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Thermally Persistent Fluorosulfonyl Nitrene and Unexpected Formation of the Fluorosulfonyl Radical

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S *Supporting Information*

ABSTRACT: Thermally persistent triplet sulfonyl nitrene, FSO_2N, was produced in the gas phase in high yields (up to 66%) by flash vacuum pyrolysis of FSO_2N_3. Surprisingly, no rearrangement of FSO_2N was observed, but the long-sought radical FSO_2 (22%) and traces of SO_2 (3%) were identified by IR (^{15}N, ^{18}O, ^{34}S) spectroscopy. The photoinduced Curtius rearrangement of the nitrene to $FNSO_2$ was observed in solid noble gas matrices, and reactions of the nitrene with O_2, NO, and CO were studied.

Nitrenes play important roles in chemistry, biology, and material science. Their spectroscopy, structure, and reactivity are of fundamental importance.[1] Common nitrenes have a triplet ground state, and they can be readily produced through decomposition of covalent azides by eliminating N_2 molecules. Photodecomposition of azides has shown to efficiently generate nitrenes either in solutions or in low-temperature solid matrices for their direct spectroscopic characterization and reaction studies.[1] However, photolysis was found to produce highly reactive intermediates in exited states,[2] while thermally generated nitrenes are liable to facile secondary reactions like nitrene rearrangement and insertion reactions.[3] Direct observation of thermally produced nitrenes, such as CH_3N,[4] NCN,[5] PhN,[6] and various hetarylnitrenes[7] was, however, rendered possible using highly sensitive spectroscopic methods. Thus, the selective high-yield production of a thermally persistent triplet nitrene in the gas phase is a rare case.

In the past half century, α-oxo nitrenes RC(O)N,[8] $R_2P(O)N$,[9] and RSO_2N[10] have attracted experimental and computational interests due to their rich fundamental and applied chemistry. Many α-oxo nitrenes have already been spectroscopically detected, and they exclusively were generated through photolysis of appropriate precursors, mostly azides $RC(O)N_3$, $R_2P(O)N_3$, and RSO_2N_3, respectively.[8−10] However, pyrolysis of these azides mainly yields rearrangement and insertion products of the nitrene. Thus, α-oxo nitrene species were assumed to be too short-lived in the gas phase to survive the pyrolysis conditions.

Sulfonyl azides, RSO_2N_3, are commonly used as diazo and azide transfer reagents in organic synthesis. The corresponding sulfonyl nitrenes, RSO_2N, have been proposed as key intermediates for the synthesis of sulfonamides, sulfonylanilines, and sulfonylimido−metal complexes.[11] Herein, we report a rare example of a high-yield thermal production of triplet α-oxo nitrene (FSO_2N) in the gas phase from FSO_2N_3. Prior to this study, this nitrene has already been identified as the photolysis product of FSO_2N_3 in solid noble gas matrices.[12] In contrast to the observations in the photolysis study, traces of SO_2 and the long-sought sulfur-centered radical FSO_2 were obtained as byproducts of the flash vacuum pyrolysis.

Flash vacuum pyrolysis of FSO_2N_3 diluted in noble gas (azide:noble gas, 1: 500) was performed by passing the mixture through a quartz furnace (i.d., 1.0 mm; length, 30 mm), which was heated (~1000 K) over a length of ~10 mm by a platinum wire. The decomposition mixture was then immediately deposited as a solid film on the matrix support and subjected to IR and UV/vis spectroscopy studies (see Supporting Information (SI)).

A typical IR spectrum of the matrix-isolated pyrolysis products in the mid-IR region is shown in Figure 1. The assignment of the spectrum is straightforward by comparison with that of the azide (Figure S1)[13] and its photolysis products.[12] In addition to the weak IR bands of the precursor (Figure 1 asterisks) and SO_2 (Figure 1c), four strong bands at 1426.2, 1206.5, 835.2, and 730.1 cm^{-1} (Figure 1a) belongs to triplet nitrene FSO_2N (X^3A''). The band positions agree nicely with the values (1426.4, 1206.5, 835.2, and 730.5 cm^{-1}) observed in the photolysis experiments. This assignment is

