ClONO_2$, respectively, as the primary products. Whereas $FClO_3$ does not react with $LiNO_3$ at temperatures as high as 75 °C, $FClO_2$ readily reacts with either $LiNO_3$ or N_2O_5 to give $ClONO_2$ and O_2 in high yield, probably via the formation of an unstable O_2ClONO_2 intermediate. With an excess of ClF, chlorine nitrate undergoes a slow reaction to give FNO_2 and Cl_2O as the primary products, followed by Cl_2O reacting with ClF to give Cl_2, ClF, and $FClO_2$. The alkali-metal fluorides CsF, RbF, and KF catalyze the decomposition of ClF_5 to ClF_3 and F_2, which can result in the generation of substantial F_2 pressures at temperatures as low as 25 °C.

Introduction

Ionic nitrates are surprisingly reactive toward the fluorides and oxyfluorides of bromine,[1,2] xenon,[3,4] and iodine.[5] The observed reaction chemistry is fascinating and often unpredictable. Thus, BrF_5 undergoes fluorine–oxygen exchange reactions that, depending on the choice of the nitrate salt or the reagent used in excess, yield either BrF_4O^- salts, free BrF_3O, or bromine nitrates. In the cases of XeF_6, $XeOF_4$, and IF_5, stepwise fluorine–oxygen exchange occurs, whereas for the closely related IF_7 molecule, reduction to IF_5 with simultaneous oxygen evolution was observed. In view of these results it was interesting to study the behavior of chlorine fluorides and oxyfluorides toward ionic nitrates.

The previous reports on reactions of ionic nitrates with chlorine fluorides are limited to a statement by Ruff and Krug that KNO_3 does not react with liquid ClF_3 while $AgNO_3$ does[6] and a synthesis of $ClONO_2$ from ClF and $M(NO_3)_2$ where M is either Ca, Sr, Ba, or Pb.[7] In addition, the reactions of ClF,[8,9] ClF_3,[9] ClF_5,[9] and $FClO_2$[9] with the covalent nitrate $HONO_2$ have previously been studied.

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%), KNO_3 (J. T. Baker, 99.1%), and $RbNO_3$ (K&K Labs, Inc., 99.9%) were dried in vacuo at 120 °C for 1 day prior to their use. $CsNO_3$ was prepared from Cs_2CO_3 and HNO_3 and dried in the same manner. N_2O_5,[10] ClF_5,[11] ClF,[12] and $FClO_2$[13] were prepared by literature methods. $FClO_3$ (Pennsalt) and ClF_3 (Matheson) were commercial materials and were purified by fractional condensation prior to their use.

Caution! Chlorine fluorides and oxyfluorides are powerful oxidizers and can react violently with most organic substances. The materials should be handled only in well-passivated metal–Teflon equipment with all the necessary safety precautions.

Reaction of ClF with an Excess of $NaNO_3$. A mixture of $NaNO_3$ (17.32 mmol) and ClF (11.53 mmol) in a 30-mL stainless steel cylinder was allowed to slowly warm in a dry ice–liquid N_2 slush bath from −196 to −78 °C and then toward 0 °C. The cylinder was recooled to −196 °C and did not contain any gas noncondensible at this temperature. The material volatile at room temperature was separated on warm up of the cylinder from −196 °C by fractional condensation through traps kept at −112, −126, −142, and −196 °C. The −112 °C trap contained $ClONO_2$[14] (8.89 mmol) and Cl_2O[15] (0.68 mmol), the one at −126 °C had $ClONO_2$ (0.09 mmol), the one at −142 °C had Cl_2 (0.35 mmol), while the one at −196 °C contained FNO_2[16] (1.01 mmol). The white solid residue in the cylinder was a mixture of NaF and $NaNO_3$ (1046 mg; weight calculated for 9.99 mmol of NaF and 7.33 mmol of $NaNO_3$ = 1043 mg). The yield of $ClONO_2$, based on ClF, was 76%.

Reaction of $NaNO_3$ with an Excess of ClF. Finely powdered $NaNO_3$ (5.15 mmol) was loaded in the drybox into a prepassivated 30-mL stainless steel cylinder equipped with a valve. On the vacuum line, ClF (8.00 mmol) was added at −196 °C. The cylinder was allowed to slowly warm to room temperature, where it was kept for 3 days. It was cooled again to −196 °C and did not contain any gas noncondensible at this temperature. The material volatile at room temperature was separated on warm up of the cylinder from −196 °C by fractional condensation through traps kept at −142 and −196 °C. The −196 °C trap contained FNO_2 (2.88 mmol) and the one at −142 °C had 5.14 mmol of a mixture

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consisting mainly of $ClONO_2$ and Cl_2O and small amounts of $FClO_2$[17] and Cl_2. The cylinder contained 215 mg of NaF (weight calculated for 5.15 mmol of NaF = 216 mg).

