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3. PHOTODEGRADATION OF CF_3I

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3.1 Introduction

CF_3I has been identified as a leading candidate for the replacement of halon fire extinguishing agents because of its high degree of effectiveness as a flame suppressant and its short tropospheric lifetime and low ozone depletion potential (Nyden, 1994). Although this compound is known to undergo rapid photolysis in the presence of sunlight, the byproducts of the photodegradation process have not been determined. It is also not known whether this agent will photolyze significantly when it is exposed to radiation from fluorescent lamps and other common sources of indoor light. This knowledge is essential to assess the stability of this agent and the risk of human exposure to it and its byproducts.

The ultraviolet absorption spectrum of CF_3I, which is displayed in Figure 1 (Fahr, 1994), exhibits a peak which is centered near 270 nm and extends beyond 350 nm. This is the so-called A band which is attributed to the superposition of electronic transitions from the ground state (X) to three low lying excited states which are designated, in order of increasing energy, $^3Q_1$, $^3Q_0$ and $^1Q_1$ (Mulliken, 1935, 1940). These states correspond to the spin orbit couplings which arise from the promotion of an electron from a lone pair orbital (5 pπ) on the iodine to an antibonding orbital (σ^*) which is localized in the region between the carbon and iodine nuclei.

Photoexcitation of the A band results in the dissociation of the C-I bond with unit quantum yield in accordance with Equation (1) (Felder, 1992; Van Veen, *et al.*, 1985).

$$CF_3I \rightarrow \begin{matrix} CF_3 + I\,(^2P_{\frac{3}{2}}) \\ CF_3 + I^*\,(^2P_{\frac{1}{2}}) \end{matrix} \qquad (1)$$

The excited spin orbit state of the iodine (I^*) correlates with the $^3Q_0$ state, whereas the ground state iodine (I) corresponds to the separated atom limit of the $^1Q_1$ and $^3Q_1$ potential energy curves. The dissociation energy of the C-I bond is about 222 kJ/mole (Felder, 1992).

The spectrum of a fluorescent lamp, obtained in this laboratory (Figure 2), indicates a measurable radiative flux out to about 310 nm. The observation that this spectrum overlaps with the absorption spectrum of CF_3I suggests that this agent should undergo appreciable photolysis when it is exposed to radiation from fluorescent lights. The objectives of this study are to determine the extent of this degradation and the nature of the compounds which are likely to be produced when CF_3I is released in an indoor environment.

3.2 Experimental

The photodegradation experiments were conducted in a quartz cell which is transparent to ultraviolet and visible radiation with wavelengths longer than 200 nm. The cell was cylindrical in shape with a diameter of 5 cm. The long axis of the cell provided an optical path length of 10 cm for the spectroscopic measurements which were made before and after irradiation of the sample. The windows of the cell were made out of CaF_2 which is transparent from about 10000 nm (1000 cm^{-1}) in the infrared all the way to about 165 nm (60606 cm^{-1}) in the ultraviolet. Independent experiments were conducted using either a 1000 watt xenon arc or a 40 watt fluorescent lamp as the photolytic source. A schematic of the experimental setup is depicted in Figure 3.

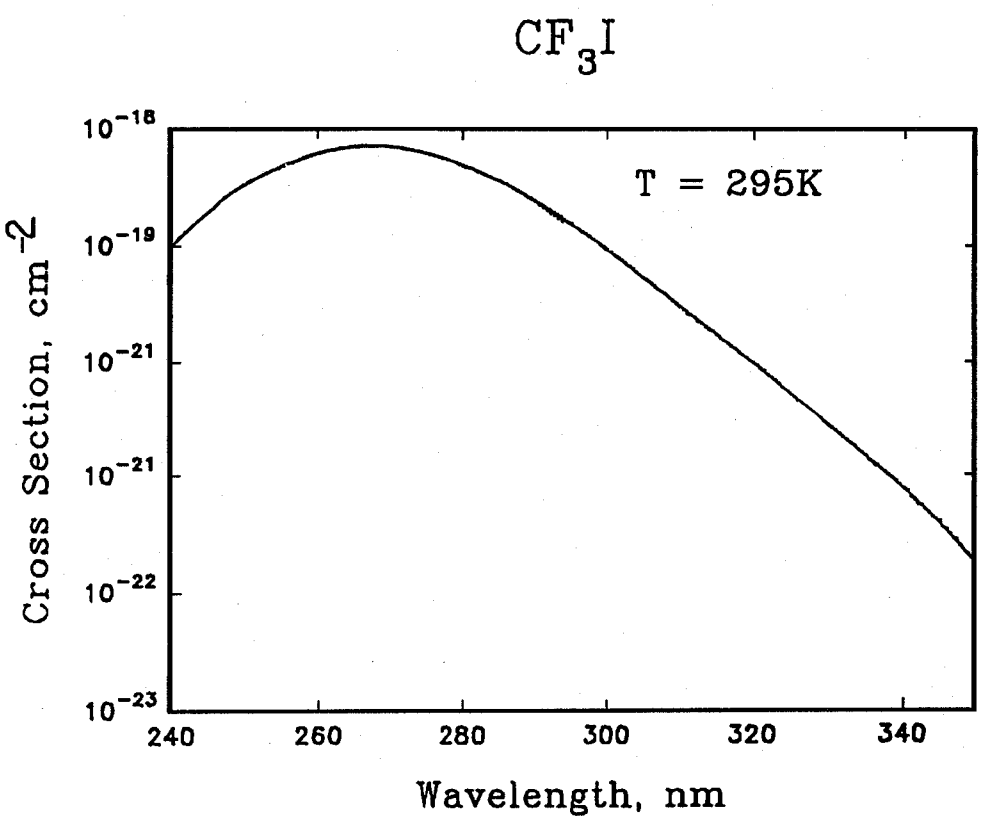

Figure 1. The UV spectrum of CF_3I at 295 K.