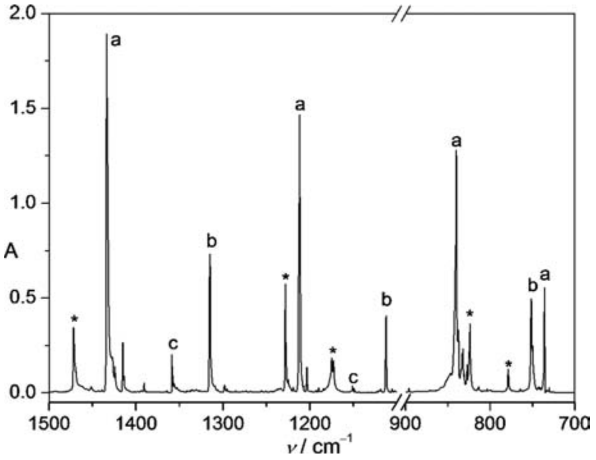

Figure 1. Argon matrix (16 K) mid-IR spectrum of the pyrolysis products of FSO_2N_3. Bands of FSO_2N_3 (*), FSO_2N (a), FSO_2 (b), and SO_2 (c) are labeled.

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unambiguously ascertained by their $^{14/15}N$ and $^{16/18}O$ isotopic shifts (Figure S2).[12] As can be seen in Figure 1, these bands are strong enough to allow a clear identification of weak bands of the naturally abundant ^{34}S isotopologues (4.2%). Interestingly, another set of less intense bands at 1307.6, 1107.0, and 744.7 cm^{-1} (Figure 1b) occurred with very similar $^{16/18}O$ isotopic patterns using a 1:2.7:1.9 mixture of $FS(^{16}O)_2N_3$, $FS(^{16}O)(^{18}O)N_3$, and $FS(^{18}O)_2N_3$. However, no $^{14/15}N$ shift was observed for these bands using a 1:1 mixture of $FSO_2{}^{15}NNN$ and $FSO_2NN^{15}N$. The weak bands of naturally abundant ^{34}S isotopologues were also observed for these bands.

A liquid-He-cooled bolometer was utilized for recording the far-IR spectrum in the 700−200 cm^{-1} region. The far-IR spectrum of the flash pyrolysis products of FSO_2N_3 is shown in Figure 2. The low intensity of the bands for the azide precursor (Figure 2*) indicates an almost complete decomposition. Additional five IR fundamental bands of the nitrene (Figure 2a) appeared in the spectrum at 515.1, 487.9, 457.6, 311.7, and 301.8 cm^{-1}. Another set of bands at 524.3, 424.1, and 405.0 cm^{-1} (Figure 2b) show no $^{14/15}N$ but distinct $^{16/18}O$ shifts (Figure S3) and are attributed to the same carrier, which gives rise to the aforementioned three unassigned bands in Figure 1b.

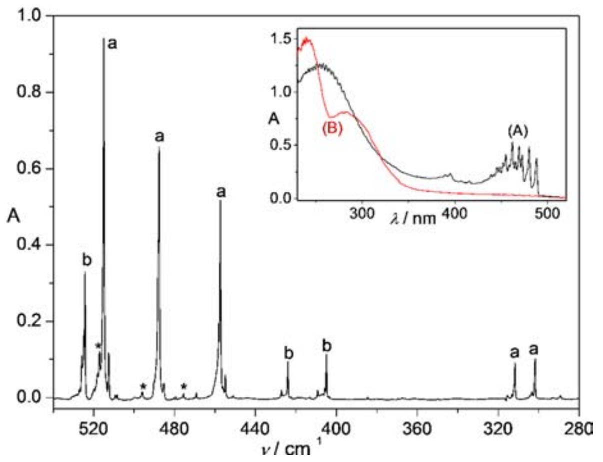


Figure 2. Argon matrix (16 K) far-IR spectrum of the pyrolysis products of FSO_2N_3. Bands of FSO_2N_3 (*), FSO_2N (a), and FSO_2 (b) are labeled. Inset: Neon matrix (6 K) UV/vis spectra of the pyrolysis products of FSO_2N_3 before (A) and after (B) UV light irradiation of $\lambda = 266$ nm.

