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Short Communication

A new synthesis of $NO^+BF_4^-$ from boron nitride

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Nitrosyl tetrafluoroborate is used in organic synthesis as a convenient source of NO^+ ions for diazotation[1] and as nitrosating agents[2]. This reagent has the advantage of being a completely anhydrous source of the NO^+ ion.

We wish to report a new synthesis for $NO^+BF_4^-$ from boron nitride, oxygen and fluorine. This has been accomplished by the reaction of solid boron nitride in a quartz reactor at room temperature under irradiation with mercury vapor lamps with a 4/1 mixture of fluorine and oxygen.

Experimental

Flow rates of fluorine and oxygen were measured using Hastings Model LF-50X mass flowmeters. The reactions were carried out in fused quartz reactors. Swagelok/UltraTorr reducing unions were used at quartz/copper junctions. The reactor was sealed using Hoke # 3212 M4M Monel needle valves adapted to 6 mm UltraTorr couplings. Access to the sample was through a 29/42 quartz joint, sealed with Fluorolube. Boron nitride powder which passed through a 325 mesh sieve was heated under vacuum in the reactor to approximately 600°. Heating was continued for 5 min, and then the sample was allowed to cool. The tube was filled with argon and sealed. The quartz reactor vessel was transferred to the UV reactor and connected to the fluorine–oxygen system using UltraTorr fittings. The reactor tube was purged for 0.5 h using a helium flow of about 150 $cm^3\ min^{-1}$. The helium flow was shut off, the mercury vapor lamps lit and a flow of 12.0 $cm^3\ min^{-1}$ fluorine and 3.0 $cm^3\ min^{-1}$ oxygen initiated. The reaction was allowed to proceed for 7 days to insure complete reaction. A test of the exhaused gas for BF_3 showed a minor concentration and BF_3 was completely eliminated by increasing the oxygen flow to 3.5 to 4.0 $cm^3\ min^{-1}$. However, excess oxygen flow is disadvantageous because it dilutes the fluorine and reduces the reaction rate. Yields averaged 25% with complete conversion to $NO^+BF_4^-$. Occasionally the yields are much higher.

Analysis of the reaction product with no further purification gave the following results: Calculated for $NO^+BF_4^-$: B, 9.25; N, 12.0; F, 65.1%. Found: B, 10.48; N, 10.50; F, 61.43%.

The X-ray powder pattern (Cu radiation) of the $NO^+BF_4^-$ contained "d" lines at 3.50, 3.13, 2.82, 2.25, 4.40, 2.50, 2.09 and 5.50 in agreement with the reported lines in the powder diffraction file[3].

The infrared spectra contained a peak at 2320 (Nujol mull) or 2310 cm^{-1} (Fluorolube mull) due to the NO^+ ion. The tetrafluoroborate ion was identified by its characteristic absorption pattern of 1045 cm^{-1} and weaker bands at 495, 510 and 1290 cm^{-1}. The ^{19}F NMR resonance of the tetrafluoroborate ion was observed at +147.2 ppm relative to $CFCl_3$ in acetontrile solution. The mass spectrum of the compounds contained peaks corresponding to BF_3 at m/e 68, BF_2 and NOF at 49, and NO and BF at 30. The isotope ratio of ^{10}B to ^{11}B indicates that both species are present as indicated.

Discussion

It appears that reaction occurs in the solid phase and probably is not the result of gaseous recombination of boron trifluoride and nitrosyl fluoride because the solid product is not formed outside the boat. A deficiency of oxygen in the system, however, increases the production of boron trifluoride. During one step in the reaction, incipient boron trifluoride evolution may be prevented by reaction with another species presumably containing oxidized nitrogen or with oxygen to form nitrosyl tetrafluoroborate. These species are probably still bonded to the lattice or held in reactive proximity of one another by covalent bonds or electrostatic attractions. The interplanar distance in boron nitride would be likely to permit free diffusion of fluorine atoms but inhibit the diffusion of molecular oxygen suggesting that the reaction may be a surface reaction in its initial stages. Nitrosyl tetrafluoroborate is made commercially by the reaction[4]

$$NOCl + HF + BF_3 \xrightarrow[-30^\circ \text{ to } -15^\circ]{SO_2} NO^+BF_4^- + HCl \ (88\text{–}100\%)$$

There is a possibility that the process we report may be less expensive because boron nitride is an inexpensive starting material, no solvent is required and fluorine is less expensive than BF_3. The net reaction may be written:

$$\frac{2}{x}(BN)_x + 4F_2 + O_2 \rightarrow 2NO^+BF_4^-$$

and has the industrial advantage that no by-products are produced and the long reaction times we report may possibly be reduced by agitating the solid. It is possible that air could be used as an oxygen source unless the dilution with nitrogen is so detrimental to the reaction rate that this is undesirable. This reaction also occurs in good yield at temperatures of 60° to 100° without ultraviolet activation.

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