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Spectroscopic Evidence for the Existence of the CF_3OSO_3 Radical

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The first spectrosopic evidence for the existence of the CF_3OSO_3 radical has been obtained from matrix isolation and FT-IR and UV spectroscopic studies. The vibrational frequencies measured are in reasonable agreement with predictions from density functional calculations. Upon visible and UV photolysis of the CF_3OSO_3 radical, SO_3 is produced and provides experimental support for a new light-driven route for the oxidation of SO_2 to SO_3 assisted by CF_3O radicals.

A fundamental and key species produced in the degradation of alternative halocarbons and chlorofluorocarbons is the CF_3O radical.[1−3] Its formation is dominated by the degradation of the CF_3 group contained in the halocarbon. The processes that dictate the atmospheric fate of CF_3O radicals are widely accepted to be the reactions either with methane or with nitrogen monoxide. Methane is present in the atmosphere in a mixing ratio of 1800 ppb (parts per billion, 1 in 10^9), while NO is less abundant (1 ppb). However, the reaction with NO is 2000 times faster than that with methane and, hence, is comparable in significance.[4,5] However, other reactions of CF_3O radicals are usually neglected because of the low concentrations of possible reaction partners or comparably slow reaction rates. Nonetheless, one atmospheric species that has been largely ignored until recently is SO_2.[6] The abundance of SO_2 in the atmosphere is highly variable. Its concentrations can reach levels of 1000 ppb.[5] The reaction of CF_3O with SO_2 has been shown to produce the CF_3OSO_2 radical, which is quite stable.[6] One expected atmospheric fate of the CF_3OSO_2 radical is the rapid reaction with molecular oxygen leading to the peroxy radical $CF_3OS(O)_2OO$. Peroxy radicals readily convert to the corresponding oxy radicals under atmospheric conditions. This is done by rapid reaction with trace gases such as NO, CO, or ozone;[7] consequently, it is expected that CF_3OSO_2 forms CF_3OSO_3 in the atmosphere. Oxy radicals, such as CF_3OSO_3, are generally more reactive than their corresponding peroxy radicals. They are highly oxidizing species, as with, for example, the FSO_3 radical.[8−10] The CF_3OSO_3 radical has not been observed, and there are no reports of its existence in the literature. In this communication, we report the discovery of the hitherto unknown CF_3OSO_3 radical.

To generate the CF_3OSO_3 radical, we performed low-pressure flash thermolysis experiments of highly diluted $CF_3OS(O)_2OOS(O)_2OCF_3$ (this previously unknown peroxide is the radical dimer), held in a U-trap at −85 °C with Ar or Ne flow over the solid sample to give a diluted mixture. The peroxide is prepared from a 1:7:100 mixture of $CF_3C(O)OC(O)CF_3$, SO_2, and O_2 (300 mbar total pressure in a 5 L reaction bulb) that is held at −40 °C and irradiated for 4 h with UV light from a 15 W mercury low-pressure lamp. Lowering the temperature to −50 °C allows evaporation of the volatile compounds, as there are the excess oxygen and SO_2, unreacted acetic acid anhydride, and COF_2 as the product of a minor side reaction. The $CF_3OS(O)_2OOS(O)_2OCF_3$ product is further purified by trap-to-trap condensation where it proved to be immobile in a trap held at −40 °C.

The peroxide is transferred into a U-trap that is connected by one side to the Ar or Ne storage volume and the other side to the thermolysis device mounted directly in front of the matrix support. The thermolysis oven temperatures are adjusted to various temperatures between room temperature and 400 °C, while the matrix support is held at 16 or 6 K for Ar or Ne matrixes, respectively. A noble gas flow is allowed to pass over the U-trapped sample, taking some peroxide with it as it moves through the thermolysis oven. The thermolyzed mixture is then immediately frozen on the matrix support. Details of the matrix apparatus are given elsewhere.[11] IR spectra of the matrix-isolated species are recorded with an IFS 66v/S FT-IR spectrometer (Bruker) with a resolution of 1 cm^{-1} (Ar) or 0.25 cm^{-1} (Ne). The UV−vis spectra of the Ne matrix-isolated products were recorded with a Lambda 900 UV−vis spectrometer (Perkin-Elmer) with a resolution of 1 nm under use of a quartz fiber and condensor optics (Hellma). All spectra are recorded in reflectance mode. For photolysis experiments on the matrix-isolated samples, a 150 W mercury high-pressure lamp (Heraeus) is used with and without 280 or 385 nm cutoff filters (Schott).

