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Journal of Fluorine Chemistry 89 (1998) 97–99

JOURNAL OF FLUORINE CHEMISTRY

Dinitramide anion as a reagent for the controlled replacement of fluorine by oxygen in halogen fluorides

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Received 8 August 1996; accepted 22 October 1997

Abstract

The reactions of $KN(NO_2)_2$ with BrF_5, ClF_5 and IF_7 were investigated. It is shown that the $N(NO_2)_2^-$ anion is superior to NO_3^- as a reagent for the controlled, stepwise replacement of two fluorine ligands by a doubly bonded oxygen atom. Thus, $KN(NO_2)_2$ readily reacts with BrF_5 at −45°C to give $KBrOF_4$, N_2O and FNO_2 in quantitative yield. With ClF_5 at −13°C, an equimolar mixture of $KClOF_4$ and $KClF_4$ was obtained. The formation of $KClOF_4$ is remarkable because with most other fluorine–oxygen exchange reagents, such as NO_3^-, the exchange process cannot be arrested at the $ClOF_4^-$ stage and yields $FClO_2$ as the only product. In the case of IF_7, deoxygenation of the desired IOF_6^- product occurred resulting instead in the formation of KIF_6, which, in the presence of excess IF_7, formed the novel $KIF_6 \cdot 2IF_7$ adduct.

Keywords: Fluorine–oxygen exchange; Dinitramide anion; Halogen fluorides; Bromine pentafluoride; Chlorine pentafluoride; Iodine heptafluoride

1. Introduction

Fluorine–oxygen exchange reactions are of importance in synthetic chemistry. Whereas most of the known methods are concerned with the replacement of a doubly bonded oxygen atom by two fluorine atoms, only little systematic work had been done on the reverse problem, i.e., the controlled replacement of fluorine by oxygen. In a recent paper, the principal methods for fluorine–oxygen exchange have been reviewed, and a new method, based on the use of the NO_3^- anion, has been described [1]. Although the NO_3^- anion was found to be a highly effective and generally useful reagent, it was not capable of achieving a controlled stepwise fluorine–oxygen exchange in either IF_7 or ClF_5. Since recent work in our laboratory on the dinitramide anion [2] had indicated that the $N(NO_2)_2^-$ anion is more reactive than the NO_3^- ion, it was of interest to examine its potential as a reagent for fluorine–oxygen exchange and, in particular, for the two problem cases, ClF_5 and IF_7.

2. Experimental details

Literature methods were used for the syntheses of $KN(NO_2)_2$ [2], ClF_5 [3], IF_7 [4] and KIF_6 [5]. The BrF_5 (Matheson) was treated with 35 atm of F_2 at 100°C for 24 h and then purified by fractional condensation through traps kept at −64° and −95°C, with the material retained at −95°C being used. Volatile materials were handled in a well-passivated (with ClF_3) stainless-steel Teflon-FEP vacuum line [6] and solids in the dry nitrogen atmosphere of a glove box. Raman spectra were recorded on either a Cary Model 83 or a Spex Model 1403 spectrophotometer using the 488-nm exciting line of an Ar ion or the 647.1-nm line of a Kr ion laser, respectively. Baked-out Pyrex melting point capillaries were used as sample containers. Infrared spectra were recorded on a Perkin-Elmer Model 283 spectrophotometer. For gases, a 5-cm path length Teflon cell equipped with AgCl windows was used. For solids, the finely powdered samples were sandwiched between two thin AgCl or AgBr disks and pressed together in a Wilks minipress inside the drybox.

2.1. *Reaction of $KN(NO_2)_2$ with BrF_5*

Inside the drybox, $KN(NO_2)_2$ (1.00 mmol) was placed into a pre-passivated Teflon–FEP ampoule which was closed by a stainless-steel valve. On the vacuum line, BrF_5 (14.46 mmol) was added at −196°C. The resulting mixture was warmed to −45°C for 30 min and then cooled back to −196°C. All material volatile at room temperature was pumped off and fractionated through a series of cold traps

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PII S0022-1139(98)00092-X

kept at −45, −95 and −196°C. The −45°C trap contained nothing, while the −95°C trap contained unreacted BrF_5 (13.40 mmol), and the −196°C trap had an equimolar mixture (1.98 mmol) of FNO_2 and N_2O. The white solid residue (214 mg, weight calculated for 1.00 mmol of $KBrOF_4 = 211.0$ mg), left behind in the Teflon ampoule, was identified by infrared and Raman spectroscopy as pure $KBrOF_4$.

