Synthesis, Characterization and Chemistry of the Fluoronitramide Anion

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In fond memory of our esteemed colleague Robert J. Schmitt

Abstract: The fluoronitramide anion, as its potassium, tetraisopropyl *p*-phenylenediguanidinium, and tetraphenylphosphonium salts, have been synthesized. The latter salt was characterized in detail as it was by far the most stable. The free acid $HN(F)(NO_2)$ was found to be unstable, as was the ammonium salt of fluoronitramide. The fluorine atom was shown to be capable of displacement by nucleophiles. In contrast to dinitramide, which at room temperature is unreactive towards aqueous alkali, fluoronitramide reacts instantly with aqueous hydroxide. Single crystal X-ray diffraction data show an unusual degree of uncertainty in the position of the fluorine atom in all of the salts that were examined.

Key words: fluoronitramide, dinitramide, difluoramide, nitrocyanamide

The recent synthesis of the dinitramide ion (**1**; Figure 1)[1] as well as the reputed instability of the difluoroamide anion (**2**)[2] lead directly to the question of the existence and stability of the structurally hybrid fluoronitramide ion. The potential uses for fluoronitramide salts in propellant technology are numerous, as it is a source of oxidizing oxygen and fluorine, giving further motivation to pursue the synthesis of this system. We report here on the synthesis and characterization of a few salts of the fluoronitramide anion.

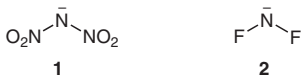
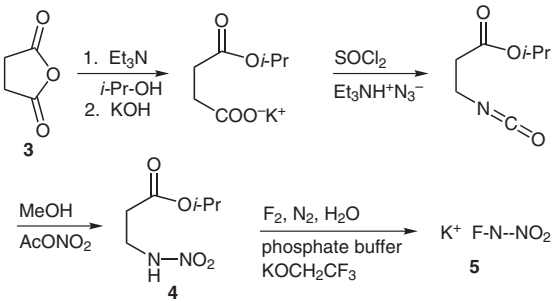


Figure 1 Dinitramide (**1**) and difluoroamide (**2**) anions

The potassium salt of fluoronitramide ion was synthesized by the route shown in Scheme 1. The synthesis begins with converting succinic anhydride into its isopropyl half ester. The free acid chloride is then converted into the acylazide, which is then transformed by Curtius rearrangement to the isocyanate. Methanolysis of the isocyanate produces the methyl carbamate, which in turn can be converted into the nitramine function by treatment with acetyl nitrate, followed by a brief and quantitative ammonolysis. The resulting isopropyl β-nitraminopropionate was fluorinated on the nitrogen in a buffered aqueous media in 90% yield and the potassium salt of fluoronitramide was obtained in nearly quantitative yield by base-catalyzed elimination in isopropanol as solvent; however, the crystal quality of his hygroscopic, hydrolytically unstable solid was poor. A much better crystal quality with a diminished surface area was derived using ethanol as solvent with only a slight reduction in yield. The product precipitated from the solution in 90% yield. This synthetic route is amenable to scale-up to a multimole scale, although this was not undertaken in our laboratories.



Scheme 1 Synthesis of potassium fluoronitramide

The tetraphenylphosphonium salt was prepared by the rapid preparation and mixing of aqueous solutions of tetraphenylphosphonium chloride and potassium fluoronitramide (fluoronitramide salts decompose quickly in aqueous solutions), which resulted in precipitation of fine needles of the tetraphenylphosphonium salt. The crude product was dried and crystallized from hot acetonitrile, to obtain pale yellow prisms in ~80% yield. Attempts to isolate the ammonium salt by analogous ion exchange procedures were unsuccessful. The superior polarizing capacity of the ammonium ion, compared with that of the potassium ion, arises from the localized, interactive nature of the hydrogen bond; even though the ammonium ion has an ostensibly larger radius than the potassium ion, its charge is anisotropically configured by its four protons and it also has the capacity to act simultaneously as a Lewis and a Brønsted acid, thus expanding its mechanistic capacity.

Dependency of Stability of Fluoronitramide Salts on the Counterion

The thermal stability of the fluoronitramide salts was investigated by differential scanning calorimetry (DSC).