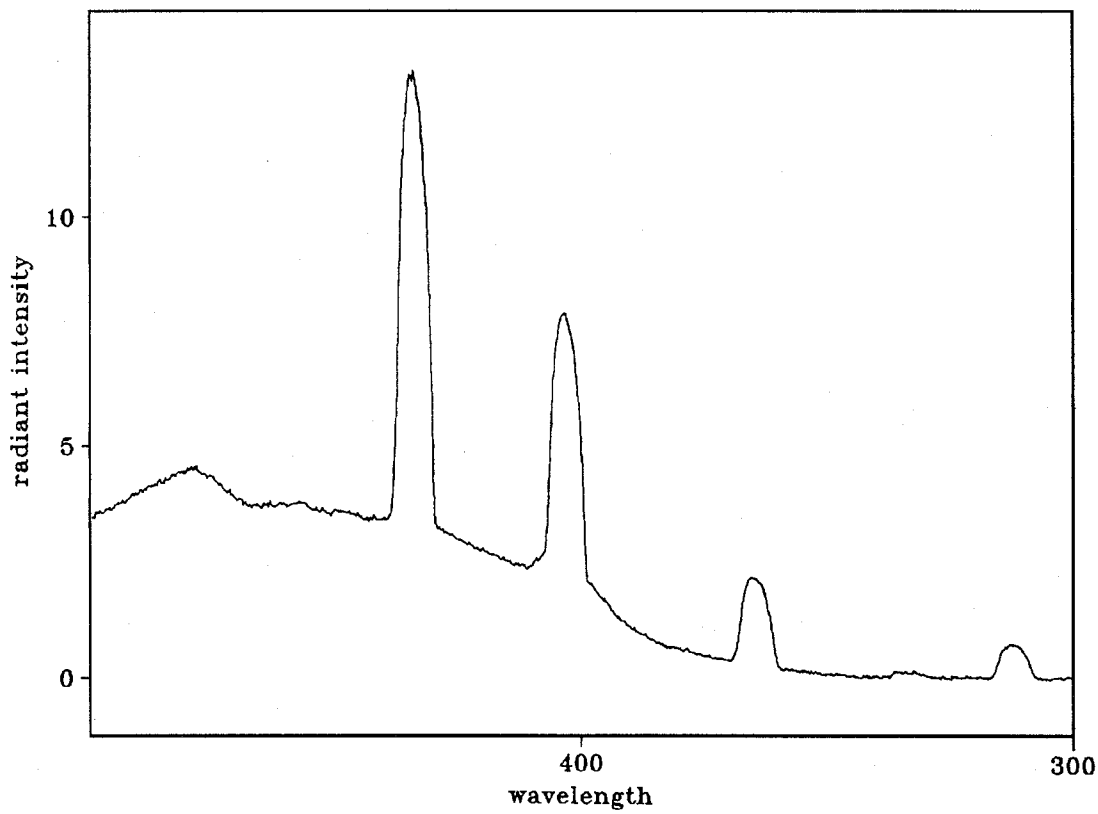

Figure 2. The near UV-VIS spectrum of a common fluorescent lamp.

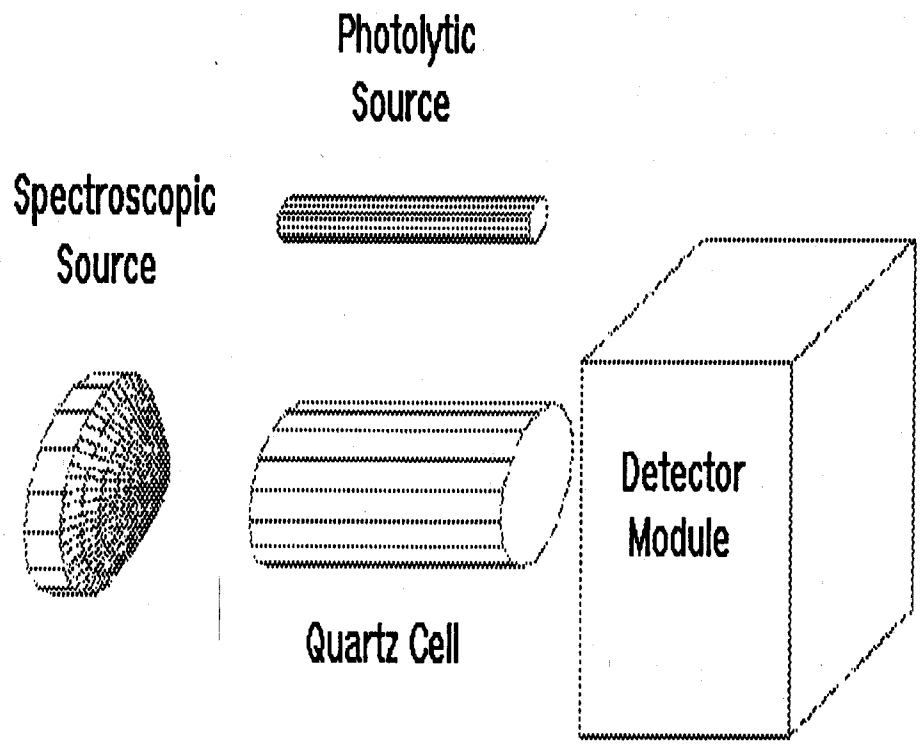

Figure 3. Schematic showing the experimental setup for the photodegradation experiments.