Reaction of $NaNO_3$ with an Excess of ClF_3. Finely powdered $NaNO_3$ (1.02 mmol) was loaded in the drybox into a prepassivated 30-mL stainless-steel reactor, and ClF_3 (5.36 mmol) was added at −196 °C on the vacuum line. The cylinder was allowed to slowly warm to room temperature where it was kept for 10 days. It was recooled to −196 °C and checked for noncondensible gas (0.26 mmol of O_2). The material volatile at room temperature was separated by fractional condensation through traps kept at −112, −126, and −196 °C. The −112 °C trap contained ClF_3[18] (4.36 mmol), and one at −126 °C had $FClO_2$[17] (0.25 mmol), and the one at −196 °C showed FNO_2[16] (1.02 mmol) and ClF[15] (0.77 mmol). The white solid residue (47 mg) consisted of NaF (weight calculated for 1.02 mmol of NaF = 43 mg).

Reaction of $LiNO_3$ with an Excess of ClF_5. A 30-mL stainless-steel cylinder was loaded in the drybox with $LiNO_3$ (2.68 mmol). ClF_5 (40.54 mmol) was added at −196 °C on the vacuum line. The cylinder was warmed from −196 °C to room temperature and kept at this temperature for 3 h with frequent agitation. The reactor was cooled back to −196 °C and did not contain any significant amount of noncondensible gas. The material volatile at room temperature was separated by fractional condensation through a series of traps kept at −95, −142, and −196 °C, while the cylinder was allowed to warm from −196 °C to room temperature. The −95 °C trap was empty, and the −196 °C trap contained FNO_2[16] (2.48 mmol). The contents of the −142 °C trap (40.67 mmol) consisted of unreacted ClF_5,[19] $FClO_2$,[17] and a very small amount of FNO_2.[16] The amount of $FClO_2$ and FNO_2 in the ClF_5 was estimated by infrared spectroscopy and verified by complexing with AsF_5 and weighing of the resulting $ClO_2^+AsF_6^-$[20] and $NO_2^+AsF_6^-$[15] (409 mg, weight calculated for 1.34 mmol of $ClO_2^+AsF_6^-$ and 0.20 mmol of $NO_2^+AsF_6^-$ = 391 mg). The white solid residue in the cylinder (71 mg; weight calculated for 2.68 mmol of LiF = 70 mg) consisted of LiF.

Reaction of $NaNO_3$ with ClF_5. The reaction between $NaNO_3$ and ClF_5 was carried out as described for the $LiNO_3$–ClF_5 system. After 10 days at 25 °C, the $NaNO_3$ had quantitatively reacted to yield 1 mol of NaF and FNO_2 and 0.5 mol of $FClO_2$/mol of $NaNO_3$.

Reaction of KNO_3 with ClF_5. The reaction between KNO_3 and ClF_5 was carried out as described above for $LiNO_3$. After 28 days at 25 °C, the KNO_3 had quantitatively reacted to yield FNO_2 and $FClO_2$ in a 2:1 mole ratio. About 16% of the byproduct KF had been converted to $KClF_4$,[21] and fluorine was found as noncondensible gas at −196 °C and identified by its reaction with mercury.

Reaction of $RbNO_3$ with ClF_5. The reaction between $RbNO_3$ and ClF_5 was carried out as described above. After 31 days at 25 °C, 90% of the $RbNO_3$ had reacted to yield FNO_2[16] and $FClO_2$[17] in a 2:1 mole ratio. About 35% of the byproduct RbF had been converted to $RbClF_4$,[21] and fluorine was identified as noncondensible gas at −196 °C.

Reaction of $CsNO_3$ with ClF_5. The reactions between $CsNO_3$ and ClF_5 were carried out as described above. After 32 days at 25 °C, 16% of the $CsNO_3$ had reacted to yield FNO_2[16] and $FClO_2$[17] in a 2:1 mole ratio. About half of the CsF byproduct had been converted to $CsClF_4$.[21] When the reaction was carried out at 0 °C for 2 h, the conversion of $CsNO_3$ was 4.4%, whereas at 70 °C for 3 days it was 46%. The amount of fluorine evolved in these reactions increased with increasing temperature.