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Figure 2 shows the DSC scans for the potassium and the tetraphenylphosphonium salts. They both display a sharp exothermic decomposition. Evidently, the decomposition is strongly dependent upon the polarizing capability of the counterion. Thus, the potassium salt decomposed at 145 °C and the tetraphenylphosphonium salt at 215 °C; the ammonium salt could not be isolated at room temperature (20 °C).

One attractive mechanistic possibility for the decomposition is the counterion-mediated dissociation of the fluoride ion to give the singlet nitronitrene, which undergoes migratory rearrangement to the nitric oxide dimer which, in turn, dissociates to NO (see Scheme 2). This hypothesis was tested by decomposing approximately two milligrams of the potassium salt in an evacuated 10-cm pathlength IR cell and analyzing the gases. The IR spectrum clearly showed the PQR branches, characteristic of NO, centered around 1880 cm^{-1}. This band was accompanied by a slightly weaker band due to NO_2 between 1750 and 1800 cm^{-1}. The formation of NO was further confirmed by letting in air, which converted the resulting NO into NO_2 and dramatically increased the intensity of the NO_2 band to more than fifty times its original intensity. In view of the substantially stronger absorption coefficient of NO_2, we can surmise that greater than 95% of the decomposition gas was NO.

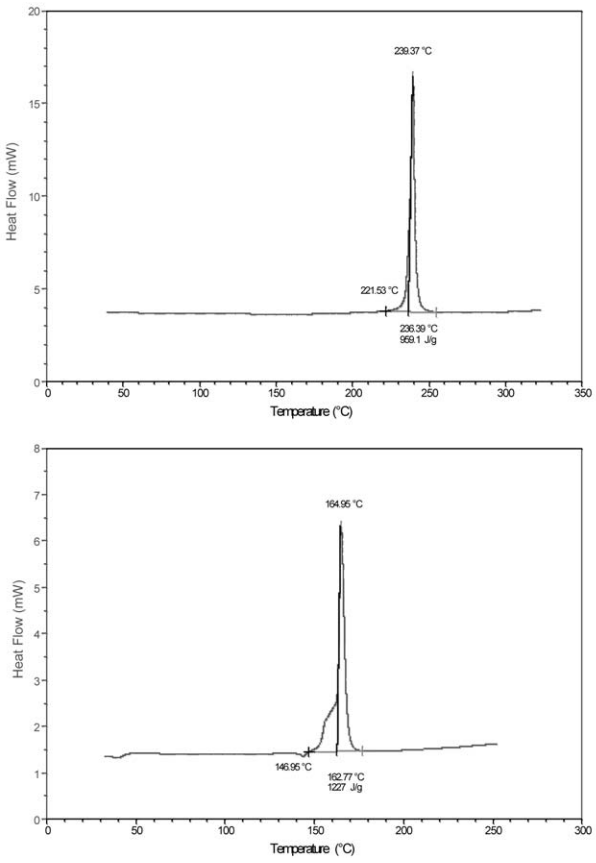
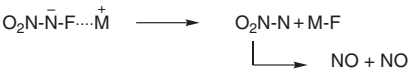


Figure 2 DSC scans for the decomposition of fluoronitramide salts: tetraphenylphosphonium (top panel) and potassium (bottom panel)



Scheme 2 Decomposition of fluoronitramide salts

Preliminary Assessment of the Chemistry of Fluoronitramide Anion

Fluoronitramide behaves as an electrophilic nitroaminating agent. In an attempted ion exchange of potassium fluoronitramide with ammonium ions, using an ammonia-charged ABERLYST®15 polysulfonic acid resin in methanol, only ammonium methoxynitramide was isolated, indicating methanolysis of the N–F bond had occurred. Heating potassium fluoronitramide to 85 °C with sodium nitrite in dimethylformamide (DMF) gave a 20% (unoptimized) yield of potassium dinitramide.