The CF_3I used in these experiments was obtained from PCR, Inc.[1] The stated purity was 99 % which was confirmed by GC/MS analyses performed on a Hewlett Packard 5710A gas chromatograph with an open split interface to a HP 5970 mass selective detector. Samples containing approximately 6.7 kPa of the agent, either by itself or mixed with a variety of other gases, were irradiated for 30 min with the high intensity Xe arc lamp. The experiments designed to measure the extent of degradation in the radiation field generated by the fluorescent lamp, however, were conducted over a much longer period of time (several days) because the rate of photolysis was much slower than it was with the Xe arc. The effects of adding various gases including O_2, Ar and air were also investigated.

The products of the photolysis of CF_3I were characterized by ultraviolet (UV), visible (VIS) and infrared (IR) spectroscopy. The UV/VIS spectra were measured over the range extending from about 250 nm to 850 nm using a fiber optic spectrometer manufactured by Ocean Optics, Inc. in conjunction with either a xenon flash (UV) or a tungsten halogen (VIS) source. The IR spectra, which were measured at 1 cm^{-1} resolution and signal averaged over 64 scans, were obtained using a Midac open path Fourier transform infrared (FTIR) spectrometer.

Quantitative estimates of the fraction of unreacted agent (f) were obtained from least squares fits of the spectra of the original to the spectra of the photolyzed mixtures in accordance with Equation (2).

$$f = \frac{\int_{\nu} A_o(\nu) A_p(\nu) d\nu}{\int_{\nu} A_o(\nu)^2 d\nu}, \tag{2}$$

where $A_0(\nu)$ and $A_p(\nu)$ are the measured values of the IR absorbance of the original and photolyzed mixtures at the frequency, ν, and the integration is over the band in CF_3I which extends from 2272 - 2230 cm^{-1}. The extent of degradation is the fraction of reacted agent which is given by 1-f. The uncertainties in the spectroscopic measurements were computed as the standard error of the estimated concentration using Equation (3) (Haaland, 1980).

$$\Delta f = \sqrt{\frac{\int_{\nu} [f A_o(\nu) - A_p(\nu)]^2 d\nu}{(n-1)\int_{\nu} A_o(\nu)^2 d\nu}}, \tag{3}$$

where n is the number of data points in the specified frequency range.

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[1] Certain trade names and company products are mentioned in the text or identified in an illustration in order to specify adequately the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

In addition, there were a number of sources of systematic error which might have affected the reproducibility of the experimental results. These include variations in the composition of the sample mixtures resulting from leaks and contamination of the photolytic cell, as well as variations in exposure times and in the intensity of the photolytic source which could have affected the amount of energy absorbed by the sample. The magnitudes of the resulting errors are difficult to quantify, however, past experience suggests that they can be as much as an order of magnitude larger than the uncertainties in the spectroscopic measurements calculated from Equation (3).

3.3 Results

The first set of experiments was designed to determine the extent of degradation of the pure agent in the presence of high intensity radiation from the Xe arc lamp. The expected reactions are summarized in Equation (4).

$$2CF_3I \xrightarrow{h\nu} 2CF_3\bullet + 2I\bullet \rightarrow \begin{matrix} C_2F_6 + I_2 \\ 2CF_3I \end{matrix} \tag{4}$$

In fact, a comparison of the IR spectra measured before an after the irradiation (Figure 4) indicate that the net effect of the photolysis was minimal, presumably because the reverse reaction is favored over the reactions leading to the formation of new products. This is consistent with the entries in the NIST kinetic database which indicate that the rate constant for the formation of CF_3I from CF_3 + I is about twice as fast as the corresponding value for the formation of C_2F_6 + I_2 (Mallard, 1993). The observed extent of degradation, as estimated by least squares analysis over the region between 2230 cm^{-1} - 2272 cm^{-1}, was only 5.5 % (Table 1). The formation of a small amount of C_2F_6, however, is apparent from the presence of a sharp peak centered at about 1250 cm^{-1} in the difference spectrum displayed at the top of Figure 5. This assignment may be confirmed by comparing the spectrum in Figure 5 with the reference spectrum of C_2F_6 in Figure 6 (Sadtler, 1993).

Additional measurements were performed to determine whether the presence of an inert gas would have an effect on the photolysis of CF_3I. In these experiments, a mixture consisting of 8.6 kPa of Ar and 6.7 kPa of CF_3I was exposed to the radiation from the Xe arc lamp for 30 min. The extent of degradation was about 4.1 % (Table 1); which is comparable to the value obtained in the photolysis of the pure agent. The small discrepancy in the extent of degradation (1.4 %) is indicative of the range of values obtained in repetitive experiments and is most likely due to the systematic errors delineated in the previous section. On this basis, it was concluded that the effect of the inert gas was minor.

The presence of even a small amount of O_2, however, has a dramatic effect on the photodegradation chemistry of CF_3I. This is apparent in the comparison of the UV spectra (Figure 7) of a mixture containing 6.7 kPa of CF_3I and 0.94 kPa of O_2 taken before (top) and after (bottom) irradiation for 30 min with the Xe arc lamp. A thick, white smoke formed almost immediately upon applying voltage to the arc. Shortly thereafter, a brown residue was observed to form in the crevices where the windows were joined to the cell. The IR spectra displayed in Figure 8 exhibit a significant loss of spectral intensity in the region between 2230 cm^{-1} and 2272 cm^{-1}, which correlates with depletion of the agent, and a concomitant increase in absorbance in the region between 2300 cm^{-1} and 2400 cm^{-1}, which is associated with the formation of CO_2. At the same time, the presence of I_2 was indicated by the appearance of a new feature centered at about 530 nm in the VIS spectrum which is

