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Spectroscopic and Photochemical Properties of CH_3SNO

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UV and IR absorption cross sections were measured for methyl thionitrite at 298 K. This compound was found to undergo photochemical reactions in the wavelength region of 300–400 nm via $CH_3SNO + h\nu \rightarrow CH_3S + NO$ followed by $CH_3S + NO \rightarrow CH_3SNO$ and $2CH_3S \rightarrow CH_3SSCH_3$. Preliminary results on the mechanism of the reaction of CH_3S with O_2 were also obtained.

Introduction

In a recent FT IR study of the HO-radical initiated oxidation of CH_3SCH_3 in the presence of NO,[1] CH_3SNO was observed as an intermediate presumably formed by the addition reaction of CH_3S radical with NO, reaction 1.[2]

$$CH_3S + NO \rightarrow CH_3SNO \quad (1)$$

Since CH_3SNO is analogous to CH_3ONO, it is expected to photodissociate readily in the near-UV region.[3]

$$CH_3SNO + h\nu(300\text{–}400\ \text{nm}) \rightarrow CH_3S + NO \quad (2)$$

However, to date, no studies have been made of the gas-phase photochemistry of CH_3SNO. Higher members of the alkyl thionitrites have been recently used for synthetic purposes in the liquid phase.[4] In 1961, Philippe reported the preparation method and low-resolution IR spectrum of CH_3SNO.[5] More recently, we have found that this compound can be formed heterogeneously in gaseous mixtures containing CH_3NO and CH_3SH according to the stoichiometric relation $CH_3ONO + CH_3SH \rightarrow CH_3OH + CH_3SNO$.[1] A medium-resolution IR spectrum of CH_3SNO recorded with the FT IR method in such a mixture has led to the positive identification of its formation in the reaction $HO + CH_3SCH_3$ as mentioned above. Reported briefly in the present paper are experimental data on its spectroscopic (UV and IR) and photochemical properties.

Experimental Section

The FT IR facility and the general experimental procedures were identical with those used for the several recent studies of the gas-phase reactions of atmospheric interest.[6] Three IR cells (1-, 20-, and 180-m path lengths) served as static reactors to handle reagent gases at partial pressures over the mtorr to torr range in the presence of 700 torr of diluent air or N_2. A theoretical resolution of 1/16 cm^{-1} and 1.5-min data acquisition (16 scans) were used throughout the present study to record IR spectra in the frequency region of 500–4000 cm^{-1}. UV–visible spectra were recorded by use of a Cary 14 double-beam spectrometer with a matched pair of sample and reference cells (50 mL quartz, 10 cm path length).

Pure samples of methyl thionitrite were prepared by reacting equimolar concentrations of N_2O_3, i.e. ($NO + NO_2$), with CH_3SH at dry ice temperature, as indicated by the color change of the condensate from blue to red, and by taking the mid-fraction during slow warming.[5] ^{15}NO and $^{15}NO_2$ were used to prepare $CH_3S^{15}NO$. The CH_3SNO is thermally stable but is highly susceptible to photodissociation at wavelengths shorter than that of yellow light. Thus, the CH_3SNO samples were usually stored in the dark at dry ice temperature prior to use.

Results and Discussion

IR and UV–Visible Spectra. IR absorbance spectra of $CH_3S^{14}NO$ and $CH_3S^{15}NO$ are shown in Figure 1, together with that of CH_3ONO for comparison. All the bands seen in Figure 1A for $CH_3S^{14}NO$ were previously observed and were assigned by Philippe.[5] In the present study, the absolute absorption cross section was determined for the entire spectrum ranging from 500 to 4000 cm^{-1}. The N-15 isotope effect on the N=O stretch and S–N stretch bands is readily discernible in Figure 1B. Namely, the peak height at 1536.1 cm^{-1} was found to correspond to $\sigma = 1.2 \times 10^{-18}$ cm^2. Also, as discussed by Philippe, CH_3SNO in contrast to CH_3ONO does not exhibit distinct bands attributable to the cis and trans isomers.

