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## REACTIONS OF $\text{BrF}_5$ WITH THE AZIDE, NITRITE AND SULFATE ANIONS

KARL O. CHRIS<sup>T</sup>E\*, WILLIAM W. WILSON and CARL J. SCHACK

Rocketdyne, A Division of Rockwell International Corporation, Canoga Park, California  
91303 (U.S.A)

### SUMMARY

Bromine pentafluoride undergoes a facile fluorine-oxygen exchange reaction with the sulfate anion to yield an equimolar mixture of  $\text{BrF}_4\text{O}^-$  and  $\text{SO}_3\text{F}^-$  salts. With  $\text{CsN}_3$  it ignites producing  $\text{N}_2$  and a mixture of  $\text{CsBrF}_4$  and  $\text{CsBrF}_6$ . With an excess of  $\text{NaNO}_2$  it forms  $\text{NaF}$ ,  $\text{Br}_2$ , and  $\text{FNO}_2$ . When  $\text{BrF}_5$  is used in excess with  $\text{KNO}_2$  its reduction is halted at the  $\text{BrF}_3$  stage producing  $\text{KBrF}_4$  and  $\text{FNO}_2$  as the primary products. The  $\text{FNO}_2$  can undergo a secondary reaction with  $\text{KNO}_2$  to give  $\text{N}_2\text{O}_4$  and  $\text{KF}$  which react further to  $\text{FNO}$  and  $\text{KNO}_3$ . The latter and excess  $\text{BrF}_5$  yield some  $\text{KBrF}_4\text{O}$  and  $\text{FNO}_2$ .

### INTRODUCTION

The  $\text{NF}_4^+$  and  $\text{ClF}_6^+$  cations possess surprising kinetic stability and by metathesis in suitable solvents can be coupled with a variety of anions [1,2]. Since one of the best solvents for this purpose is  $\text{BrF}_5$ , its compatibility with the  $\text{N}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{SO}_4^{2-}$  anions was studied. Although these anions were found to be unstable in  $\text{BrF}_5$ , the observed reactions are interesting and are reported in this paper.

### EXPERIMENTAL

Apparatus and Materials. The vacuum lines, handling techniques and spectrometers used in this study have been described elsewhere [3]. The  $\text{BrF}_5$  (Matheson) was treated with 35 atm

of  $F_2$  at  $100^\circ C$  for 24 hours in the presence of NaF and then purified by fractional condensation through traps kept at  $-64^\circ$  and  $-95^\circ C$ , with the material retained at  $-95^\circ C$  being used. The  $KNO_2$  (J.T. Baker, 99.0%) and  $NaNO_2$  (J.T. Baker, 98.0%) were dried in vacuo at  $120^\circ C$  for one day prior to their use. The  $Cs_2SO_4$  was prepared from  $Cs_2CO_3$  and  $H_2SO_4$  and dried in vacuo at  $200^\circ C$  for one day. The  $CsN_3$  (Eastman Kodak) was used as received.

Reaction of  $Cs_2SO_4$  with  $BrF_5$ . A mixture of  $Cs_2SO_4$  (1.30 mmol) and  $BrF_5$  (106.4 mmol) in a 3/4" o.d. Teflon ampule was kept at  $25^\circ C$  for one hour. The material volatile at  $25^\circ C$  was pumped off and consisted of 105.1 mmol of  $BrF_5$ . The white solid residue (698.4 mg, weight calcd for 1.30 mmol of  $CsBrF_4O$  and 1.30 mmol of  $CsSO_3F$  = 698.2 mg) was identified by infrared and Raman spectroscopy as a mixture of  $CsBrF_4O$  and  $CsSO_3F$ .

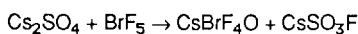
Reaction of  $CsN_3$  with  $BrF_5$ . When a mixture of  $CsN_3$  and a fivefold excess of  $BrF_5$  in a Teflon-FEP ampule was warmed from  $-196^\circ C$  towards ambient temperature, the mixture ignited on melting of the  $BrF_5$  and burned with a bright red flame breaching the container. To achieve better temperature control, the experiment was repeated in a 95 ml Monel cylinder.  $CsN_3$  (2.41 mmol) was added to the cylinder in the drybox, and  $BrF_5$  (12.36 mmol) was added at  $-196^\circ C$  on the vacuum line. The cylinder was allowed to slowly warm to room temperature and then cooled back again to  $-196^\circ C$ . The gas noncondensable at  $-196^\circ$  ( $N_2$ , 3.65 mmol) was pumped off, and the excess of unreacted  $BrF_5$  (9.98 mmol) was removed at  $25^\circ C$ . The white solid residue (730 mg, weight calcd for 1.20 mmol each of  $CsBrF_4$  and  $CsBrF_6$  = 739 mg) was shown by Raman and infrared spectroscopy to be an about equimolar mixture of  $CsBrF_4$  and  $CsBrF_6$ .