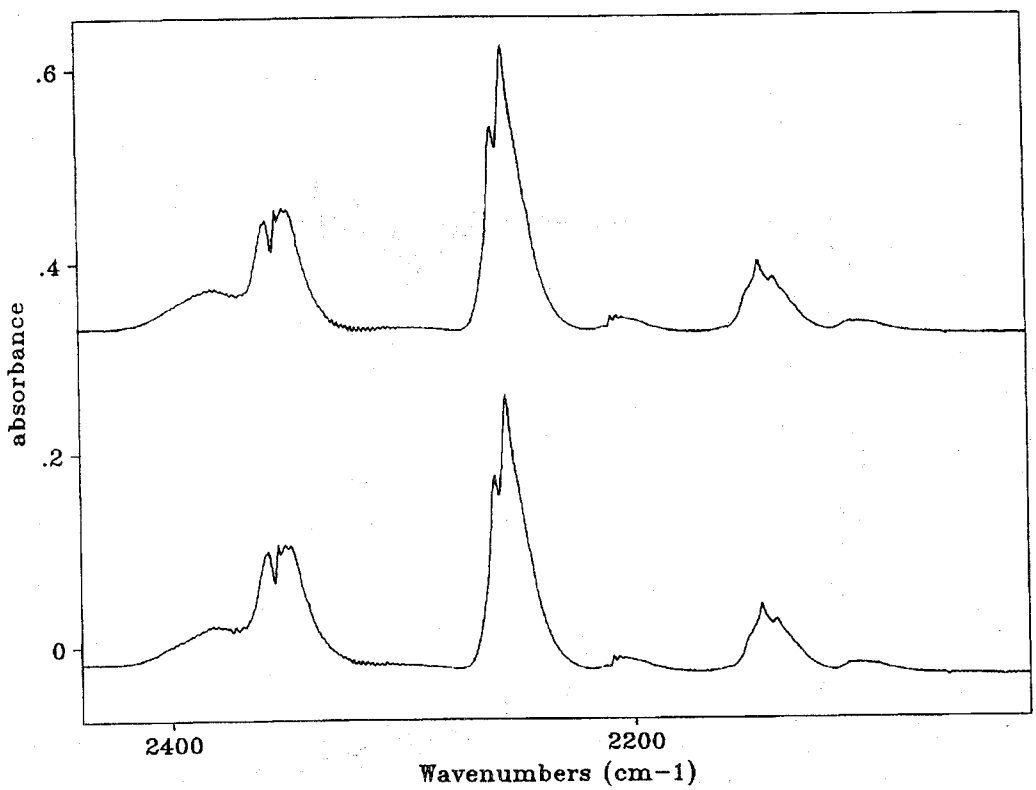

Figure 4. The IR spectra of CF_3I taken before (top) and after (bottom) irradiation for 30 min with the Xe arc lamp.