The thermal dissociation of the $CF_3OS(O)_2OOS(O)_2OCF_3$ peroxide is performed at room temperature. The precursor dissociates slowly at temperatures above −40 °C, and the dissociation occurs too slowly for detection. After increasing

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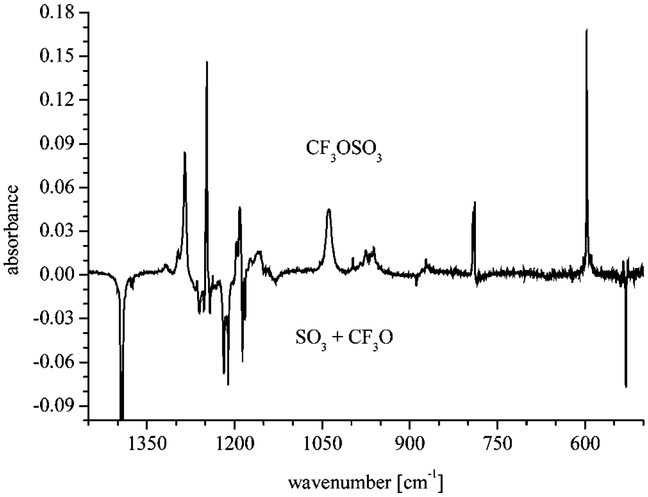

Figure 1. Difference IR spectrum (before minus after photolysis) of the thermolysis products of $CF_3OS(O)_2OOS(O)_2OCF_3$ isolated in Ne matrix. The bands of the CF_3OSO_3 radical, vanishing upon photolysis, point upward. The absorptions of the photoproducts CF_3O and SO_3 are displayed in negative direction.

TABLE 1: Observed and Calculated IR Absorptions of CF_3OSO_3

Ne matrix		Ar matrix		calculated[a]		
ν [cm^{-1}]	rel int.	ν [cm^{-1}]	rel int.	ν [cm^{-1}]	intensity [km·mol^{-1}]	mode
1284.9	100	1281	100	1255	364	ν_1
1247.2	58	1244	55	1217	308	ν_2
				1202	47	ν_3
1190.0	40	1186	24	1161	236	ν_4
1039.0	61	1037	89	1048	353	ν_5
961.7	5.8	961	11	963	153	ν_6
866.7	0.8	866	2.1	929	27	ν_7
791.4	24	791	40	775	82	ν_8
				687	0.78	ν_9
				615	3.4	ν_{10}
597.1	46	594	69	597	157	ν_{11}
		536	1.7	520	6.3	ν_{12}

[a] B3LYP/6-311+G(3df); calculated low-frequency modes $\nu_{13}-\nu_{21}$ are (intensities in brackets) as follows: 468 (0.45), 346 (0.28), 337 (0.90), 333 (0.19), 273 (3.7), 165 (2.6), 144 (0.50), 71 (0.04), 44 (0.05).