The positions of these six new IR bands and their $^{32/34}S$ and $^{16/18}O$ isotopic shifts are collected in Table 1. Their assignment to the long-sought radical FSO_2[14] is supported by the good agreement with calculations at the B3LYP/6-311+G(3df) level. The two SO_2 stretching frequencies for FSO_2 ($\nu_{asym}(SO_2) = 1307.6$ cm^{-1}, $\nu_{sym}(SO_2) = 1107.0$ cm^{-1}) are close to those of sulfonyl radical $ClSO_2$ (1309.6, 1098.2 cm^{-1}).[15]

Since N_3 radicals were not observed among the pyrolysis products, the formation of FSO_2 from FSO_2N_3 is intriguing. A plausible explanation is the dimerization of triplet FSO_2N to $FSO_2N{=}NSO_2F$, which then undergoes fragmentation into N_2 and two FSO_2 radicals. This assumption is consistent with the observed dimerization of triplet nitrenes through N−N coupling in condensed phases.[16] Our attempts to capture the nitrene or its dimer by condensation of the pyrolysis products of FSO_2N_3 on a coldfinger held at 77 K failed. A deep brownish-yellow solid mixture was observed, which turned into a white solid and released N_2 on warming up to ~133 K, eventually, FSO_2N_3, F_2SO_2, SO_2, F_2SO, and SO_3 were identified by IR spectroscopy (Figure S4).

Flash pyrolysis of FSO_2N_3 offers an efficient and also selective way of producing the α-oxo nitrene FSO_2N in the gas phase. It has a triplet ground state[12] and is thermally robust against rearrangements under the described pyrolysis conditions. The yields of azide pyrolysis products were estimated based on observed and calculated IR intensities for their two SO_2 stretches (antisymmetric and symmetric). Both bands give consistent results, and the averaged yield of FSO_2N is ~66%, together with 22% of FSO_2 and 3% of SO_2; still less than 10% of azide was left.

The high yield of nitrene enables us to significantly improve its UV/vis spectrum which was recently obtained through laser (193 nm) photolysis of the azide.[12] The structured visible absorption band with the onset at 488 nm is assigned to the $A^3A'' \leftarrow X^3A''$ transition of FSO_2N (Figure 2 inset, spectrum A). However, according to its photobehavior, FSO_2 also contributes partially to the visible band (*vide infra*). FSO_2 can also likely be associated with the regular vibrational spacing of 510 ± 20 cm^{-1} superimposed to the broad band at $\lambda_{max} = 260$ nm. This latter feature was absent in the UV/vis spectrum obtained in the photolysis experiments (Figure S5), where FSO_2 radicals were not formed.[12] In fact, both FSO_2N and FSO_2 were depleted when the matrix was exposed to 266 nm laser irradiation (Figures S6 and S7), indicating that also the nitrene has some contributions to the broad UV band at $\lambda_{max} = 260$ nm. The UV photolysis of matrix isolated FSO_2 furnished SO_2 as the only detectable product, suggesting its fragmentation into SO_2 and fluorine atom.

Table 1. Calculated and Experimentally Observed IR Frequencies and Isotopic Shifts (cm^{-1}) of FSO_2 (C_s, $^2A'$)

IR fundamentals (cm^{-1})		isotopic shifts (cm^{-1})[a]										
$F^{32}S^{16}O_2$		$F^{34}S^{16}O_2$		$F^{32}S^{16}O^{18}O$		$F^{32}S^{18}O_2$		$F^{34}S^{16}O^{18}O$		$F^{34}S^{18}O_2$		
cal[c]	exp[d]	cal	exp	cal	exp	cal	exp	cal	exp	cal	exp	symmetry, assignment[b]
1115 (52)	1107.0 (48)	6.8	6.9	27.5	26.1	49.9	47.7	34.7	33.4	57.3	55.2	a′, SO_2 sym. stretch
719 (171)	744.7 (100)	8.8	8.4	1.1	1.3	2.3	2.7	9.8	9.6	10.9	10.9	a′, SF stretch
518 (27)	524.3 (16)	7.0	−[e]	7.0	6.8	14.1	13.7	14.0	−[e]	21.1	20.8	a′, FSO_2 umbrella
414 (5)	424.1 (3)	1.4	1.5	6.5	6.6	15.0	15.2	7.9	8.0	16.4	17.1	a′, SO_2 bending
1308 (134)	1307.6 (95)	17.2	17.0	18.0	17.7	41.0	39.8	35.3	34.7	58.8	57.3	a″, SO_2 antisym. stretch
391 (8)	405.0 (5)	1.5	1.5	6.2	6.5	10.5	10.8	7.7	7.4	11.9	12.1	a″, FSO bending