The UV–visible absorption spectrum of CH_3SNO was recorded in the wavelength region of 190–600 nm. As will be discussed later, an excess of NO was added to the CH_3SNO samples used in this experiment to minimize the formation of the major photochemical product CH_3SSCH_3 during the data acquisition. The resulting spectral data were free of absorption due to CH_3SSCH_3. Figure 2 shows the UV spectrum of CH_3SNO in the wavelength region of 190–430 nm. This spectrum is somewhat similar to that of CH_3ONO owing to singlet–singlet n-π^* transitions.[3,8,9] However, CH_3ONO does not exhibit the doublet structure in the region of 190–250 nm as seen for CH_3SNO.[9] Furthermore, the band centered at about 340 nm is approximately 10 times stronger than the corresponding band of CH_3ONO.[9] Also, CH_3SNO appears to have two bands at 510 and 545 nm with $\sigma = 2.4 \times 10^{-20}$ and 5.8×10^{-20} cm^2, respectively, although possible contribution of some unknown impurity to these weak bands has not been ruled out.

Photochemistry. The UV irradiation of CH_3SNO in the wavelength region of 300–400 nm resulted in the formation

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[1] H. Niki, P. D. Maker, C. M. Savage, and L. P. Breitenbach, International Symposium on Chemical Kinetics related to Atmospheric Chemistry, Tsukuba, Japan, June 6–10, 1982, Abstracts pp 17–21.

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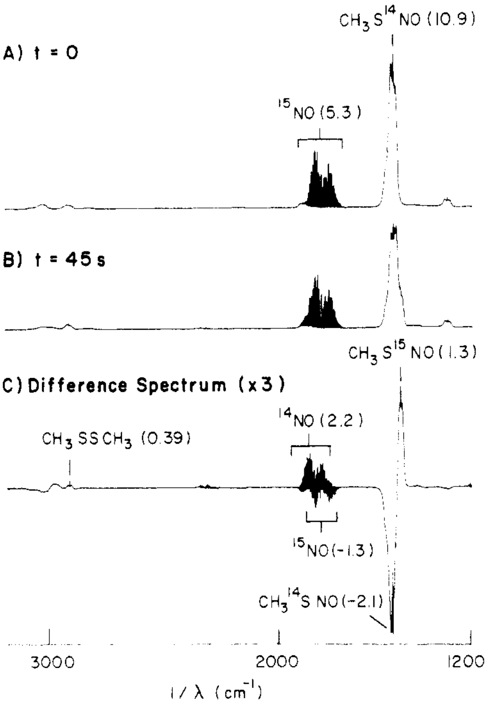

Figure 1. IR absorbance spectra of CH$_3$S^{14}NO, CH$_3$^{15}NO, and CH$_3$O^{14}NO in the frequency region of 550–2000 cm^{-1}. Frequencies are indicated for the most intense peaks and not necessarily for the band centers. (C) and (T) denote the cis and trans isomers for CH$_3$ONO.

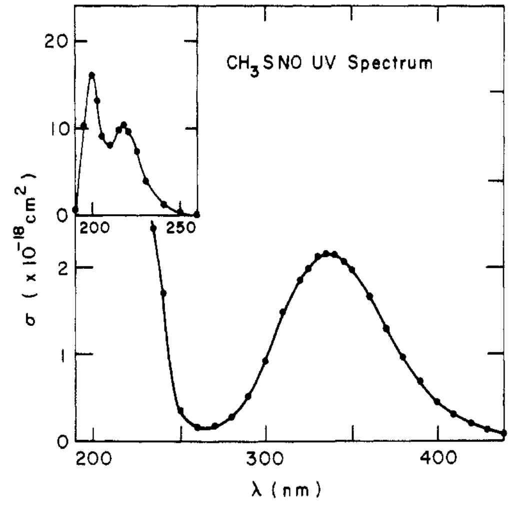

Figure 2. UV absorption cross section of CH$_3$SNO in the wavelength region of 190–430 nm.

of CH$_3$SSCH$_3$ and NO in stoichiometric amounts. These results are consistent with the occurrence of the primary step, reaction 2, followed by the self-reaction of the CH$_3$S radicals, i.e. reaction 3.[2,10,11]

$$2CH_3S \rightarrow CH_3SSCH_3 \qquad (3)$$

In addition, some evidence was obtained for the regeneration of CH$_3$SNO by the reaction of the CH$_3$S with NO, reaction 1. Namely, the observed decay rates of CH$_3$SNO decreased markedly with increase in [NO] either formed during the photolysis or added initially to the mixtures. More direct evidence for reactions 1–4 was provided by the product study in the photolysis of mixtures containing