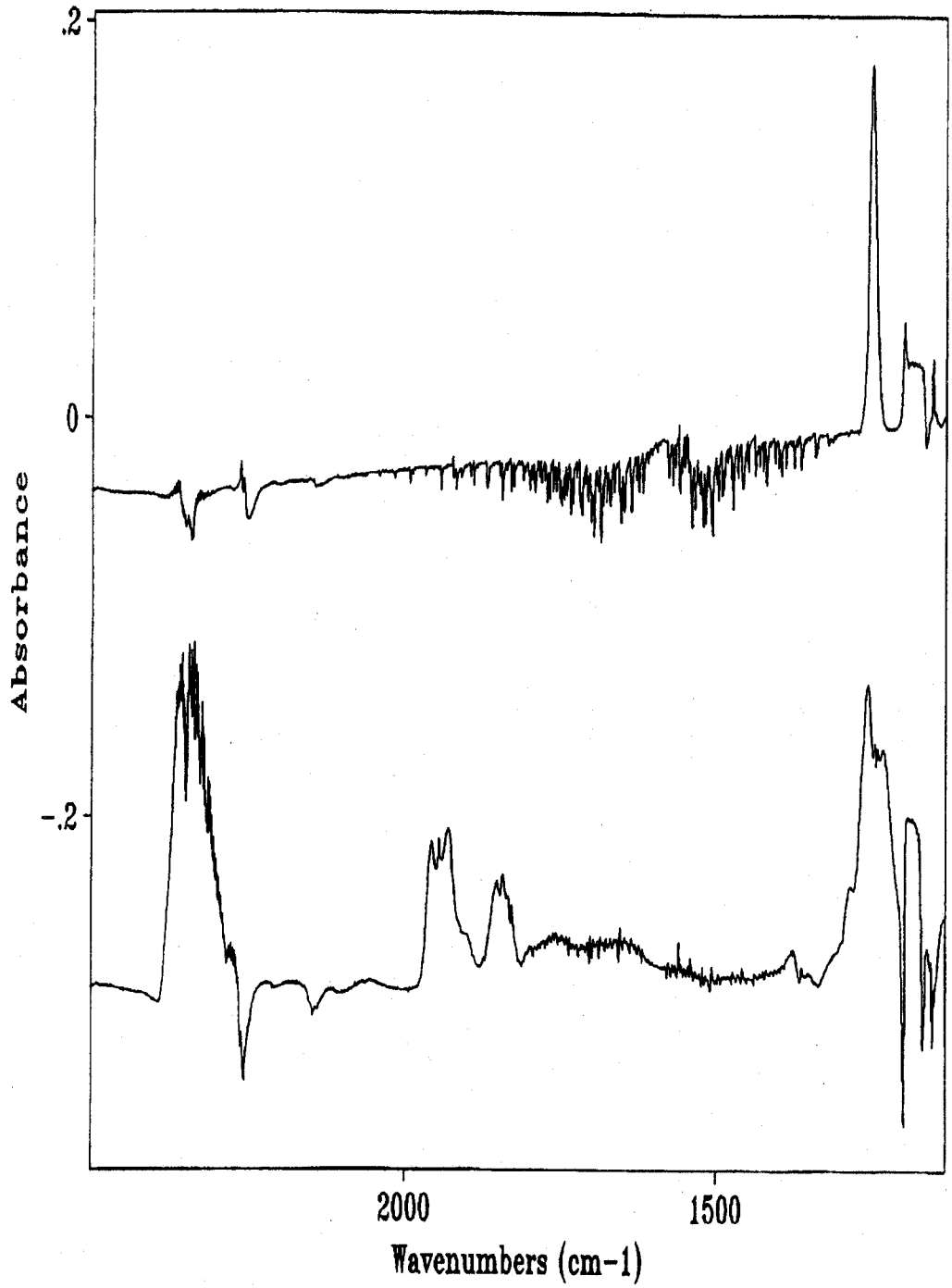

Figure 5. The differences in the IR spectra taken before and after irradiation with the Xe arc lamp of pure CF_3I (top) and a mixture of CF_3I and O_2 (bottom).

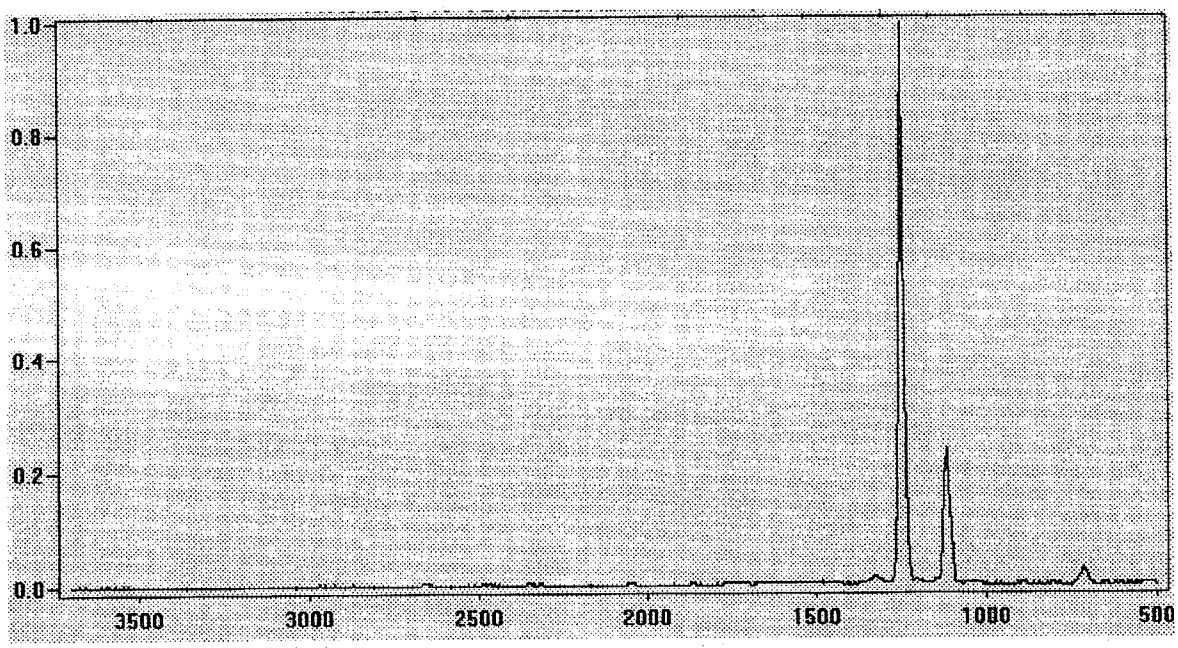

Figure 6. Library spectrum of C_2F_6.