[a] Calculated and observed isotopic shifts are given relative to $F^{32}S^{16}O_2$ ($^2A'$). [b] Vibration modes according to calculated displacement vectors. [c] B3LYP/6-311+G(3df) calculated frequencies and IR intensities (km mol^{-1}, in parentheses). [d] Observed IR band positions in argon matrix (16 K, most-intense matrix sites) and relative intensities based on integrated absorbances of all matrix sites (in parentheses). [e] Bands overlap.

Upon UV radiation FSO_2N is subjected to an unusual oxo nitrene−nitroso Curtius-type rearrangement, furnishing nitroso sulfinyl fluoride, FS(O)NO.[12] This rearrangement was observed in the former photolysis study using near-UV visible (>320 nm) and UV (260−400 nm) light irradiations[12] and is verified in this study by 266 nm laser photolysis of FSO_2N (Figures S6 and S7). This experiment establishes the assignment of two broad absorptions at λ_{max} = 285 and 240 nm to FS(O)NO (Figure 2 inset, spectrum B). Apart from the formation of FS(O)NO, 266 nm laser photolysis of FSO_2N afforded another set of 9 very weak IR bands at 1420.0, 1230.4, 959.2, 844.2, 543.6, 453.3, 377.5, 240.9, and 245.5 cm^{-1} (Figures S8 and S9). These bands turned out to be associated with a novel isomer of FSO_2N. The absence of characteristic NO or NO_2 stretching frequencies ruled out the formation of as yet unknown nitrosooxy or nitro derivatives, FSONO and $FSNO_2$, respectively. The large $^{14/15}N$ isotopic shifts of 19.3 and 17.0 cm^{-1} for the respective two bands at 959.2 and 844.2 cm^{-1} suggest the presence of both N−F and S−N vibrations. The two bands at 1420.0 and 1230.4 cm^{-1} can be reasonably assigned to SO_2 stretching vibrations. Thus the new set of bands is assigned to the N-sulfonyl imine $FNSO_2$. This assignment is supported by an excellent agreement between experimental and calculated vibrational data (Table S1). Due to the low abundance of $FNSO_2$, distinct $^{16/18}O$ isotopic shifts were difficult to extract for most of the bands. However, the out-of-plane NSO_2 bending mode at 377.5 cm^{-1} clearly splits into four components with $^{16/18}O$ isotopic shifts of 1.9, 3.6, and 5.5 cm^{-1} upon ^{18}O labeling (Figure S10), proving the structural nonequivalence of the two oxygen atoms in this planar molecule. The unambiguous identification of $FNSO_2$ provides the first clear evidence for the formation of N-sulfonyl imines via Curtius rearrangement of sulfonyl nitrenes.[10]

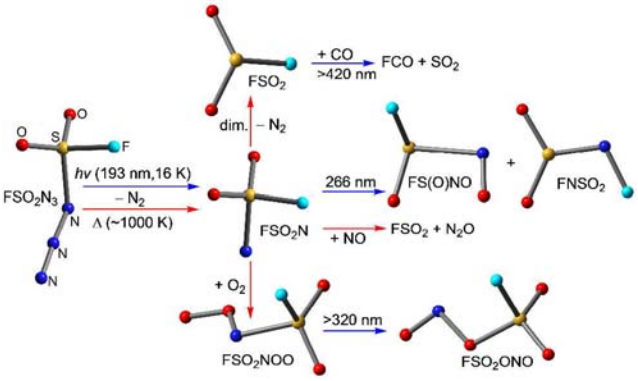
The gas-phase generation of FSO_2N enabled us to study gas-phase reactions between the triplet nitrene and small molecules like O_2 and NO, which do not react with the azide precursor at room temperatures. Reactions of triplet nitrenes with O_2 have already been studied in solid noble gas matrices.[17] Thus, a mixture of the azide with either O_2 or NO diluted in argon gas was pyrolyzed and deposited onto the matrix support at 16 K. Triplet FSO_2N was efficiently scavenged by O_2 and mainly singlet nitroso-*O*-oxide FSO_2NOO was obtained in the deposit (Figure S11). The peroxide selectively rearranged to FSO_2ONO upon subsequent irradiation (λ > 320 nm) of the deposit (Figure S12). The matrix was then slowly warmed to room temperature and FSO_2ONO converted into solid $NO^+SO_3F^-$ (Figure S12). The IR spectrum obtained from the nitrosonium salt agrees well with that reported previously,[18] while the vibrational spectra of the nitroso-*O*-oxide and the nitrosooxy derivatives were assigned by comparison with calculated data and based on $^{14/15}N$ isotopic shifts (Tables S2 and S3).