Reaction of  $BrF_5$  with an Excess of  $NaNO_2$ . To a prepassivated 30 ml stainless steel cylinder that contained  $NaNO_2$  (10.3 mmol),  $BrF_5$  (2.54 mmol) was added at  $-196^\circ C$ . The cylinder was allowed to warm to room temperature where it was kept for two hours. The material volatile at  $25^\circ C$  was separated by fractional condensation through  $-142^\circ C$  and  $-196^\circ C$  traps. The  $-142^\circ$  trap contained  $Br_2$  (1.27 mmol), and the one at  $-196^\circ$  had  $FNO_2$  (5.33 mmol, corresponding to an 84% yield based on  $BrF_5$ ). The white solid residue was shown to be a mixture of NaF and unreacted  $NaNO_2$ .

Reaction of  $\text{KNO}_2$  with an Excess of  $\text{BrF}_5$ . A mixture of  $\text{KNO}_2$  (2.55 mmol) and  $\text{BrF}_5$  (12.06 mmol) in a 30 ml stainless steel cylinder was kept at  $25^\circ\text{C}$  for four hours. Then, the cylinder was cooled to  $-196^\circ\text{C}$  and shown to contain no material noncondensable at this temperature. The material volatile at  $25^\circ\text{C}$  was pumped off and separated by fractional condensation. It consisted of  $\text{FNO}_2$ ,  $\text{FNO}$  and  $\text{BrF}_5$ . The light yellow-orange residue (290 mg) was identified by spectroscopic methods as a mixture of  $\text{KBrF}_4$ ,  $\text{KNO}_3$ ,  $\text{KBrF}_4\text{O}$  and  $\text{KF}$ .

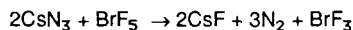
## RESULTS AND DISCUSSION

At room temperature  $\text{Cs}_2\text{SO}_4$  readily undergoes the following quantitative reaction with  $\text{BrF}_5$ .

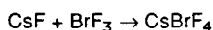


Even in the presence of a large excess of  $\text{BrF}_5$ , a further fluorine-oxygen exchange to a second mole of  $\text{CsBrF}_4\text{O}$  and  $\text{SO}_2\text{F}_2$  does not take place. Although the above reaction is quantitative, it is not as useful as that of  $\text{CsNO}_3$  with  $\text{BrF}_5$  [4] for the preparation of pure  $\text{CsBrF}_4\text{O}$  because of the difficulty of separating  $\text{CsBrF}_4\text{O}$  from  $\text{CsSO}_3\text{F}$ .

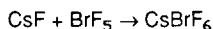
The reaction of  $\text{CsN}_3$  with an excess of  $\text{BrF}_5$  is quite violent and, unless carefully controlled, results in ignition upon melting of the  $\text{BrF}_5$ . With careful temperature control, the following quantitative reaction is observed:



The  $\text{CsF}$  product reacts with the  $\text{BrF}_3$  and excess of  $\text{BrF}_5$  to give  $\text{CsBrF}_4$  [5] and  $\text{CsBrF}_6$  [6], respectively:

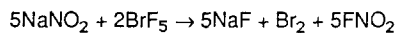


and



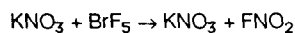
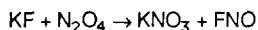
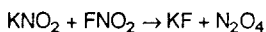
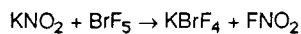
Since  $\text{BrF}_3$  is a stronger Lewis Acid than  $\text{BrF}_5$  [7], all of the  $\text{BrF}_3$  reacts with half of the  $\text{CsF}$  available leaving the other half for complexing with excess  $\text{BrF}_5$ . The reaction of  $\text{CsN}_3$  with  $\text{BrF}_5$  can, therefore, be regarded as a redox reaction in which  $\text{N}_3^-$  is oxidized to  $\text{N}_2$  and  $\text{BrF}_5$  is reduced to  $\text{BrF}_3$ .

The products observed for the reaction of  $\text{BrF}_5$  with  $\text{NO}_2^-$  depend on which reagent is used in excess. As with the  $\text{N}_3^-$  anion, the  $\text{NO}_2^-$  anion acts as a reducing agent toward  $\text{BrF}_5$ . If an excess of  $\text{NO}_2^-$  is used,  $\text{BrF}_5$  is reduced all the way to  $\text{Br}_2$  as shown by the following equation:



This reaction has potential as a relatively simple, high yield synthesis for  $\text{FNO}_2$ .

If an excess of  $\text{BrF}_5$  is used, the reaction products are  $\text{KBrF}_4$ ,  $\text{KNO}_3$ ,  $\text{KBrF}_4\text{O}$ ,  $\text{KF}$ ,  $\text{FNO}$ , and  $\text{FNO}_2$ . These products are best rationalized by the following reaction sequence in which not all of the steps may go to completion:



Of these reactions, the third one involving  $\text{KF} + \text{N}_2\text{O}_4$  and the last one involving  $\text{KNO}_3 + \text{BrF}_5$  have previously been demonstrated [8,4] in separate experiments.

In summary,  $\text{BrF}_5$  is not only capable of undergoing smooth fluorine-oxygen exchange reactions, as for example with  $\text{NO}_3^-$  [4],  $\text{SO}_4^{2-}$ ,  $\text{BrO}_3^-$  [9],  $\text{BrO}_4^-$  [10], or  $\text{IO}_4^-$  [11], but also can act as an oxidative fluorinator toward anions of lower oxidizing power such as  $\text{N}_3^-$  or  $\text{NO}_2^-$ .

#### ACKNOWLEDGEMENT

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