

Registry No. 1-C₂H₅-2,4-C₂B₅H₆, 118319-03-2; 3-C₂H₅-2,4-C₂B₅H₆, 118319-04-3; 5-C₂H₅-2,4-C₂B₅H₆, 93243-43-7; 1,3-(C₂H₅)₂-2,4-C₂B₅H₅, 118319-05-4; 1,5-(C₂H₅)₂-2,4-C₂B₅H₅, 118319-06-5; 1,7-(C₂H₅)₂-2,4-C₂B₅H₅, 118319-07-6; 3,5-(C₂H₅)₂-2,4-C₂B₅H₅, 105930-51-6; 5,6-(C₂H₅)₂-2,4-C₂B₅H₅, 93243-42-6; 1-Cl-3,5-(C₂H₅)₂-2,4-C₂B₅H₄, 118319-08-7; 1-Cl-3,7-(C₂H₅)₂-2,4-C₂B₅H₄, 118319-09-8; 1-Cl-5,6-(C₂H₅)₂-2,4-C₂B₅H₄, 118319-10-1; 1-Cl-5,7-(C₂H₅)₂-2,4-C₂B₅H₄,

118319-11-2; 3-Cl-1,5-(C₂H₅)₂-2,4-C₂B₅H₄, 118319-12-3; 3-Cl-1,7-(C₂H₅)₂-2,4-C₂B₅H₄, 118319-13-4; 3-Cl-5,6-(C₂H₅)₂-2,4-C₂B₅H₄, 105930-50-5; 5-Cl-1,3-(C₂H₅)₂-2,4-C₂B₅H₄, 118319-14-5; 5-Cl-1,6-(C₂H₅)₂-2,4-C₂B₅H₄, 118319-15-6; 5-Cl-1,7-(C₂H₅)₂-2,4-C₂B₅H₄, 118319-16-7; 5-Cl-3,6-(C₂H₅)₂-2,4-C₂B₅H₄, 118319-17-8; 3-Cl-5-C₂H₅-2,4-C₂B₅H₅, 118334-42-2; 3-Cl-2,4-C₂B₅H₆, 28347-93-5; C₂B₅H₇, 20693-69-0; C₂H₅Cl, 75-00-3.

Contribution from Rocketdyne, A Division of Rockwell International, Canoga Park, California 91303

Reactions of Chlorine Fluorides and Oxyfluorides with the Nitrate Anion and Alkali-Metal Fluoride Catalyzed Decomposition of ClF₃

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The binary chlorine fluorides ClF₂, ClF₃, and ClF, when used in an excess, all undergo facile fluorine-oxygen exchange reactions with the nitrate anion, forming FClO₂, unstable FClO, and ClONO₂, respectively, as the primary products. Whereas FClO₃ does not react with LiNO₃ at temperatures as high as 75 °C, FClO₂ readily reacts with either LiNO₃ or N₂O₅ to give ClONO₂ and O₂ in high yield, probably via the formation of an unstable O₂ClONO₂ intermediate. With an excess of ClF, chlorine nitrate undergoes a slow reaction to give FNO₂ and Cl₂O as the primary products, followed by Cl₂O reacting with ClF to give Cl₂, ClF, and FClO₂. The alkali-metal fluorides CsF, RbF, and KF catalyze the decomposition of ClF₃ to ClF₂ and F₂, which can result in the generation of substantial F₂ 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, BrF₅ undergoes fluorine-oxygen exchange reactions that, depending on the choice of the nitrate salt or the reagent used in excess, yield either BrF₄O⁻ salts, free BrF₃O, or bromine nitrates. In the cases of XeF₆, XeOF₄, and IF₅, stepwise fluorine-oxygen exchange occurs, whereas for the closely related IF₇ molecule, reduction to IF₃ 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 KNO₃ does not react with liquid ClF₃ while AgNO₃ does⁶ and a synthesis of ClONO₂ from ClF and M(NO₃)₂ where M is either Ca, Sr, Ba, or Pb.⁷ In addition, the reactions of ClF,^{8,9} ClF₃,⁹ ClF₅,⁹ and FClO₂⁹ with the covalent nitrate HONO₂ 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 LiNO₃ (J. T. Baker, 99.7%), NaNO₃ (J. T. Baker, 99.5%), KNO₃ (J. T. Baker, 99.1%), and RbNO₃ (K&K Labs, Inc., 99.9%) were dried in vacuo at 120 °C for 1 day prior to their use. CsNO₃ was prepared from Cs₂CO₃ and HNO₃ and dried in the same manner. N₂O₅,¹⁰ ClF₃,¹¹ ClF,¹² and FClO₂¹³ were prepared by literature methods.