the thermolysis temperature to 90 °C, the peroxide precursor dissociates quantitatively, and new IR absorption bands could be detected in the product IR spectra. After further increase of the thermolysis temperature above 200 °C, these new bands vanish, while the known absorptions of CF_3O and SO_3 appear. Finally, further reaction temperature increases result in the production of COF_2, which is the result of secondary decomposition of the CF_3O radical. The new bands detected under "mild" thermolysis conditions also vanished when the product matrix is irradiated with UV light. In these experiments, CF_3O and SO_3 are produced parallel to the consumption of the species responsible for the new bands. A difference IR spectrum (before minus after photolysis) is shown in Figure 1. The new bands, vanishing upon photolysis, are plotted in the positive direction (*y*-axis represents absorbance) and are assigned to CF_3OSO_3. The photolysis experiments and additional support from quantum chemical calculations also suggest that the new species is CF_3OSO_3. The observed and quantum chemical prediction of the vibrational modes of the CF_3OSO_3 radical is presented in Table 1. The broad band at 1039 cm^{-1} is assigned to the ν_s-(SO_3) vibrational mode. However, vibrational coupling between the SO_3 and CF_3 moieties is expected, and a description of a particular mode with one characteristic motion (like the C−F stretching mode) is not plausible for most of the fundamentals for CF_3OSO_3 . From the 21 fundamental normal vibrational modes of CF_3OSO_3 , only 9 are identified. The other missing modes do not contradict the assignment of the new species, as these modes are expected to be either too low in intensity to be detected or outside our experimental detection region of our instrumentation.

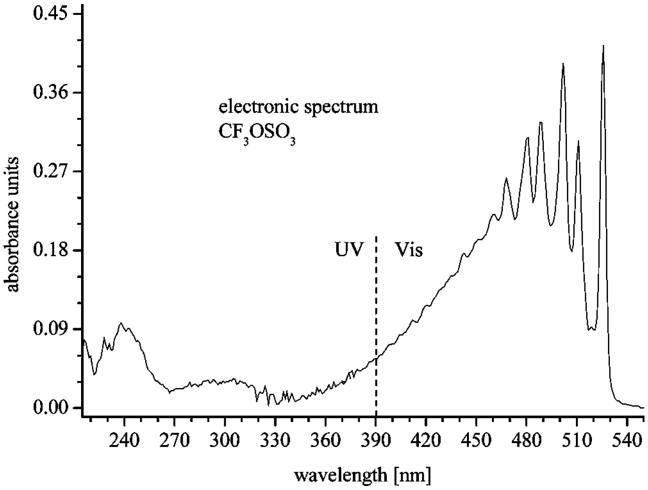

Figure 2. UV−vis spectrum of Ne matrix-isolated CF_3OSO_3 radicals.

The UV−vis spectrum of CF_3OSO_3 isolated in Ne matrix is shown in Figure 2. A well-structured absorption band with a clearly visible progression (910 cm^{-1}) and additional fine structure (250 and 550 cm^{-1}) is found with an onset τ_{00} at 19 020 cm^{-1} (526.8 nm). The light absorption continues into the UV region where two additional but smaller absorption maxima are found at 305 and 238 nm together with an increasing absorption toward shorter wavelengths than 210 nm. As the exact concentration of the radical and the thickness of the matrix are unknown, no absolute absorption cross-sections could be determined directly. However, by comparing the radical's photochemical behavior, IR, vis, and UV absorbance with similar radicals, a cross-section at the absorbance maximum in the visible region could be estimated to be in the magnitude of $4 \cdot 10^{-18}$ cm^2. Reinforcing the similarity between CF_3O and F as substituent,[12] the visible spectrum of the CF_3OSO_3 radical is similar to that of FSO_3 radicals[13,14] in band contour and intensity. Detailed spectroscopic assignment of the UV−vis spectrum of CF_3OSO_3 is given in Table S1 in the Supporting Information.