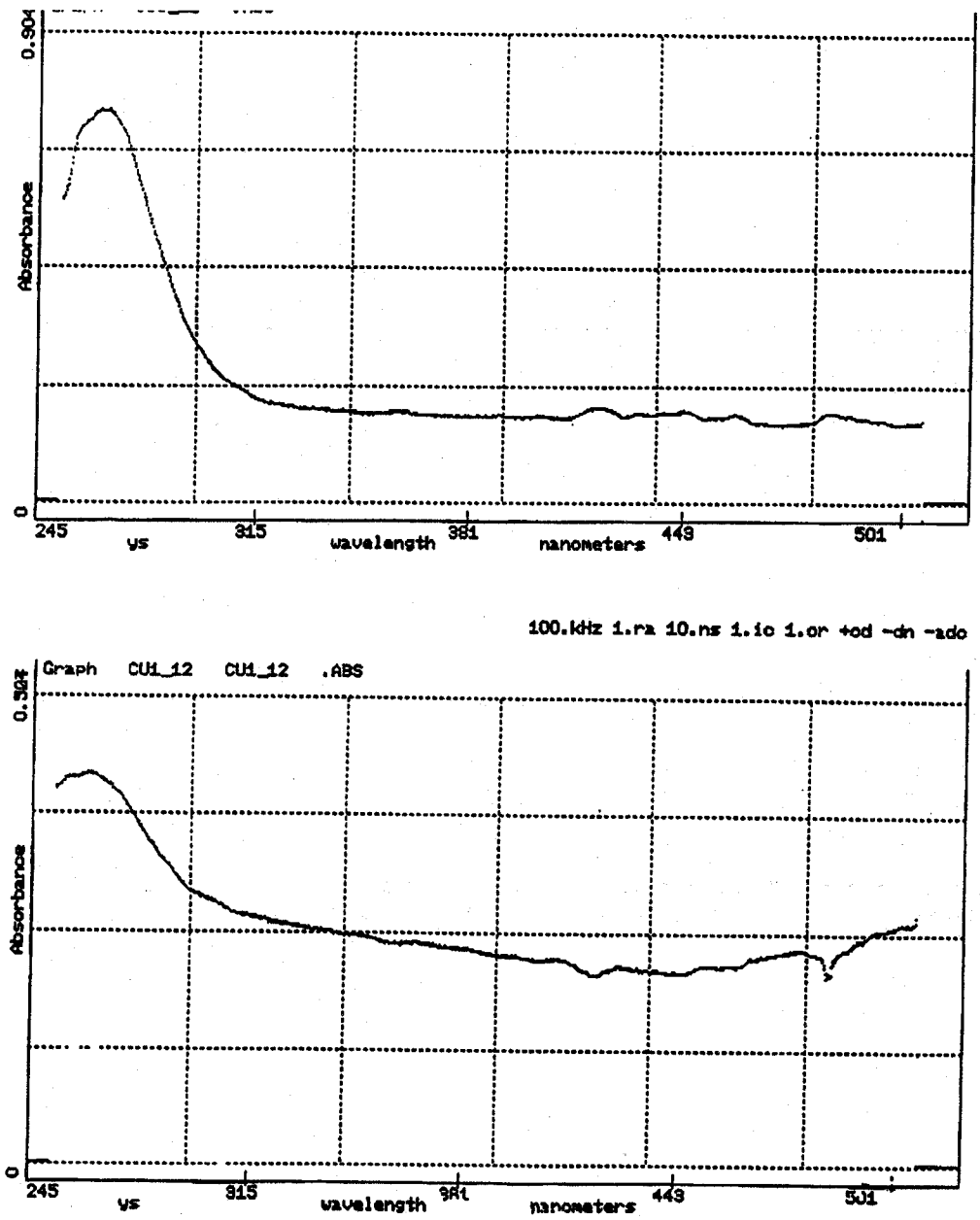

Figure 7. The UV spectra of a mixture of CF_3I and O_2 taken before (top) and after (bottom) irradiation for 30 min with the Xe arc lamp.

displayed in Figure 9. The extent of degradation, based on the change in optical density in the region between 2230 cm^{-1} and 2272 cm^{-1} in the spectra of the original and photolyzed mixtures in Figure 8, was approximately 32 %. This result implies that the stoichiometry of the photo-oxidation process is 2.3 mol of CF_3I per mole of O_2 (i.e., 6.7(.32)/0.94). A ratio of approximately 2:1 is obtained if the 5 % degradation of the agent, which would be expected to occur upon depletion of all of the available O_2, is taken into account.

The peak centered at 1950 cm^{-1} in the difference spectrum displayed at the bottom of Figure 5 is attributable to COF_2. A spectrum of this compound, which was measured in this laboratory, is displayed in Figure 10. Carbonyl fluoride is an extremely toxic compound (Sax and Lewis, 1987) which can react further with H_2O to produce HF as summarized in Equation (5).

$$COF_2 + H_2O \rightarrow CO_2 + 2HF \tag{5}$$

The smaller peak at about 1850 cm^{-1} was not definitively assigned but it is consistent with the presence of compounds possessing a carbonyl group (C=O). There was an indication in the IR spectra that ethanol, which was used to clean the cell, was present as a contaminant during some of the photolytic experiments. It is possible, therefore, that this peak is associated with a product of a photochemical reaction involving the ethanol and that is not related to the photodegradation of the agent.

A mechanism for the photo-oxidation of CF_3I was put forward in a recent paper by Clemitshaw and Sodeau who used FTIR spectroscopy to measure the quantum yield of the formation of COF_2 in the photolysis of CF_3I at 253.7 nm (Clemitshaw and Sodeau, 1995). Their mechanism, which is consistent with the reaction stoichiometry of 2 mol of CF_3I to 1 mol of O_2 which was observed in this study, is summarized in Equation (6).

$$\begin{aligned}
&CF_3I \xrightarrow{h\nu} CF_3\bullet + I\bullet \\
&CF_3\bullet + O_2 + M \rightarrow CF_3O_2\bullet + M \\
&CF_3O_2\bullet + I\bullet + M \rightarrow CF_3OOI + M \\
&CF_3OOI \rightarrow COF_2 + FOI \\
&FOI + M \rightarrow I\bullet + OF + M \\
&I\bullet + I\bullet + M \rightarrow I_2 + M \\
&OF + OF + M \rightarrow F_2 + O_2 + M
\end{aligned} \tag{6}$$

Another set of experiments were performed to determine the extent of degradation of CF_3I in the presence of radiation from a common fluorescent lamp. The photolysis of a mixture of 6.7 kPa of CF_3I and 82 kPa of O_2 was monitored for about 5 days. During this period of time, about 28 % of the CF_3I was transformed into products. The brown residue, which had been observed in the previous photo-oxidation measurements, formed after the first few hours of exposure to the lamp.