No nitrocyanamide ion[3] was observed to evolve from the attempted reaction of potassium cyanide with potassium fluoronitramide in DMF. The study of the reactivity of fluoronitramide with other nucleophilic reagents is currently underway. In the reaction of potassium fluoronitramide with quinuclidine, the most nucleophilic amine known, there was TLC evidence of a trace of quinuclidine-*N*-nitro imine ylide, by comparison to the known ylide, $(CH_3)_3N^+N^-NO_2$. The dissolution of fluoronitramide salts in basic aqueous media results in rapid hydrolysis, whereas dinitramide salts are not visibly reactive in alkaline solutions at room temperature.

X-ray Crystallography

X-ray diffraction studies of the potassium, tetraphenylphosphonium, and tetraisopropyl *p*-phenylenediguanidinium salts yielded an anomalous uncertainty in the position of the fluorine atom.

In conclusion, a novel inorganic anion (the fluoronitramide anion) has been synthesized and characterized. Although it does not possess the stability to a variety of environmental challenges displayed by the dinitramide anion, it has a well-defined profile of reactivity, and can undergo displacement of fluorine by active nucleophiles such as water or methanol to give Angeli's salt, (trioxodinitrate), or methoxy nitramide, respectively.

^{19}F NMR spectra were recorded on a Varian Gemini 300 NMR spectrometer at 282 MHz in benzene-d_6 using 2,2,2-trifluoroethanol (0 ppm) as an external reference. Thermal stability measurements were carried out on a DuPont Model DSC2920 differentially scanning calorimeter, and the data were analyzed using TA Instruments Universal Analysis version 4.0D. IR spectra were recorded on a Perkin Elmer Model 1420 infrared spectrometer. The samples were sent to Galbraith Laboratories for elemental microanalyses.

Isopropyl β-Nitraminopropionate (4)

To a solution of Et_3N (10 g, 100 mmol) in *i*-PrOH (100 mL) was added succinic anhydride (10 g, 100 mmol). The resulting mixture was stirred for 12 h, concentrated in vacuo, redissolved in MeOH (100 mL) and treated with a solution of KOH (2 M, 100 mL) in

MeOH (50 mL). The resulting solution was mixed with toluene (200 mL) and the resulting suspension was concentrated in vacuo. The solid residue was dried in vacuo at 100 °C then added to a solution of $SOCl_2$ (200 mmol) in chlorobenzene (100 mL). The mixture was stirred for 4 h, filtered and the filtrate was concentrated in vacuo to give the crude isopropyl β-(chlorocarbonyl)propionate (not isolated).

The entirety of the crude acid chloride was added to a preformed suspension of triethyl ammonium azide [110 mmol; prepared by mixing Et_3N (110 mmol), EtOH (110 mmol) and trimethylsilyl azide (110 mmol) in EtOAc (200 mL)] and the mixture was stirred for 1 h, filtered and concentrated to 100 mL in vacuo. The resulting concentrate was eluted through a SiO_2 column (4″ × 1″; EtOAc) and the fractions eluting with $R_f = 0.8$ were collected. The effluent from the column (~150 mL in all) was mixed with chlorobenzene (150 mL), concentrated in vacuo to 100 mL and heated to 90 °C for 1 h, at which point nitrogen evolution ceased. The crude isopropyl β-isocyanatopropionate was dissolved in MeOH (100 mL) then treated with Et_3N (1 g, 10 mmol) and allowed to stand at r.t. for 12 h. The solution was then concentrated and distilled under high vacuum (bp 120 °C, 100 mTorr) to give crude isopropyl β-(methoxycarbonylamino)propionate (17 g). This was added to a solution of acetyl nitrate (100 mmol) in $CHCl_3$ (100 mL) and stirred at r.t. for 12 h. The resulting solution was washed with K_2HPO_4 (2 M, 2 × 200 mL), dried ($MgSO_4$), concentrated in vacuo and eluted through a SiO_2 column (1″ × 4″; EtOAc) with the fractions eluting with $R_f = 0.9$ collected. The combined fractions were treated with excess NH_3 and the resulting solid was partitioned between H_3PO_4 (1 M, 100 mL) and toluene (100 mL). The organic layer was dried ($MgSO_4$), concentrated and passed through a SiO_2 column (1″ × 2″; EtOAc) with the fractions eluting with $R_f = 0.6$ collected. The combined fractions were concentrated and the residue was stirred for 1 h at 50 °C, under high vacuum, to give isopropyl β-nitraminopropionate (**4**; 14 g, 80% overall from **3**) of sufficient purity to be used for further synthesis.