FClO₃ (Pennsalt) and ClF₃ (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 NaNO₃. A mixture of NaNO₃ (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 N₂ 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 noncondensable 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 ClONO₂¹⁴ (8.89 mmol) and Cl₂O¹⁵ (0.68 mmol), the one at -126 °C had ClONO₂ (0.09 mmol), the one at -142 °C had Cl₂ (0.35 mmol), while the one at -196 °C contained FNO₂¹⁶ (1.01 mmol). The white solid residue in the cylinder was a mixture of NaF and NaNO₃ (1046 mg; weight calculated for 9.99 mmol of NaF and 7.33 mmol of NaNO₃ = 1043 mg). The yield of ClONO₂, based on ClF, was 76%.

Reaction of NaNO₃ with an Excess of ClF. Finely powdered NaNO₃ (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 noncondensable 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 FNO₂ (2.88 mmol) and the one at -142 °C had 5.14 mmol of a mixture

- (1) Wilson, W. W.; Christe, K. O. *Inorg. Chem.* **1987**, *26*, 916.
- (2) Wilson, W. W.; Christe, K. O. *Inorg. Chem.* **1987**, *26*, 1573.
- (3) Christe, K. O.; Wilson, W. W. *Inorg. Chem.* **1988**, *27*, 1296.
- (4) Christe, K. O.; Wilson, W. W. *Inorg. Chem.*, in press.
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- (6) Ruff, O.; Krug, H. Z. *Angew. Allg. Chem.* **1930**, *190*, 270.
- (7) Schmeisser, M.; Eckermann, W.; Gundlach, K. P.; Naumann, D. Z. *Naturforsch.* **1980**, *35B*, 1143.
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- (13) Christe, K. O.; Wilson, R. D.; Schack, C. J. *Inorg. Synth.* **1986**, *24*, 3.
- (14) Christe, K. O.; Schack, C. J.; Wilson, R. D. *Inorg. Chem.* **1974**, *13*, 2811.
- (15) Siebert, H. *Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie. Anorganische und Allgemeine Chemie in Einzeldarstellungen*; Springer Verlag: Berlin, Heidelberg, FRG, New York, **1966**; Vol. VII.
- (16) Bernitt, D. L.; Miller, R. J.; Hisatsune, I. C. *Spectrochim. Acta, Part A* **1967**, *23*, 237.

consisting mainly of ClONO₂ and Cl₂O and small amounts of FClO₂¹⁷ and Cl₂. The cylinder contained 215 mg of NaF (weight calculated for 5.15 mmol of NaF = 216 mg).

Reaction of NaNO₃ with an Excess of ClF₃. Finely powdered NaNO₃ (1.02 mmol) was loaded in the drybox into a prepassivated 30-mL stainless-steel reactor, and ClF₃ (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 noncondensable gas (0.26 mmol of O₂). 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 ClF₃¹⁸ (4.36 mmol), and one at -126 °C had FClO₂¹⁷ (0.25 mmol), and the one at -196 °C showed FNO₂¹⁶ (1.02 mmol) and ClF₃¹⁵ (0.77 mmol). The white solid residue (47 mg) consisted of NaF (weight calculated for 1.02 mmol of NaF = 43 mg).

Reaction of LiNO₃ with an Excess of ClF₃. A 30-mL stainless-steel cylinder was loaded in the drybox with LiNO₃ (2.68 mmol). ClF₃ (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 noncondensable 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 FNO₂¹⁶ (2.48 mmol). The contents of the -142 °C trap (40.67 mmol) consisted of unreacted ClF₃,¹⁹ FClO₂,¹⁷ and a very small amount of FNO₂.¹⁶ The amount of FClO₂ and FNO₂ in the ClF₃ was estimated by infrared spectroscopy and verified by complexing with AsF₅ and weighing of the resulting ClO₂⁺AsF₆⁻²⁰ and NO₂⁺AsF₆⁻¹⁵ (409 mg, weight calculated for 1.34 mmol of ClO₂⁺AsF₆⁻ and 0.20 mmol of NO₂⁺AsF₆⁻ = 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 NaNO₃ with ClF₃. The reaction between NaNO₃ and ClF₃ was carried out as described for the LiNO₃-ClF₃ system. After 10 days at 25 °C, the NaNO₃ had quantitatively reacted to yield 1 mol of NaF and FNO₂ and 0.5 mol of FClO₂/mol of NaNO₃.

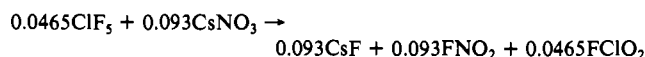
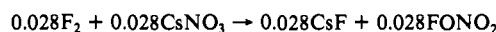
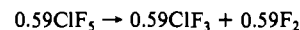
Reaction of KNO₃ with ClF₃. The reaction between KNO₃ and ClF₃ was carried out as described above for LiNO₃. After 28 days at 25 °C, the KNO₃ had quantitatively reacted to yield FNO₂ and FClO₂ in a 2:1 mole ratio. About 16% of the byproduct KF had been converted to KClF₄,²¹ and fluorine was found as noncondensable gas at -196 °C and identified by its reaction with mercury.