Reaction of $CsNO_3$ with ClF_5 in the Presence of Excess CsF. A mixture of finely powdered $CsNO_3$ (0.97 mmol) and CsF (8.89 mmol) was placed in the drybox into a prepassivated stainless-steel reactor of 32.3-mL volume. On the vacuum line, ClF_5 (14.57 mmol) was added at −196 °C. The cylinder was agitated on a shaker at 25 °C for 18 days and then cooled to −196 °C. It contained 0.56 mmol of a noncondensible gas, which reacted quantitatively with Hg giving a weight increase of 21 mg (weight increase calculated for 0.56 mmol of F_2 = 21.3 mg). The material volatile at 25 °C was separated by fractional condensation through traps kept at −142 and −196 °C. The −196 °C trap contained FNO_2[16] (0.093 mmol) and $FONO_2$[14] (0.028 mmol), while the one at −142 °C had ClF_5[19] (13.97 mmol) corresponding to a ClF_5 consumption of 0.60 mmol. The white solid residue (1610 mg, weight calculated for the below given material balance = 1593 mg) was shown by Raman spectroscopy to contain significant amounts of $CsNO_3$ and $CsClF_4$.[21] These results are in excellent agreement with the following material balance:

$$0.59ClF_5 \rightarrow 0.59ClF_3 + 0.59F_2$$

$$0.028F_2 + 0.028CsNO_3 \rightarrow 0.028CsF + 0.028FONO_2$$

$$0.0465ClF_5 + 0.093CsNO_3 \rightarrow 0.093CsF + 0.093FNO_2 + 0.0465FClO_2$$

$$0.59ClF_3 + 0.59CsF \rightarrow 0.59CsClF_4$$

$$0.0465CsF + 0.0465FClO_2 \rightarrow 0.0465CsClF_2O_2$$

Reaction of $FClO_2$ with $LiNO_3$. Finely powdered $LiNO_3$ (2.41 mmol) was placed in the drybox into a prepassivated 30-mL stainless-steel reactor, and $FClO_2$ (1.62 mmol) was added at −196 °C on the vacuum line. The cylinder was allowed to slowly warm to room temperature where it was kept for 15 h. It was recooled to −196 °C, and the noncondensible gas (1.58 mmol of O_2) was pumped off. The material volatile at room temperature consisted of $ClONO_2$[14] (1.59 mmol). The white, solid residue (96 mg) was a mixture of LiF and $LiNO_3$ (weight calculated for 1.62 mmol of LiF and 0.79 mmol of $LiNO_3$ = 96 mg).

Reaction of $FClO_2$ with N_2O_5. N_2O_5 (0.83 mmol) was condensed at −31 °C in a dynamic vacuum into a 5-mm-o.d. glass NMR tube, which was attached to a flamed-out 96-mL Pyrex vessel equipped with two Teflon valves. $FClO_2$ (1.87 mmol) was added to the NMR tube at −196 °C. No appreciable reaction between N_2O_5 and $FClO_2$ was observed at temperatures as high as −31 °C. When the mixture was kept at 0 °C for 18 h, about 64% of the N_2O_5 had reacted with $FClO_2$ to yield $ClONO_2$[14] and O_2 as the main products. In addition, there was an attack of $FClO_2$ on the Pyrex vessel, resulting in substantial amounts of ClO_2 and SiF_4 and a trace amount of $NO_2^+ClO_4^-$.[22] The residue left behind at −78 °C in the NMR tube was identified by Raman spectroscopy as unreacted N_2O_5.[10]

Results and Discussion

MNO_3–ClF System. ClF readily reacts with $NaNO_3$ at subambient temperature to give NaF and $ClONO_2$ (eq 1). However,

$$NaNO_3 + ClF \rightarrow NaF + ClONO_2 \tag{1}$$

the yield of $ClONO_2$ was found to be less than quantitative because of the competing reaction 2. Reaction 2 might be explained by

$$NaNO_3 + 2ClF \rightarrow NaF + Cl_2O + FNO_2 \tag{2}$$

a secondary reaction of $ClONO_2$, formed in (1), with a second mole of ClF (eq 3). In a previous study,[9] $ClONO_2$ and ClF were

$$ClONO_2 + ClF \rightarrow Cl_2O + FNO_2 \tag{3}$$

found not to interact appreciably below room temperature and with relatively short reaction times. However, it was shown in this study that at room temperature and with reaction times of several days reaction 3 slowly proceeds to give Cl_2O and FNO_2 as the main products with Cl_2 and $FClO_2$ as the byproducts. The byproducts are readily explained by the previously reported,[9,23] relatively fast reactions 4 and 5, which are summarized in (6).

$$2Cl_2O + 2ClF \rightarrow 2Cl_2 + 2FClO \tag{4}$$

$$2FClO \rightarrow ClF + FClO_2 \tag{5}$$

$$\text{net:}\quad 2Cl_2O + ClF \rightarrow 2Cl_2 + FClO_2 \tag{6}$$

The fact that, for reaction 1, side reaction 2 could not be completely suppressed even at low temperatures indicates either acceleration of (3) under the conditions of (1) or a slightly different reaction path.