2.2. *Reaction of $KN(NO_2)_2$ with ClF_5*

A mixture of $KN(NO_2)_2$ (1.01 mmol) and ClF_5 (17.05 mmol) was prepared as described above and allowed to warm from −196°C to −13°C. It was kept at this temperature for 3 h with agitation, before being cooled again to −196°C. While warming up to room temperature, all volatile material was fractionated in a dynamic vacuum through two cold traps kept at −126°C and −196°C. The −126°C trap contained most of the unreacted ClF_5 (15.86 mmol), while the −196°C one contained a mixture (2.17 mmol) of FNO_2, ClF_5, N_2O, FNO and a trace of $FClO_2$. The FNO is believed to result from the fluorination of some N_2O which, therefore, was present in an amount smaller than that of FNO_2. The white solid residue (140 mg, weight calculated for 1.01 mmol of an equimolar mixture of $KClF_4$ and $KClOF_4 = 160$ mg) was identified by its infrared and Raman spectra as an approximately equimolar mixture of $KClF_4$ and $KClOF_4$.

2.3. *Reaction of $KN(NO_2)_2$ with IF_7*

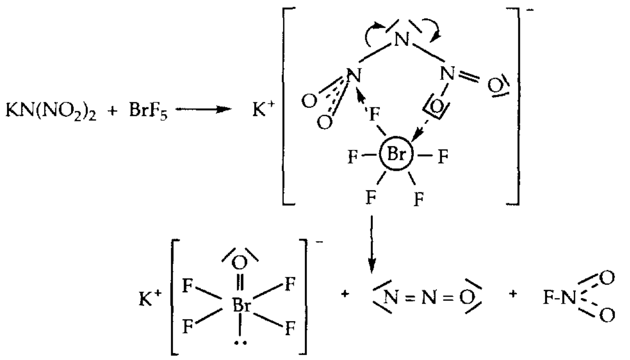
A mixture of $KN(NO_2)_2$ (1.02 mmol) and IF_7 (16.61 mmol) was prepared as described above and allowed to warm from −196°C to room temperature. At the beginning the white, solid $KN(NO_2)_2$ floated on top of the liquid IF_7, but after 1 h at room temperature and frequent agitation the solid sank to the bottom. The Teflon–FEP ampoule was re-cooled to −196°C and the material volatile at room temperature was fractionated on warm up in a dynamic vacuum through traps kept at −126 and −196°C. The −126°C trap contained unreacted IF_7 (15.17 mmol) and the −196°C trap had a mixture of N_2O and FNO_2 (1.46 mmol). The white solid residue (461 mg, weight calculated for 0.525 mmol of KNO_3 and 0.495 mmol of $KIF_6 \cdot 2IF_7 = 457$ mg) was shown from its vibrational spectra and their comparison with those of known samples to be a mixture of $KIF_6 \cdot 2IF_7$ and KNO_3.

3. Results and discussion

Bromine pentafluoride readily reacted with $KN(NO_2)_2$ according to the equation:

$$BrF_5 + KN(NO_2)_2 \rightarrow KBrOF_4 + FNO_2 + N_2O$$

After 30 min at −45°C, the yield of $KBrOF_4$ was quantitative and no side reactions were observed. Therefore, no other reaction conditions were explored. Clearly, $KN(NO_2)_2$ is more reactive than KNO_3 which under similar conditions (−31°C, 1 h reaction time) yielded only 34.3% of $KBrOF_4$. To achieve quantitative yields of $KBrOF_4$ with KNO_3, either a temperature of about 100°C and reaction times of about 20 h or continuous ball-milling for 20 h at 25°C were required [7]. For the $KN(NO_2)_2/BrF_5$ reaction, the following mechanism is proposed in which an oxygen atom of one nitro group attacks the bromine atom of BrF_5 whose free valence electron pair can become temporarily sterically inactive by occupation of an *s*-orbital as for example, in BrF_6^- [8,9]. A fluorine ligand of BrF_5 is then transferred to the nitrogen atom of the second nitro group, followed by N_2O elimination giving $BrOF_4^-$ and FNO_2.



The formation of the postulated intermediate anion which requires a twisting of the NO_2 groups in the $N(NO_2)_2^-$ anion is facilitated by the dihedral angle and the very low (<3 kcal mol^{-1}) rotational barrier of these groups [2].

