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Novel Synthesis of Trifluoromethylnitrate, CF_3ONO_2

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Irradiation of the equilibrated gas mixture $CF_3O_2NO_2 \leftrightarrows CF_3O_2 + NO_2$ at room temperature using the output from UV fluorescent "blacklamps" provides a rapid and simple method for the production of pure samples of CF_3ONO_2 in high yield (ca. 80%). This synthetic procedure is superior to that described in the literature in two aspects: (i) the yield of CF_3ONO_2 is approximately a factor of 5 greater, and (ii) the present method avoids the need for a high pressure (70 bar) reactor.

Introduction

CF_3ONO_2 is a colorless gas with a boiling point of −18 °C and a melting point of −163 °C.[1] It was first identified by Chen et al.[2] by virtue of its IR features observed during a smog chamber study of the reactions of CF_3O_2 and CF_3O with NO_2. CF_3ONO_2 has been synthesized and characterized recently by Sander et al.[1] While the method of Sander et al.[1] is capable of producing substantial quantities of pure CF_3ONO_2 it involves the reaction of CF_3OF with NO_2 at high pressure (70 bar) for long periods of time (1−2 days) and is not convenient in most laboratories.

To support laboratory studies of the atmospheric degradation mechanisms of fluorinated organic compounds, we have developed a convenient synthesis for CF_3ONO_2. The peroxy nitrate $CF_3O_2NO_2$ can be prepared readily, either by direct reaction between CF_3OOH and excess N_2O_5 at −50 °C[3] or by photolysis of a suitable CF_3 radical precursor (e.g., CF_3I, $(CF_3CO)_2O$, or $CF_3N_2CF_3$) in the presence of NO_2 in O_2 diluent. The latter method was chosen for this work. $CF_3O_2NO_2$ is well characterized[3,4] and exists in equilibrium with CF_3O_2 radicals and NO_2 (reactions 1, −1).

$$CF_3O_2NO_2 + M \rightarrow CF_3O_2 + NO_2 + M \qquad (1)$$

$$CF_3O_2 + NO_2 + M \rightarrow CF_3O_2NO_2 + M \qquad (-1)$$

Irradiation of an equilibrated mixture of $CF_3O_2NO_2$ using the output of UV fluorescent blacklamps ($\lambda_{max} \approx 355$ nm) converts NO_2 into NO, which is then oxidized back to NO_2 via reaction with CF_3O_2 radicals.[5] The resulting CF_3O radicals react with NO_2 to give CF_3ONO_2.[1] The result is photochemical conversion of $CF_3O_2NO_2$ into CF_3ONO_2 in high yield.

$$CF_3O_2NO_2 \rightleftharpoons CF_3O_2 + NO_2 \qquad (1, -1)$$

$$NO_2 + h\nu \rightarrow NO + {}^1\!/_2O_2 \qquad (2)$$

$$CF_3O_2 + NO \rightarrow CF_3O + NO_2 \qquad (3)$$

$$CF_3O + NO_2 + M \rightarrow CF_3ONO_2 + M \qquad (4)$$

with an overall stoichiometry of

$$CF_3O_2NO_2 \rightleftharpoons CF_3ONO_2 + {}^1\!/_2O_2$$

Experimental Section

Gas mixtures were prepared using a conventional greaseless gas handling vacuum system. The photolytic reactions were carried out in a 23 cm long quartz cell fitted at both ends with KBr windows that was illuminated by two black lights (GE FL6 BLB). The quartz cell was mounted in the sample compartment of a Bruker IFS28

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10.1021/ic035425b CCC: $27.50

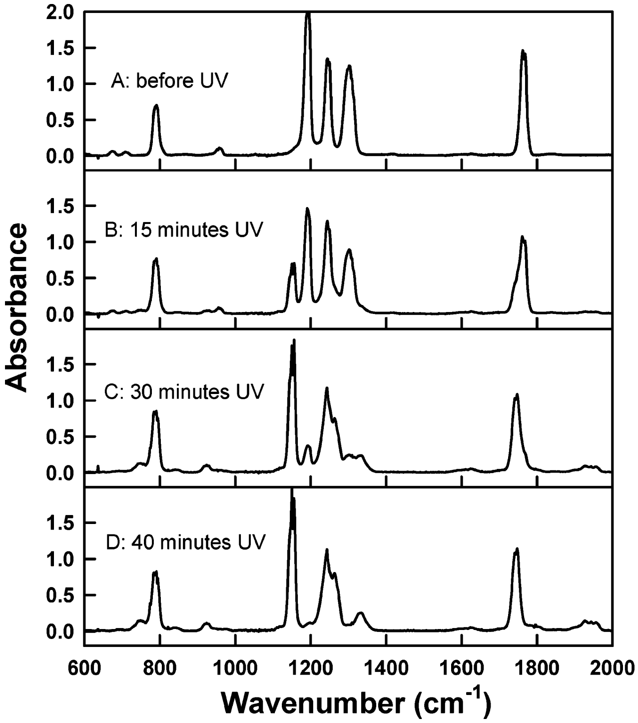

Figure 1. IR spectra acquired before (A) and after 15 (B), 30 (C), and 40 (D) min UV irradiation of 2.6 mbar of $CF_3O_2NO_2$.