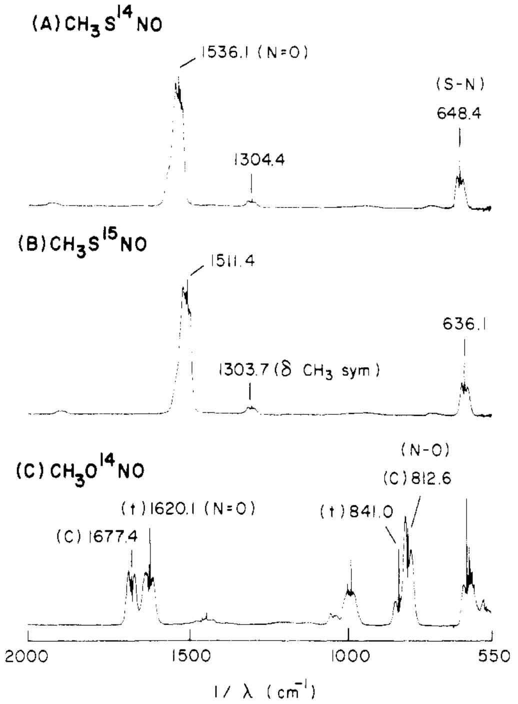

Figure 3. IR spectral data from the photolysis of a mixture containing CH$_3$S^{14}NO (10.9 ppm) and ^{15}NO (5.3 ppm) in 700 torr of N$_2$. Values in parentheses are concentrations in ppm (1 ppm = 2.46 × 10^{13} molecule cm^{-3}).

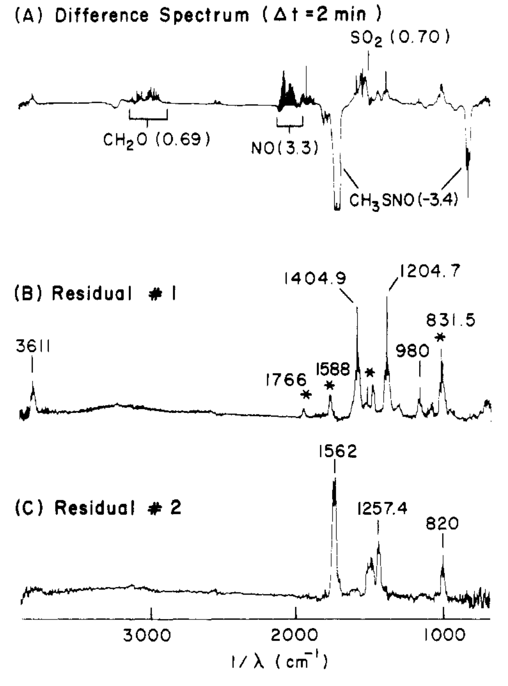

Figure 4. IR spectra of the reaction products in the photolysis of a mixture containing CH$_3$SNO (20 ppm) in 700 torr of air. The difference spectrum in (A) corresponds to the spectral changes during 2-min irradiation.

CH$_3$S^{14}NO and ^{15}NO in N$_2$ diluent. Figure 3 shows the results obtained from the UV irradiation of a mixture containing CH$_3$S^{14}NO (10.9 ppm) and ^{15}NO (5.3 ppm). The occurrence of a rapid N-14 and N-15 isotopic mixing in the CH$_3$SNO and NO is clearly seen in the difference spectrum Figure 3C. Also, in this run, the initial yield of CH$_3$SSCH$_3$ was negligibly small as compared with those of the isotopically scrambled products. Thus, reaction 1 can become dominant over reaction 4. These results clearly indicate that the primary photochemical step for CH$_3$SNO is indeed analogous to that of CH$_3$ONO.[3] On the other

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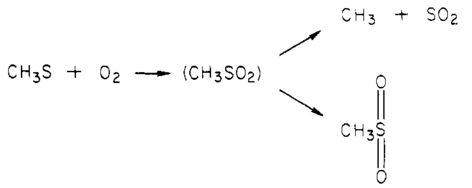
(10) M. Rao, J. A. Copek, and A. R. Knight, *Can. J. Chem.*, **45**, 1369 (1967).