Table 1. Extent of Photodegradation Based on Eq.(2)

Conditions	$\int A_o(\nu)d\nu$	$\int A_p(\nu)d\nu$	% Degradation
Vacuum Xe arc lamp	4.55	4.32	5.5 ± 0.1
8.6 kPa Ar Xe arc lamp	5.80	5.53	4.1 ± 0.2
0.94 kPa O_2 Xe arc lamp	3.59	2.37	31.7 ± 0.3
82 kPa O_2 fluorescent lamp	3.20	2.30	28.1 ± 0.2
95 kPa air fluorescent lamp	4.33	3.34	23.2 ± 0.1

In the final experiment, the valve on the cell containing 6.7 kPa of CF_3I was opened to the atmosphere and allowed to equilibrate. The valve was closed after a few minutes and the resulting mixture of CF_3I and air was placed under the fluorescent lamp for approximately 24 hours. The idea was to simulate as closely as possible the environment inside of a building during a release of the agent. The IR spectra before (top) and after 24 hours of exposure to the radiation from the fluorescent lamp (bottom) are displayed in Figure 11. A comparison of these spectra indicate a 23 % reduction in optical density in the region between 2230 cm^{-1} and 2272 cm^{-1} which is attributable to the loss of CF_3I, and a concomitant increase in optical density in the region between 2300 cm^{-1} and 2400 cm^{-1} which is due to the formation of CO_2.

The first order rate constant obtained from the observation of a reduction of 23 % in the concentration of agent in 24 hours is 3×10^{-6} s^{-1}. Not surprisingly, this is of the same order of magnitude as the value which was calculated for the rate constant of the photolysis of CF_3I in direct sunlight (Nyden, 1994).

It is then useful to estimate the extent of degradation of CF_3I and to assess the potential hazard to occupants should an accidental discharge take place. The magnitude of the threat to public safety will vary significantly depending on the ventilation and lighting in the vicinity of the release. Thus, for example, the rupture of a cylinder of CF_3I in a well-lit storage area will pose a more serious threat than a controlled release of the same agent into a dark dry bay.

As an example of the former, consider an accidental release into 100 m^3 room which is uniformly lit with a series of 40 watt fluorescent fixtures. This is a conservative scenario as the mean photon flux incident on the agent in this room (at ground level) would be expected to be far lower than it was in the experiment where the photolytic cell was positioned only a few centimeters from the lamp. If the contents of a 5 kg storage cylinder were to be distributed uniformly throughout the space, the concentration of agent would be about 0.6 % by volume (assuming a ventilation rate of zero). The degree of degradation of the agent 5 min after the release, based on the value of the rate constant for

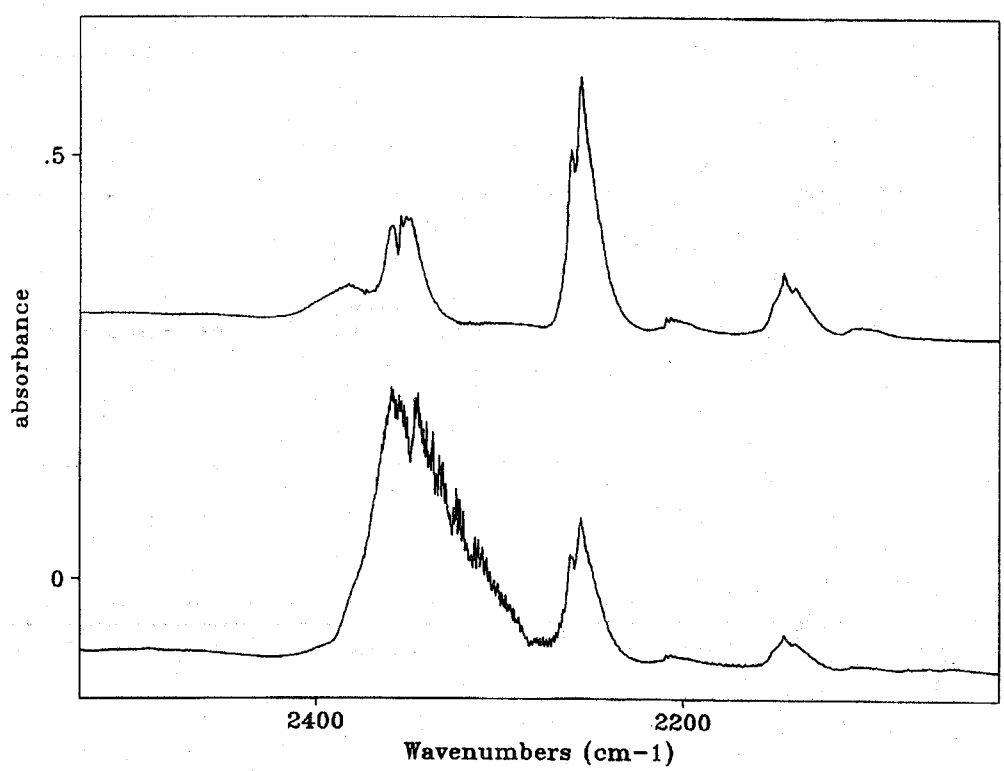

Figure 8. The IR spectra of a mixture of CF_3I and O_2 taken before (top) and after (bottom) irradiation for 30 min with the Xe arc lamp.