The reaction of ClF_5 with $KN(NO_2)_2$ was not as clean-cut as that of BrF_5 (see above). In addition to the fluorine–oxygen exchange reaction,

$$ClF_5 + KN(NO_2)_2 \rightarrow KClOF_4 + FNO_2 + N_2O$$

deoxygenation of $ClOF_4^-$ to ClF_4^- also occurred producing an approximately equimolar amount of $KClF_4$. Surprisingly, only a small amount of $FClO_2$ was formed due to a double oxygen–fluorine exchange. In the case of the corresponding NO_3^- reaction [10] and also during the hydrolysis of ClF_5 [11], $FClO_2$ was always obtained as the main product without any evidence for $ClOF_3$ or $ClOF_4^-$ formation. The exclusive formation of $FClO_2$ in the NO_3^- or hydrolysis reactions was ascribed [1,12] to kinetic effects, i.e., the much higher reactivity of $ClOF_3$ compared to that of ClF_5. This extraordinary reactivity of $ClOF_3$ has also rendered the synthesis of $ClOF_3$ difficult and usually involves either the low-temperature fluorination of shock sensitive materials, such as chlorine oxides or chlorine nitrate, or UV-photolysis [12]. Therefore, a method involving a controllable stepwise fluorine–oxygen exchange in the readily accessible [3] ClF_5 is highly desirable. There has been only one other report on a successful stepwise fluorine–oxygen exchange in ClF_5. In a paper presented at the 10th International Symposium on Fluorine Chemistry [13], it was reported that ClF_5, although its hydrolysis yielded only $FClO_2$, reacts with $OH_3^+BF_4^-$ in HF solution at −50° to −70°C to give $ClOF_2^+BF_4^-$. However to our knowledge, no further details have been published on this process.

The third problem case for fluorine–oxygen exchange reactions is the conversion of IF_7 to IOF_5. By analogy to the NO_3^-/IF_7 reactions [14], only the deoxygenated IF_6^- salt was formed when $KN(NO_2)_2$ was treated with an excess of liquid IF_7 at room temperature.

$$3IF_7 + KN(NO_2)_2 \rightarrow KIF_6 \cdot 2IF_7 + FNO_2 + N_2O + 0.5O_2$$

In addition to this deoxygenation reaction, about half of the $KN(NO_2)_2$ starting material decomposed under the above conditions according to:

$$KN(NO_2)_2 \rightarrow KNO_3 + N_2O$$

Hence, neither $N(NO_2)_2^-$ nor NO_3^- is suitable for the conversion of IF_7 to IOF_5 or IOF_6^-.

Although the desired conversion of IF_7 to IOF_5 was not achieved, an interesting observation of a stable and previously unknown adduct having the composition $KIF_6 \cdot 2IF_7$ was made. This new compound is a white solid which is stable at room temperature but slowly loses IF_7 in a dynamic vacuum at 100°C and IF_5 between 180 and 240°C. Its vibrational spectra (Raman: 647(10), 628(1.5), 594(0.1), 560(4), 543(0.8), 528(1), 501(0.1), 380 (0.4), 350(0.4), 290–240(0.4, br); infrared: 630s, 550vs br, 401w, 390w, 386mw) resembled in their general appearance those of the IF_6^- and $IF_6^- \cdot 2IF_5$ anions [5] but with different frequencies and intensities. It, therefore, appears likely that the $(IF_6 \cdot 2IF_7)^-$ adduct has a polyanion structure similar to those found for $(IF_6 \cdot 2IF_5)^-$ [9] and $(XeOF_5 \cdot 2XeOF_4)^-$ [15] in which a fluoride ion is shared by three IF_5 or $XeOF_4$ molecules, respectively. The formation and identity of the $KIF_6 \cdot 2IF_7$ adduct was confirmed in a separate experiment by treating a sample of KIF_6 with a large excess of liquid IF_7 at room temperature for 12 h. After removal of the excess IF_7 in a dynamic vacuum at 25°C, a white product was obtained which exhibited the same $KIF_6 \cdot 2IF_7$ composition and vibrational spectra. Vacuum pyrolysis of the $KIF_6 \cdot 2IF_7$ adduct in the 100–120°C range resulted in IF_7 removal and produced a new compound which is stable over a relatively wide composition range. It exhibits relatively simple vibrational spectra (Raman: 569(10), 499(3), 470(4); infrared: 574s, 500vs br, 460sh, 428vs br) which cannot be assigned to any presently known iodine fluoride anion. Based on its relatively low frequencies and its loss of IF_5 on vacuum pyrolysis at about 200°C, it is assigned to the novel IF_7^{2-} anion, whose positive identification and characterization will be published elsewhere.

Acknowledgements

The work at the Air Force Research Laboratory is financially supported by the Propulsion Directorate of the US Air Force and that at USC by the National Science Foundation. The authors are grateful to Prof. G.A Olah and Dr. S. Rodgers for their support and stimulating discussions.

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