Reaction of RbNO₃ with ClF₃. The reaction between RbNO₃ and ClF₃ was carried out as described above. After 31 days at 25 °C, 90% of the RbNO₃ had reacted to yield FNO₂¹⁶ and FClO₂¹⁷ in a 2:1 mole ratio. About 35% of the byproduct RbF had been converted to RbClF₄,²¹ and fluorine was identified as noncondensable gas at -196 °C.

Reaction of CsNO₃ with ClF₃. The reactions between CsNO₃ and ClF₃ were carried out as described above. After 32 days at 25 °C, 16% of the CsNO₃ had reacted to yield FNO₂¹⁶ and FClO₂¹⁷ in a 2:1 mole ratio. About half of the CsF byproduct had been converted to CsClF₄.²¹ When the reaction was carried out at 0 °C for 2 h, the conversion of CsNO₃ 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 CsNO₃ with ClF₃ in the Presence of Excess CsF. A mixture of finely powdered CsNO₃ (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, ClF₃ (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 noncondensable gas, which reacted quantitatively with Hg giving a weight increase of 21 mg (weight increase calculated for 0.56 mmol of F₂ = 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 FNO₂¹⁶ (0.093 mmol) and FONO₂¹⁴ (0.028 mmol), while the one at -142 °C had ClF₃¹⁹ (13.97 mmol) corresponding to a ClF₃ 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 CsNO₃ and CsClF₄.²¹

These results are in excellent agreement with the following material balance:

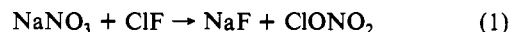


Reaction of FClO₂ with LiNO₃. Finely powdered LiNO₃ (2.41 mmol) was placed in the drybox into a prepassivated 30-mL stainless-steel reactor, and FClO₂ (1.62 mmol) was added at -196 °C on the vacuum line. The cylinder was allowed to slowly warm to room temperature where it was kept for 15 h. It was recooled to -196 °C, and the noncondensable gas (1.58 mmol of O₂) was pumped off. The material volatile at room temperature consisted of ClONO₂¹⁴ (1.59 mmol). The white, solid residue (96 mg) was a mixture of LiF and LiNO₃ (weight calculated for 1.62 mmol of LiF and 0.79 mmol of LiNO₃ = 96 mg).

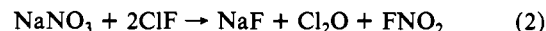
Reaction of FClO₂ with N₂O₅. N₂O₅ (0.83 mmol) was condensed at -31 °C in a dynamic vacuum into a 5-mm-o.d. glass NMR tube, which was attached to a flamed-out 96-mL Pyrex vessel equipped with two Teflon valves. FClO₂ (1.87 mmol) was added to the NMR tube at -196 °C. No appreciable reaction between N₂O₅ and FClO₂ was observed at temperatures as high as -31 °C. When the mixture was kept at 0 °C for 18 h, about 64% of the N₂O₅ had reacted with FClO₂ to yield ClONO₂¹⁴ and O₂ as the main products. In addition, there was an attack of FClO₂ on the Pyrex vessel, resulting in substantial amounts of ClO₂ and SiF₄ and a trace amount of NO₂⁺ClO₄⁻²². The residue left behind at -78 °C in the NMR tube was identified by Raman spectroscopy as unreacted N₂O₅.¹⁰

Results and Discussion

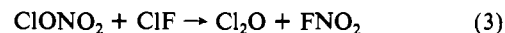
MNO₃-ClF System. ClF readily reacts with NaNO₃ at subambient temperature to give NaF and ClONO₂ (eq 1). However,



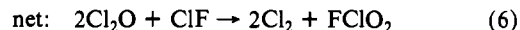
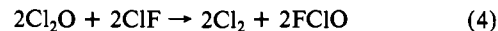
the yield of ClONO₂ was found to be less than quantitative because of the competing reaction 2. Reaction 2 might be explained by



a secondary reaction of ClONO₂, formed in (1), with a second mole of ClF (eq 3). In a previous study,⁹ ClONO₂ and ClF were



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 Cl₂O and FNO₂ as the main products with Cl₂ and FClO₂ 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).



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 ClONO₂ in (1), it is, therefore, advantageous to employ an excess of NaNO₃. Furthermore, a lowering of the reaction temperature should also favor the formation of ClONO₂. By the use of about 100% excess of NaNO₃ and subambient reaction temperatures, a ClONO₂ yield of about 76%, based on ClF, was obtained. This yield is somewhat lower than the 92% previously reported⁷ for the Pb(NO₃)₂ + ClF system,

(17) Smith, D. F.; Begun, G. M.; Fletcher, W. H. *Spectrochim. Acta* **1964**, *20*, 1763.

