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SHORT COMMUNICATION

On the Synthesis of the $N_2F_5^+$ Cation. A Critical Comment on the Paper by Toy and Stringham.

K. O. Christe, C. J. Schack, and R. D. Wilson

Rocketdyne, A Division of Rockwell International, Canoga Park, California 91304 (USA)

Toy and Stringham recently reported [1] the synthesis of $N_2F_5^+(CF_3)_3CO^-$, a salt containing the novel pentafluorohydrazinium cation. This cation would be of significant academic and practical interest [2] since it would constitute the first known example of a substituted NF_4^+ cation, i.e. an NF_4^+ cation in which a fluorine ligand is replaced by an NF_2 group. According to the authors of [1], $N_2F_5^+(CF_3)_3CO^-$ was formed in a very unusual reaction involving the transfer of a fluorine cation from $(CF_3)_3COF$ to N_2F_4 according to:

$$(CF_3)_3COF \longrightarrow (CF_3)_3CO^- + F^+ \xrightarrow{+N_2F_4} N_2F_5^+(CF_3)_3CO^-$$

Since such a heterolytic fission [3] of $(CF_3)_3COF$ with F^+ formation is unlikely, the reported [1] synthetic and spectroscopic evidence for $N_2F_5^+(CF_3)_3CO^-$ was critically reviewed. The following points indicate that the reported white solid is not $N_2F_5^+(CF_3)_3CO^-$, but most likely the known [4] compound $(NO^+)_2SiF_6^{2-}$.

(1) The reference, cited by the authors of [1] for the known existence of $N_2F_5^+$, is Sheppard and Sharts' book on Organic Fluorine Chemistry (Benjamin, New York 1969, page 328). Although this book lists the reaction of N_2F_4 with AsF_5 to yield $N_2F_5^+AsF_6^-$, this is clearly a typographical error. Examination of the original reference [5] shows that the product from this reaction is $N_2F_3^+AsF_6^-$, in agreement with other previous reports [6,7], and unpublished results from this laboratory.

(2) It was also reported [1] that the white solid was formed only in a Pyrex vessel, but not in a copper vessel. The slow reaction proceeded with the formation of a brown gas. This is charcteristic of the well known [8] attack of glass by nitrogen fluorides to form $(NO)_2SiF_6$ as the principal product. The observed [1] weight of the solid product (50% yield based presumably on the molecular weight of $N_2F_5^+(CF_3)_3CO^-$) is in fair agreement with that expected for a high yield formation of $(NO)_2SiF_6$ according to:

$$N_2F_4 + 2(CF_3)_3COF \longrightarrow 2NF_3 + (CF_3)_3COOC(CF_3)_3$$

$$2NF_3 + SiO_2 \longrightarrow (NO)_2SiF_6$$

Unfortunately, no elemental analysis was reported for the white solid, and its identification was based only on infrared, mass, and ^{19}F nmr spectroscopy.

(3) For the infrared spectrum of the solid, pressed as a NaCl disk, the following absorptions were reported [1]: 1450 (s), 1233 (s), 809 (vs), 730 (vs), and 480 (s) cm^{-1}. These bands do not agree with expectations for either a tertiary perfluorobutoxy group [9,10] or a nitrogen fluoride cation [2, 7, 11]. However, the bands at 730 and 480 cm^{-1} are in excellent agreement with those of the SiF_6^{2-} anion [12]. The bands at 1450 and 1233 cm^{-1} are characteristic [12] for the HF_2^- anion, which could readily form from $(NO)_2SiF_6$ and NaCl in the presence of moisture. No infrared data were reported for the higher frequency range which would allow a positive identification of the NO^+ cation.

(4) For the mass spectrum only 4 mass peaks were reported [1] at 104, 85, 71 and 52 m/e. The peaks at 104 and 85 were assigned to $N_2F_4^+$ and $N_2F_3^+$, respectively, but since N_2 has the same mass as Si, they can equally well be assigned to SiF_4^+ and SiF_3^+. Based on their observed relative abundances of 2 and 100, respectively, we prefer their assignment to SiF_4 [13], which is the product expected for the thermal dissociation of a SiF_6^{2-} salt. It is important to note that no fragments due to $(CF_3)_3CO^-$ could be detected [1] for the white solid.

(5) The ^{19}F nmr spectrum of an HF solution of the product showed at room temperature only one exchange broadened resonance at ϕ=204 due to HF. On cooling to -80°C a singlet at ϕ=149 appeared which was assigned [1] to the $(CF_3)_3CO^-$ anion. However, for a tertiary perfluorobutoxy group a resonance around ϕ=70 should be expected [9, 10]. Furthermore, we cannot envision a mechanism which could provide for a rapid fluorine exchange between the covalent CF_3 groups and the HF solvent. On the other hand, the observed chemical shift and exchange characteristics are in line with expectations for a silicon fluoride. Unpublished work in this laboratory has shown that the SiF_6^{2-} anion is unstable in HF solution undergoing solvolysis according to $SiF_6^{2-} + 2HF \rightleftharpoons SiF_4 + 2HF_2^-$. The chemical shifts reported for SiF_4 in CCl_4 and SiF_6^{2-} in H_2O are ϕ=160 and 126, respectively, and acid was found to catalyze fluorine exchange between SiF_6^{2-} and F^- [14].

In summary, all the experimental data available for the reported [1] white solid are consistent with a hexafluorosilicate salt, such as $(NO)_2SiF_6$, but cannot be reconciled with the proposed composition $N_2F_5^+(CF_3)_3CO^-$.

Very recently, Stringham and Toy have also claimed [15] the synthesis of $N_2F_5^+BF_4^-$ by the photolytic reaction of N_2F_4 and BF_3 in the presence of fluorine below -100°C. Based on our experience, these reaction conditions are not likely to produce an $N_2F_5^+$ salt. Generally, compounds containing-NF_2 groups readily undergo fluorination to NF_3 during photolysis, followed by formation of NF_4^+ salts [16]. If the reaction is carried out in glass, formation of FNO is also possible, which can result in the formation of $NO^+BF_4^-$. Unpublished work in this laboratory has also shown that N_2F_4 does not form a stable adduct with BF_3 at temperatures as low as -78°C. At -78°C, an equimolar mixture of N_2F_4 and BF_3 is still liquid and can be transferred quantitatively from trap to trap. Therefore, the only solid products expected from the photolysis of N_2F_4-F_2-BF_3 mixtures in glass are NF_4BF_4 and BF_4^- salts of NO^+ or NO_2^+.

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