(11) M. M. Ekwenchi, I. Safarik, O. P. Strausz, *Int. J. Chem. Kinet.*, **13**, 799 (1981).

hand, the ensuing radical CH_3S behaves somewhat differently from the CH_3O, since the latter radical apparently undergoes not only addition but H-transfer reactions to some extent, i.e., $CH_3O + O_2 \rightarrow CH_2O + HO_2$ and $2CH_3O \rightarrow CH_2O + CH_3OH$.[12-14]

When the diluent N_2 was replaced by air, the photolysis of CH_3SNO yielded numerous products presumably arising from the reaction of the CH_3S with O_2 and the subsequent secondary reactions. However, in these runs, the formation of CH_3SSCH_3 by reaction 3 persisted until the photolytic light intensity was adjusted properly. Figure 4 shows the results obtained from the photolysis of CH_3SNO (20 ppm) in 700 torr of air. Figure 4A corresponds to the spectral variations resulting from 2-min irradiation. Readily recognizable products included NO, with nearly 100% yield, and SO_2 and CH_2O both with about 20% yield of the CH_3SNO consumed. Spectral subtraction of appropriate amounts of these compounds from Figure 4A revealed the presence of several S-containing species among the remaining products, some of which are not as yet positively identified. The residual spectrum no. 1, Figure 4B, is that of the component which decayed during aging in the dark for about 10 min. Several prominent peaks at 980, 1204.7, 1404.9, and 3611 cm^{-1} were identified as those belonging to gaseous methanesulfonic acid, CH_3SO_3H, using a reference spectrum of this compound obtained at 80 °C in a 20-m pathlength cell with unknown sample pressure. These bands have been previously assigned by Chackalackal and Stafford to several stretching modes, i.e., S–OH, SO_2 sym, SO_2 asym, and O–H, respectively.[15] It was also noted that the CH_3SO_3H formed during irradiation can undergo nucleation to form aerosols as evidenced by the conspicuous presence of the liquid-phase spectrum of this compound[15] in the residual spectra at longer reaction times. Also, the several weak bands indicated by asterisks in Figure 4B do not belong to CH_3SO_3H. Runs with $CH_3S^{15}NO$ showed that the peaks at 1588 and 1766 cm^{-1} were due to the presence of two N-containing products possibly formed by the reactions of NO and NO_2 with a precursor of CH_3SO_3H. The residual spectrum no. 2, Figure 4C, corresponds to the stable component observed in this system. Upon ^{15}N-labeling, it exhibited isotopic shifts similar in magnitude to those observed for the two unknown compounds observed in the residual spectrum no. 1, Figure 4B. This compound was also formed as a major product in the photolysis of CH_3SNO in N_2 with added NO_2, and thus was tentatively identified as CH_3SNO_2 formed via the addition reaction $CH_3S + NO_2$.

In any case, these unidentified N-containing compounds constitute minor products in the photooxidation of CH_3SNO at low concentrations, since the N balance could be largely accounted for by NO. Therefore, it can be concluded that the reaction of CH_3S with O_2 mainly leads to the formation of CH_3SO_3H and SO_2. Notably, a few runs with varying amounts of added O_2 indicated that the relative yields of these two products were virtually independent of $[O_2]$. Thus, the reaction of CH_3S with O_2 appears to form an adduct which decays via two competitive channels leading to these S-containing products, i.e., reactions 4a and 4b. The oxidation of CH_3 formed in reaction 4a can account for the formation of CH_2O observed in equimolar yields (20%) with SO_2. The CH_3SO_2 radical formed in reaction 4b would eventually lead to CH_3SO_3H, although the detailed reaction mechanism remains uncertain. Thus, these results suggest $k_{4b}/k_{4a} \simeq 4$. It is interesting to note that the alternative H-abstraction reaction $CH_3S + O_2 \rightarrow CH_2S + HO_2$, analogous to the corresponding reaction of CH_3O,[16,17] is not compatible with the present results. Coincidentally, the SO_2 yield in the HO-initiated oxidation of CH_3SCH_3 was also approximately 20% and was independent of O_2 pressure.[1] Thus, oxidation of CH_3SCH_3 is likely to proceed via reactions 4a and 4b. Clearly, further quantitative studies of these CH_3S reactions using the photolysis of CH_3SNO are warranted.



$$CH_3S + O_2 \rightarrow (CH_3SO_2) \rightarrow CH_3 + SO_2 \quad (4a)$$

$$CH_3S + O_2 \rightarrow (CH_3SO_2) \rightarrow CH_3S(=O)_2 \quad (4b)$$

Registry No. CH_3SNO, 22223-61-6; CH_3S, 7175-75-9; NO, 10102-43-9; CH_3SSCH_3, 624-92-0; O_2, 7782-44-7.

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