Obviously, reactions 2, 3, and 6 are favored by an excess of ClF. In order to maximize the yield of $ClONO_2$ in (1), it is, therefore, advantageous to employ an excess of $NaNO_3$. Furthermore, a lowering of the reaction temperature should also favor the formation of $ClONO_2$. By the use of about 100% excess of $NaNO_3$ and subambient reaction temperatures, a $ClONO_2$ yield of about 76%, based on ClF, was obtained. This yield is somewhat lower than the 92% previously reported[7] for the $Pb(NO_3)_2$ + ClF system,

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but is higher than those given for $Ca(NO_3)_2$ (63%), $Sr(NO_3)_2$ (44%), and $Ba(NO_3)_2$ (<10%). The main advantage of $NaNO_3$ over these other nitrates is its lower cost.

MNO_3–ClF_3 System. An excess of ClF_3 readily reacts with $NaNO_3$ at room temperature or below to give FNO_2, ClF, $FClO_2$, and O_2 as the main products. These are best rationalized in terms of the fluorine–oxygen exchange reaction 7, which generates FClO.

$$ClF_3 + NaNO_3 \rightarrow NaF + FNO_2 + FClO \quad (7)$$

The thermally unstable FClO then undergoes either disproportionation (eq 8, or decomposition eq 9), with (8) and (9) contributing about equally.

$$2FClO \rightarrow ClF + FClO_2 \quad (8)$$

$$2FClO \rightarrow 2ClF + O_2 \quad (9)$$

In the presence of a large excess of $NaNO_3$ the FNO_2,[10] $FClO_2$, and ClF products can react further with $NaNO_3$ according to (10)–(12).

$$FNO_2 + NaNO_3 \rightarrow NaF + N_2O_5 \quad (10)$$

$$FClO_2 + NaNO_3 \rightarrow NaF + ClONO_2 + O_2 \quad (11)$$

$$ClF + NaNO_3 \rightarrow NaF + ClONO_2 \quad (12)$$

MNO_3–ClF_5 System. From a preparative point of view, the reactions of ClF_5 were most interesting. For IF_5 and BrF_5 a stepwise fluorine–oxygen exchange was possible,[1,2,5] thus allowing the isolation of either XF_4O^- salts or the free XF_3O molecule. Since ClF_3O is rather difficult to synthesize,[23] a simpler synthesis of either ClF_3O or its ClF_4O^- salts is highly desirable. Consequently, the reactions of all alkali-metal nitrates with ClF_5 were studied by using a large excess of the latter to suppress, if possible, the second fluorine–oxygen exchange step leading to $FClO_2$. However, in all cases exclusively the two-step exchange reaction shown in (13) was observed. This suggests that the reaction of

$$2MNO_3 + ClF_5 \rightarrow 2MF + 2FNO_2 + FClO_2 \quad (13)$$

$$M = Li, Na, K, Rb, Cs$$

the intermediately formed ClF_3O with MNO_3 is much faster than either that of ClF_5 with MNO_3 or the complexation of ClF_3O (eq 14). In one experiment a 10-fold excess of CsF was added to

$$MF + ClF_3O \rightarrow M^+ClF_4O^- \quad (14)$$

the $CsNO_3$–ClF_5 reaction in an attempt to trap any intermediately formed ClF_3O as $Cs^+ClF_4O^-$. Although no evidence for the formation of $Cs^+ClF_4O^-$ was obtained, a detailed material balance of the reaction revealed two very interesting side reactions.

In the first side reaction, a significant amount of ClF_5 had decomposed at 25 °C to give equimolar amounts of F_2 and ClF_3 with the latter being complexed by CsF as $Cs^+ClF_4^-$. This side reaction had also been observed for $RbNO_3$ and KNO_3, but to a lesser extent. This decomposition of ClF_5 to ClF_3 and F_2 at room temperature was surprising in view of ClF_5 normally being completely stable at this temperature.[11] Although extrapolation of the degree of dissociation of ClF_5 at 25 °C from the known equlibrium constant temperature relationship[24] gives a value of 0.087%, this dissociation should require a significant activation energy and, therefore, not proceed under normal conditions. Our observation that in the presence of excess CsF more than 4% of the ClF_5 decomposed in 18 days at 25 °C while building up a fluorine pressure of about 340 Torr in the reactor, suggests that the alkali-metal fluorides (i) lower the activation energy required for the ClF_5 decomposition and (ii) effectively remove ClF_3 from the equilibrium given in (15), thereby shifting it to the right. The

$$ClF_5 \rightleftarrows ClF_3 + F_2 \quad (15)$$

catalytic effect of alkali-metal fluorides for the backward reaction, i.e. the formation of ClF_5 from ClF_3 and F_2, has previously been recognized, and advantage of this has been taken for the ClF_5 synthesis[11] but to our knowledge has not been noted for the forward reaction.