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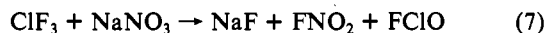
(21) Christe, K. O.; Sawodny, W. *Z. Anorg. Allg. Chem.* **1970**, *374*, 306.

(22) Nebgen, J. W.; McElroy, A. D.; Klodowski, H. F. *Inorg. Chem.* **1965**, *6*, 1796.

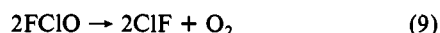
(23) Christe, K. O.; Schack, C. J. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 319.

but is higher than those given for $\text{Ca}(\text{NO}_3)_2$ (63%), $\text{Sr}(\text{NO}_3)_2$ (44%), and $\text{Ba}(\text{NO}_3)_2$ (<10%). The main advantage of NaNO_3 over these other nitrates is its lower cost.

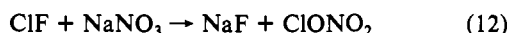
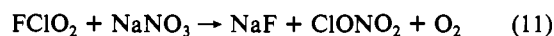
MNO_3 - ClF_3 System. An excess of ClF_3 readily reacts with NaNO_3 at room temperature or below to give FNO_2 , ClF , FCIO_2 , and O_2 as the main products. These are best rationalized in terms of the fluorine-oxygen exchange reaction 7, which generates FCIO .



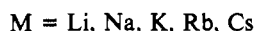
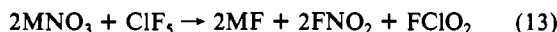
The thermally unstable FCIO then undergoes either disproportionation (eq 8, or decomposition eq 9), with (8) and (9) contributing about equally.



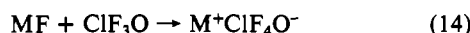
In the presence of a large excess of NaNO_3 the FNO_2 ,¹⁰ FCIO_2 , and ClF products can react further with NaNO_3 according to (10)-(12).



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 FCIO_2 . However, in all cases exclusively the two-step exchange reaction shown in (13) was observed. This suggests that the reaction of

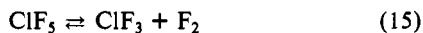


the intermediately formed ClF_3O with MNO_3 is much faster than either that of ClF_5 with MNO_3 or the complexation of ClF_3O (eq 14). In one experiment a 10-fold excess of CsF was added to



the CsNO_3 - ClF_5 reaction in an attempt to trap any intermediately formed ClF_3O as $\text{Cs}^+\text{ClF}_4\text{O}^-$. Although no evidence for the formation of $\text{Cs}^+\text{ClF}_4\text{O}^-$ was obtained, a detailed material balance of the reaction revealed two very interesting side reactions.

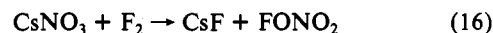
In the first side reaction, a significant amount of ClF_5 had decomposed at 25 °C to give equimolar amounts of F_2 and ClF_3 with the latter being complexed by CsF as $\text{Cs}^+\text{ClF}_4^-$. This side reaction had also been observed for RbNO_3 and KNO_3 , but to a lesser extent. This decomposition 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 equilibrium constant temperature relationship²⁴ 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



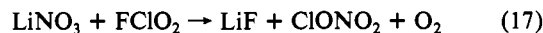
catalytic effect of alkali-metal fluorides for the backward reaction,

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 synthesis¹¹ but to our knowledge has not been noted for the forward reaction.

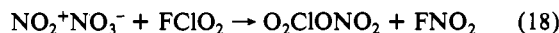
The second side reaction observed for the $\text{CsNO}_3 + \text{ClF}_5 + \text{CsF}$ system was the formation of some fluorine nitrate, FONO_2 . This can readily be explained by the known^{16,25,26} reaction given in (16). The F_2 required for (16) is generated by (15).



MNO_3 - FCIO_2 System. When a large excess of MNO_3 is used in (13), the FCIO_2 product can undergo further reaction with MNO_3 . This was confirmed in a separate experiment between LiNO_3 and FCIO_2 , which reacted according to (17). The



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



FCIO_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



this reaction was carried out in a Pyrex reactor to allow a low-temperature spectroscopic identification of the reaction product, side reactions of FCIO_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 unreactive²³ FCIO_3 , undergo facile fluorine-oxygen exchange with ionic nitrates. The observed reaction chemistry is in general agreement with that previously found⁹ for the analogous reactions with nitric acid, except for some minor deviations for FCIO_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; FCIO_2 , 13637-83-7; FCIO , 22363-68-4; ClONO_2 , 14545-72-3; FCIO_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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