To support the spectroscopic characterization, density functional theory (DFT) calculations are performed at the B3LYP/6-311+G(3df) level of theory.[15] The calculations predict C_1 symmetry of CF_3OSO_3 and incomplete delocalization of the single electron on the SO_3 unit. The calculated structural data is available as Supporting Information (Table S2). Of particular interest is the O−S bond energy. The observations from the thermolysis experiments showed that a small temperature range exists where the precursor peroxide dissociates but not the CF_3-OSO_3 radical. The calculated relative O−O bond energy for the precursor peroxide and O−S bond energy for the radical support the observation that the radical is more stable toward thermal dissociation than its precursor. The CF_3O-SO_3 bond dissociation is calculated to be $\Delta H_{diss} = +70$ kJ·mol^{-1}, while for the dissociation of the precursor $CF_3OS(O)_2OOS(O)_2OCF_3$ (breaking of the central O−O bond), a value of $\Delta H_{diss} = +49$ kJ·mol^{-1} is predicted. In addition, because of the calculated activation barrier for the CF_3OSO_3 dissociation (which represents a lower limit, as calculations often underestimate the strength of bonds weaker than 100 kJ·mol^{-1}) the radical is stable toward thermal degradation under atmospheric (upper tropospheric and stratospheric) conditions.

Further support for the existence of the CF_3OSO_3 also under atmospheric conditions is achieved by studying the precursor synthesis thermal dependency. Here, photochemically generated CF_3 radicals (from trifluoroacetic acid anhydride) react in a oxygen/SO_2 mixture. At room temperature and at 0 °C, the monoxide $CF_3OS(O)_2OS(O)_2OCF_3$ is found as the only product, identified by its known IR bands.[16] Below that, at −40 °C, the peroxide $CF_3OS(O)_2OOS(O)_2OCF_3$ becomes the main product with a minimum of 25% monoxide impurity. It is commonly accepted that CF_3 radicals in oxygen atmosphere are readily converted into CF_3O radicals via the CF_3OO intermediate.[17] CF_3O then reacts with SO_2, yielding CF_3OSO_2. The observed final products require that this radical adds oxygen, as no other explanation for the abundance of oxygen-bridged sulfur species can hold. Peroxide formation is possible by recombination of CF_3OSO_2 and $CF_3OS(O)_2OO$, but the detection of the monoxide must be due to CF_3OSO_3 formation as a result of $CF_3OS(O)OO$ self-reaction. With CF_3OSO_3 present in the reaction mixture, a dimerization of this radical is the favored formation pathway for the peroxide $CF_3OS(O)_2OOS(O)_2OCF_3$

$$CF_3O + SO_2\ (+ M) \rightarrow CF_3OSO_2\ (+ M) \tag{1}$$

$$CF_3OSO_2 + O_2\ (+ M) \leftrightarrow CF_3OS(O)_2OO\ (+ M) \tag{2}$$

$$2CF_3OS(O)_2OO \rightarrow 2CF_3OSO_3 + O_2 \tag{3}$$

$$2CF_3OSO_3\ (+ M) \rightarrow CF_3OS(O)_2OOS(O)_2OCF_3 \tag{4}$$

$$CF_3OSO_3 + CF_3OSO_2\ (+ M) \rightarrow CF_3OS(O)_2OS(O)_2OCF_3 \tag{5}$$

The abundance of the monoxide even at low temperatures and large oxygen excess indicates that the peroxy radical is not formed quantitatively, but an equilibrium (eq 2) with significant concentrations of both CF_3OSO_2 and $CF_3OS(O)_2OO$ is reached. As the reaction conditions (temperatures between −40 °C and 0 °C, O_2 pressure about 300 mbar) compare to those in the atmosphere, the reaction of CF_3O and SO_2 is suggested[6] to yield CF_3OSO_2 and CF_3OSO_4 with the latter being reduced by atmospheric trace compounds. As CF_3OSO_3 is thermally quite stable, two pathways for further reactions are possible: (i) photochemically driven dissociation of the CF_3OSO_3 radical into SO_3 and reformation of the CF_3O radical or (ii) reaction with a hydrogen donor that would yield $CF_3OS(O)_2OH$, a superacid in the atmosphere. Both cases, a conversion of S(+IV) to S(+VI) by fluorocarbon compounds or the introduction of superacid chemistry in the atmosphere, have not been addressed before.

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Supporting Information Available: Supplementary Tables 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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