The second side reaction observed for the $CsNO_3 + ClF_5 +$ CsF system was the formation of some fluorine nitrate, $FONO_2$. This can readily be explained by the known[16,25,26] reaction given in (16). The F_2 required for (16) is generated by (15).

$$CsNO_3 + F_2 \rightarrow CsF + FONO_2 \quad (16)$$

MNO_3–$FClO_2$ System. When a large excess of MNO_3 is used in (13), the $FClO_2$ product can undergo further reaction with MNO_3. This was confirmed in a separate experiment between $LiNO_3$ and $FClO_2$, which reacted according to (17). The

$$LiNO_3 + FClO_2 \rightarrow LiF + ClONO_2 + O_2 \quad (17)$$

quantitative formation of equimolar amounts of $ClONO_2$ and O_2 suggested the yet unknown O_2ClONO_2 molecule as an unstable intermediate. An attempt was made to isolate this intermediate at low temperature by reaction 18. By the use of an excess of

$$NO_2^+NO_3^- + FClO_2 \rightarrow O_2ClONO_2 + FNO_2 \quad (18)$$

$FClO_2$, it was hoped that the only product of low volatility would be O_2ClONO_2, thus allowing a convenient product purification and isolation. Unfortunately, reaction 18 required a reaction temperature of 0 °C, well above the apparent thermal stability of the desired O_2ClONO_2. Consequently, the observed products were again $ClONO_2$ and O_2, formed according to (19). Since

$$NO_2^+NO_3^- + FClO_2 \rightarrow FNO_2 + ClONO_2 + O_2 \quad (19)$$

this reaction was carried out in a Pyrex reactor to allow a low-temperature spectroscopic identification of the reaction product, side reactions of $FClO_2$ and N_2O_5 with the glass in the upper part of the reactor and each other also occurred, producing some SiF_4 and NO_2ClO_4.

Conclusion. All of the chlorine fluorides and oxyfluorides studied, except for the highly unreactive[23] $FClO_3$, undergo facile fluorine–oxygen exchange with ionic nitrates. The observed reaction chemistry is in general agreement with that previously found[9] for the analogous reactions with nitric acid, except for some minor deviations for $FClO_2$, which are attributed to thermally unstable intermediates. Depending on the exact reaction conditions, these unstable intermediates can decompose to different products.

Comparison of the nitrate–ClF_5 reactions with those of IF_5[5] and BrF_5[1,2] shows a noteworthy difference. Whereas for IF_5 and BrF_5 the fluorine–oxygen exchange could be halted at the XF_3O or XF_4O^- stage, this was not possible for ClF_5. This difference cannot be attributed to the thermal stability of the products (ClF_3O is thermally more stable than BrF_3O), but is most likely due to the extreme reactivity of ClF_3O.[23]

The alkali-metal fluoride catalyst decomposition of ClF_5 to ClF_3 and F_2 at room temperature was surprising and suggests a very low activation energy path for this reaction. It might possibly involve the attack of the free fluoride ion on a fluorine ligand of ClF_5, followed by fluorine elimination. If this assumption is indeed correct, this catalysis should be generally applicable to other high oxidation state fluorides of highly electronegative elements.

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Registry No. ClF_5, 13637-63-3; ClF_3, 7790-91-2; ClF, 7790-89-8; NO_3^-, 14797-55-8; $FClO_2$, 13637-83-7; FClO, 22363-68-4; $ClONO_2$, 14545-72-3; $FClO_3$, 7616-94-6; $LiNO_3$, 7790-69-4; N_2O_5, 10102-03-1; FNO_2, 10022-50-1; Cl_2O, 7791-21-1; Cl_2, 7782-50-5; CsF, 13400-13-0; RbF, 13446-74-7; KF, 7789-23-3; F_2, 7782-41-4; $NaNO_3$, 7631-99-4; KNO_3, 7757-79-1; $KClF_4$, 19195-69-8; $RbNO_3$, 13126-12-0; $CsNO_3$, 7789-18-6; $RbClF_4$, 15321-10-5; $CsClF_4$, 15321-04-7.

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