Copyrolysis of FSO_2N_3 and NO diluted in argon furnished N_2O and FSO_2. Apart from the NO dimer and traces of SO_2, the IR spectrum of the matrix-isolated pyrolysis products (Figure S13) revealed a further set of broad bands, which by comparison with calculated spectra (Table S4) can be assigned to FSO_2NO, very likely formed by radical recombination of FSO2 and NO. The reaction between the FSO_2N intermediate and NO resembles the radical−radical reaction between NH ($X^3\Sigma^-$) and NO to HNNO ($^2A'$).[19] Like parent HNNO, FSO_2NNO decomposed into N_2O and FSO_2 under the pyrolysis conditions.

Reaction between CO and FSO_2N was not observed in the gas phase but occurred in the solid matrix upon visible light irradiation of >420 nm (Figure S14). Upon photoexcitation the nitrene was quantitatively scavenged by CO as FSO_2NCO. Unexpectedly, FSO_2 was also efficiently depleted in the CO-doped matrix by visible light, producing FCO and SO_2. This observation is, however, consistent with a rather low S−F bond energy (169 kJ mol^{-1}),[14e] calculated vertical transition energies for the FSO_2 (Table S5), and the optical absorption spectra reported for analogous sulfonyl radicals in solution (CH_3SO_2, CH_3OSO_2). These show broad absorptions at $\lambda_{max} \approx 350$ nm which are accompanied by weaker bands extending to the visible region, where electron transfer is involved from oxygen lone pair orbitals to the mainly sulfur-centered singly occupied orbital.[20]

A summary illustrating the thermal and photochemical transformations of FSO_2N described herein is given in Scheme 1. As elucidated elsewhere, sulfonyl nitrenes have a low-lying excited singlet state of closed-shell nature.[10a,12] This configuration renders spin−orbit coupling to be a particularly effective mechanism for intersystem crossing (ISC) between this lowest singlet and the open-shell ground electronic state.[21] Thus, beside the flash vacuum pyrolysis of FSO_2N_3, preliminary studies were also performed on other sulfonyl azides RSO_2N_3 (R = CH_3, CF_3, and Cl). However, instead of the expected sulfonyl nitrene RSO_2N complex, mixtures of SO_2 and secondary products were obtained. Hence, the thermal persistency of FSO_2N in the gas phase seems to be unique and can partly be attributed to the highest X−S bond strength in the series X = F > CH_3 > CF_3 ≈ Cl. Although the fluorine derivative has the largest singlet−triplet gap (57 kJ mol^{-1} at the CBS-QB3 level) in this series, relaxation from the initially generated singlet to the triplet ground state via ISC is obviously much faster than thermal rearrangement to $FNSO_2$, even though the rearrangement barrier (125 kJ mol^{-1})[12] could be reached at the high pyrolysis temperatures (∼1000 K). These results are consistent with the rather short time scale (100−300 ps) for the ISC of naphthylsulfonyl nitrene, as estimated recently by ultrafast spectroscopy.[10a] Further experimental and theoretical studies to disclose the intriguing decomposition mechanisms for these different sulfonyl azides are currently underway.

Scheme 1. Formation and Reactions of Triplet FSO_2N[a]



[a]Blue arrows indicate photo-induced reactions obtained in solid noble gas matrices, while red arrows indicate gas-phase reactions.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and calculation methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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