Journal of Fluorine Chemistry, 43 (1989) 125–129

Received: August 8, 1988; accepted: September 7, 1988

REACTIONS OF BrF_5 WITH THE AZIDE, NITRITE AND SULFATE ANIONS

KARL O. CHRISTE*, 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 BrF_4O^- and SO_3F^- salts. With CsN_3 it ignites producing N_2 and a mixture of $CsBrF_4$ and $CsBrF_6$. With an excess of $NaNO_2$ it forms NaF, Br_2, and FNO_2. When BrF_5 is used in excess with KNO_2 its reduction is halted at the BrF_3 stage producing $KBrF_4$ and FNO_2 as the primary products. The FNO_2 can undergo a secondary reaction with KNO_2 to give N_2O_4 and KF which react further to FNO and KNO_3. The latter and excess BrF_5 yield some $KBrF_4O$ and FNO_2.

INTRODUCTION

The NF_4^+ and 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 BrF_5, its compatibility with the N_3^-, NO_2^-, and SO_4^{2-} anions was studied. Although these anions were found to be unstable in 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 BrF_5 (Matheson) was treated with 35 atm* of F_2 at 100°C for 24 hours in the presence of NaF and then purified by fractional condensation through traps kept at -64° and -95°C, with the material retained at -95°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°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°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°C for one hour. The material volatile at 25°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°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°C on the vacuum line. The cylinder was allowed to slowly warm to room temperature and then cooled back again to -196°C. The gas noncondensible at -196° (N_2, 3.65 mmol) was pumped off, and the excess of unreacted BrF_5 (9.98 mmol) was removed at 25°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°C. The cylinder was allowed to warm to room temperature where it was kept for two hours. The material volatile at 25°C was separated by fractional condensation through -142°C and -196°C traps. The -142° trap contained Br_2 (1.27 mmol), and the one at -196° 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 KNO_2 with an Excess of BrF_5. A mixture of KNO_2 (2.55 mmol) and BrF_5 (12.06 mmol) in a 30 ml stainless steel cylinder was kept at 25°C for four hours. Then, the cylinder was cooled to -196°C and shown to contain no material noncondensible at this temperature. The material volatile at 25°C was pumped off and separated by fractional condensation. It consisted of FNO_2, FNO and BrF_5. The light yellow-orange residue (290 mg) was identified by spectroscopic methods as a mixture of $KBrF_4$, KNO_3, $KBrF_4O$ and KF.

RESULTS AND DISCUSSION

At room temperature Cs_2SO_4 readily undergoes the following quantitative reaction with BrF_5.

$$Cs_2SO_4 + BrF_5 \rightarrow CsBrF_4O + CsSO_3F$$

Even in the presence of a large excess of BrF_5, a further fluorine-oxygen exchange to a second mole of $CsBrF_4O$ and SO_2F_2 does not take place. Although the above reaction is quantitative, it is not as useful as that of $CsNO_3$ with BrF_5 [4] for the preparation of pure $CsBrF_4O$ because of the difficulty of separating $CsBrF_4O$ from $CsSO_3F$.

The reaction of CsN_3 with an excess of BrF_5 is quite violent and, unless carefully controlled, results in ignition upon melting of the BrF_5. With careful temperature control, the following quantitative reaction is observed:

$$2CsN_3 + BrF_5 \rightarrow 2CsF + 3N_2 + BrF_3$$

The CsF product reacts with the BrF_3 and excess of BrF_5 to give $CsBrF_4$ [5] and $CsBrF_6$ [6], respectively:

$$CsF + BrF_3 \rightarrow CsBrF_4$$
and
$$CsF + BrF_5 \rightarrow CsBrF_6$$

Since BrF_3 is a stronger Lewis Acid than BrF_5 [7], all of the BrF_3 reacts with half of the CsF available leaving the other half for complexing with excess BrF_5. The reaction of CsN_3 with BrF_5 can, therefore, be regarded as a redox reaction in which N_3^- is oxidized to N_2 and BrF_5 is reduced to BrF_3.

The products observed for the reaction of BrF_5 with NO_2^- depend on which reagent is used in excess. As with the N_3^- anion, the NO_2^- anion acts as a reducing agent toward BrF_5. If an excess of NO_2^- is used, BrF_5 is reduced all the way to Br_2 as shown by the following equation:

$$5NaNO_2 + 2BrF_5 \rightarrow 5NaF + Br_2 + 5FNO_2$$

This reaction has potential as a relatively simple, high yield synthesis for FNO_2.

If an excess of BrF_5 is used, the reaction products are $KBrF_4$, KNO_3, $KBrF_4O$, KF, FNO, and FNO_2. These products are best rationalized by the following reaction sequence in which not all of the steps may go to completion:

$$KNO_2 + BrF_5 \rightarrow KBrF_4 + FNO_2$$
$$KNO_2 + FNO_2 \rightarrow KF + N_2O_4$$
$$KF + N_2O_4 \rightarrow KNO_3 + FNO$$
$$KNO_3 + BrF_5 \rightarrow KNO_3 + FNO_2$$

Of these reactions, the third one involving KF + N_2O_4 and the last one involving KNO_3 + BrF_5 have previously been demonstrated [8,4] in separate experiments.

In summary, BrF_5 is not only capable of undergoing smooth fluorine-oxygen exchange reactions, as for example with NO_3^- [4], SO_4^{2-}, BrO_3^- [9], BrO_4^- [10], or IO_4^- [11], but also can act as an oxidative fluorinator toward anions of lower oxidizing power such as N_3^- or NO_2^-.

ACKNOWLEDGEMENT

The authors wish to thank Mr. R.D. Wilson for his help and to the Office of Naval Research and the U.S. Army Research Office for financial support.

REFERENCES

1 For a recent review of NF_4^+ chemistry, see I.V. Nikitin and V.Ya. Rosolovskii, Russ. Chem. Rev., 54, (1985) 426.

2 K.O. Christe and W.W. Wilson, Inorg. Chem., 22, (1983) 1950.

3 K.O. Christe and W.W. Wilson, Inorg. Chem., 27, (1988) 1296.

4 K.O. Christe and W.W. Wilson, Inorg. Chem., 26, (1987) 916.

5 K.O. Christe and C.J. Schack, Inorg. Chem., 9, (1970) 1852.

6 G. Tantot and R. Bougon, C.R. Seances Acad. Sci., Ser. C, 281, (1975) 271.

7 K.O. Christe, C.J. Schack, and D. Pilipovich, Inorg. Chem., 11, (1972) 2205.

8 C.T. Ratcliffe and J.M. Shreeve, J.C.S. Chem. Commun., (1966) 674.

9 R. Bougon, T. Bui Huy, P. Charpin, and G. Tantot, C.R. Seances Acad. Sci., Ser. C, 283 (1976) 71.

10 K.O. Christe, R.D. Wilson, E.C. Curtis, W. Kuhlmann, and W. Sawodny, Inorg. Chem. 17, (1978) 533.

11 K.O. Christe, R.D. Wilson, and C.J. Schack, Inorg. Chem., 20, (1981) 2104.