^{1}H NMR (60 MHz, $CDC1_3$): δ = 1.25 (d, J = 6 Hz, 6 H), 2.7 (t, J = 6 Hz, 2 H), 3.9 (t, J = 6 Hz, 2 H), 5.15 (sept, J = 6 Hz, 1 H).

The hygroscopicity and high dissolving power of this material made determination of IR and elemental analyses somewhat difficult, and these data were not obtained on this intermediate.

Potassium Fluoronitramide (5)

Isopropyl β-nitraminopropionate (**4**, 2 g, 11 mmol) was suspended in H_2O (~40 mL) and treated with K_2HPO_4 (8.5 g, 50 mmol), cooled in an ice bath and stirred until homogeneous. This cooled solution was treated with 10% F_2 in N_2 until TLC (EtOAc) showed complete consumption of starting material and formation of the faster-eluting product ($R_f = 0.8$ versus 0.5 for the starting nitramine). The reaction mixture was extracted with EtOAc (50 mL) and the organic layer was dried ($MgSO_4$) and concentrated to give the crude *N*-fluoro-*N*-nitro ester as an oil. A solution of this oil (1 M in MeCN) was converted into the potassium fluoronitramide by treatment with a solution of potassium trifluoroethoxide (1 M in EtOH). The reaction time was typically one minute and the yield was essentially quantitative. The product was always kept at zero degrees centigrade or lower.

IR (KBr): 3300 (broad, adventitious H_2O), 1390 (strong, sharp; probable N–O stretching mode), 1300 (poorly resolved, but strong and of equal intensity), 1020 (sharp, weak), 870 (strong singlet), 690 (strong singlet) 740 (strong singlet) cm^{-1}.

Tetraisopropyl *p*-Phenylenediguanidinium Fluoronitramide

The tetraisopropyl *p*-phenylenediguanidinium fluoronitramide salt was prepared by simple ion-exchange between **5** (1 mmol) and *p*-phenylenediguanidinium chloride (0.5 mmol) in dry MeCN (5 mL) at r.t. under argon. The soluble fluoronitramide salt was separated from the insoluble by-product KCl by filtration after 1 h of stirring. The *p*-phenylenediguanidinium chloride itself was prepared by treating *p*-phenylenediammonium chloride (1 mmol) with diisopropyl carbodiimide (2 mmol) in MeCN at reflux for 1 h.

Tetraphenylphosphonium Fluoronitramide

Tetraphenylphosphonium chloride (375 mg, 1 mmol) was dissolved in cold H_2O (~5 °C; 50 mL). Potassium fluoronitramide (**5**; 120 mg, 1 mmol) was then quickly (≤30 s) dissolved in cold H_2O (5 mL) and the resulting solution was immediately added to the previously prepared aqueous solution of tetraphenylphosphonium chloride. The mixture was stirred for approximately 10 s to achieve homogeneity, placed in an ice bath and allowed to stand for 30 min. Yellow needles, which began to precipitate almost immediately after mixing, were collected by filtration and dried under high vacuum for 10 min to give the product as yellow needles (200 mg, ~50% yield). Recrystallization from MeCN (~5 mL, heated to 70 °C) gave larger yellow needles (150 mg).

IR (KBr): 1580 (sharp singlet), 1450 (sharp singlet), 1465 (sharp singlet), 1380 (broad singlet), 1425, 1380 (strong, singlet), 1280 (strong, sharp), 1105 (sharp, strong), 995 (moderate, sharp), 850–870 (moderate, sharp), 690, 720, 750 (multiplet, strong and sharp) cm^{-1}.

^{19}F NMR (benzene-F_6): 74.7 ± 2 (s).

Anal. Calcd for $C_{24}H_{20}FN_2O_2P$: C, 68.90; H, 4.78; N, 6.70; P, 7.42; F, 4.55. Found: C, 68.88; H, 4.87; N, 6.59; P, 7.54; F, 4.57.

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