FTIR spectrometer (Bruker, Karlsruhe, Germany) equipped with a DTGS detector and KBr beam splitter. All experiments were performed at room temperature, 298 K. The temporal evolution of reagents and products was monitored using FTIR spectroscopy. Spectra were obtained co-adding 8 interferograms in the range of 4000 to 400 cm^{-1} with 2 cm^{-1} resolution. $CF_3O_2NO_2$ was prepared by the photolysis of perfluoroacetic anhydride at 254 nm in the presence of NO_2 in O_2 diluent. $CF_3O_2NO_2$ was purified by allowing the reactant gas mixtures to pass slowly through a series of three traps maintained at −100 °C, −120 °C, and −196 °C. $CF_3O_2NO_2$ was retained in the second (−120 °C) trap[4] and was devoid of any impurities as determined by FTIR spectroscopy. NO_2 was made by reacting NO with O_2. Ultrahigh purity NO and O_2 reagents were obtained from commercial sources and were used as received. After photolysis, COF_2 was removed by trapping the sample at −120 °C and pumping on the sample for a few minutes, thus allowing the isolation of CF_3ONO_2. COF_2 boils at −83 °C while CF_3ONO_2 has a bp of −18 °C. The thermal stability of CF_3ONO_2 has been informed in ref 1 and should be stored at liquid nitrogen temperatures.

Results

Control experiments were performed in which samples of $CF_3O_2NO_2$ were admitted into the IR cell and left to stand in the dark for up to 30 min. There was no observable (<2%) loss of $CF_3O_2NO_2$ showing the absence of unwanted losses of $CF_3O_2NO_2$ in the cell over these time periods.

Figure 1 shows IR spectra of 2.6 mbar of $CF_3O_2NO_2$ in the cell before (A) and after 15 (B), 30 (C), and 40 (D) min of UV irradiation. IR features attributable to $CF_3O_2NO_2$ at 792, 1192, 1244, 1303, and 1762 cm^{-1} [3,4] are visible in panel A.

As seen in Figure 1, UV irradiation of the sample leads to a loss of $CF_3O_2NO_2$ and the formation of product features at 788, 1156, 1243, 1265, and 1748 cm^{-1} which can be assigned to CF_3ONO_2.[1] The small product feature at 1944 cm^{-1} reflects the formation of COF_2 in the system. Using the absorption cross section data reported by Sander et al.[1] we calculate that 80 ± 10% of $CF_3O_2NO_2$ initially present in the cell was converted into CF_3ONO_2. Quoted errors reflect uncertainties in the IR cross section data for CF_3ONO_2 combined with our assessment of the reproducibility of the spectral analysis. COF_2 was the major impurity in the samples; it was present at a level of approximately 10−20% (as determined by FTIR spectroscopy) of that of the CF_3ONO_2 and was removed as described in the Experimental Section.

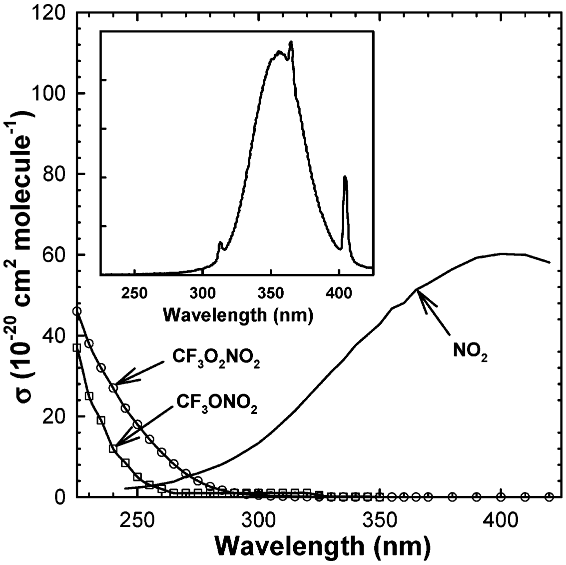

Figure 2. UV spectra of $CF_3O_2NO_2$ (circles),[4] CF_3ONO_2 (squares),[1] and NO_2.[6] The inset shows the spectral output of the UV blacklamps used in this work.

Discussion

The data presented above show that the UV irradiation of an equilibrated mixture of $CF_3O_2NO_2$ results in facile conversion of a large fraction of the $CF_3O_2NO_2$ into CF_3ONO_2. Figure 2 shows the UV spectra of the key species present in the cell, $CF_3O_2NO_2$,[4] CF_3ONO_2,[1] and NO_2,[6] together with the spectral distribution of the UV fluorescent lamps.

Inspection of Figure 2 shows that while there is little, or no, overlap between the lamp output and the absorption of $CF_3O_2NO_2$ and CF_3ONO_2, there is significant overlap with the NO_2 spectrum. As discussed in the Introduction, the photolysis of NO_2 to give NO will lead to conversion of $CF_3O_2NO_2$ into CF_3ONO_2 via reaction 1, 3, and 4. The presence of COF_2 impurity is explained by (1) the competition of reaction 5 with reaction 4 for the available CF_3O radicals and (2) the propensity of CF_3ONO_2 to decompose slowly to COF_2 and FNO_2 as noted previously.[1]

$$CF_3O + NO \rightarrow COF_2 + FNO \qquad (5)$$

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The addition of either NO_2 (to produce more NO through photolysis) or NO to the equilibrated mixture led to a decreased CF_3ONO_2 yield. This observation is explained by the increased importance of reaction 5 with increased [NO]/[NO_2] ratio. This finding is consistent with the reported formation of COF_2 and FNO following thermal decomposition of $CF_3O_2NO_2$ in the presence of excess NO,[7] and formation of COF_2, FNO, and CF_3ONO_2 following photolysis of CF_3I in the presence of NO and NO_2 with [NO]/[NO_2] ≈ 1.[7]

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