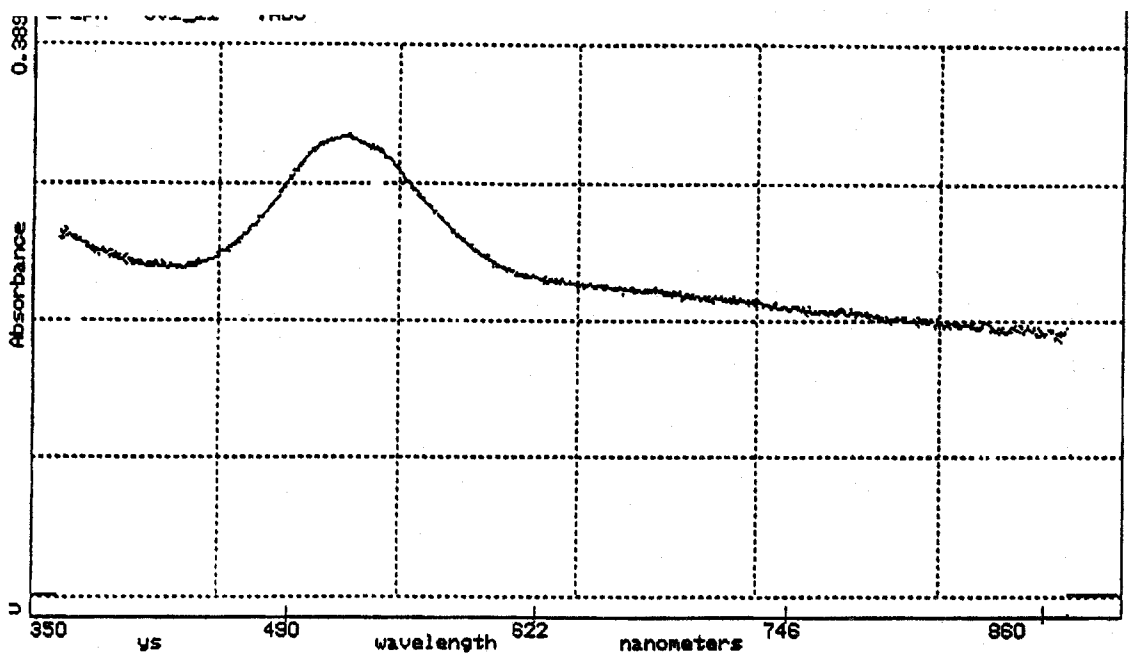

Figure 9. The VIS spectrum of a mixture of CF_3I and O_2 taken after irradiation for 30 min with the Xe arc lamp.

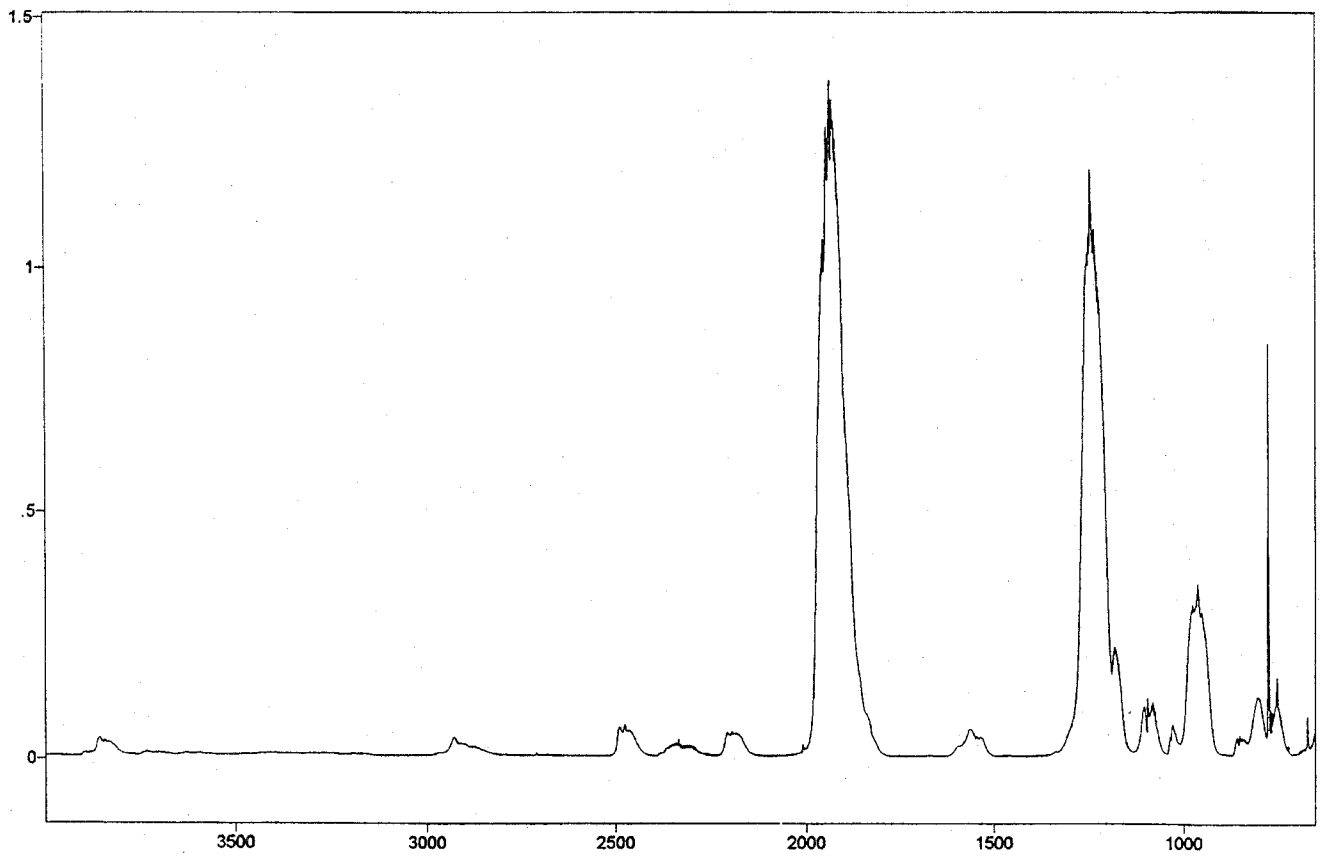

Figure 10. Spectrum of COF_2.

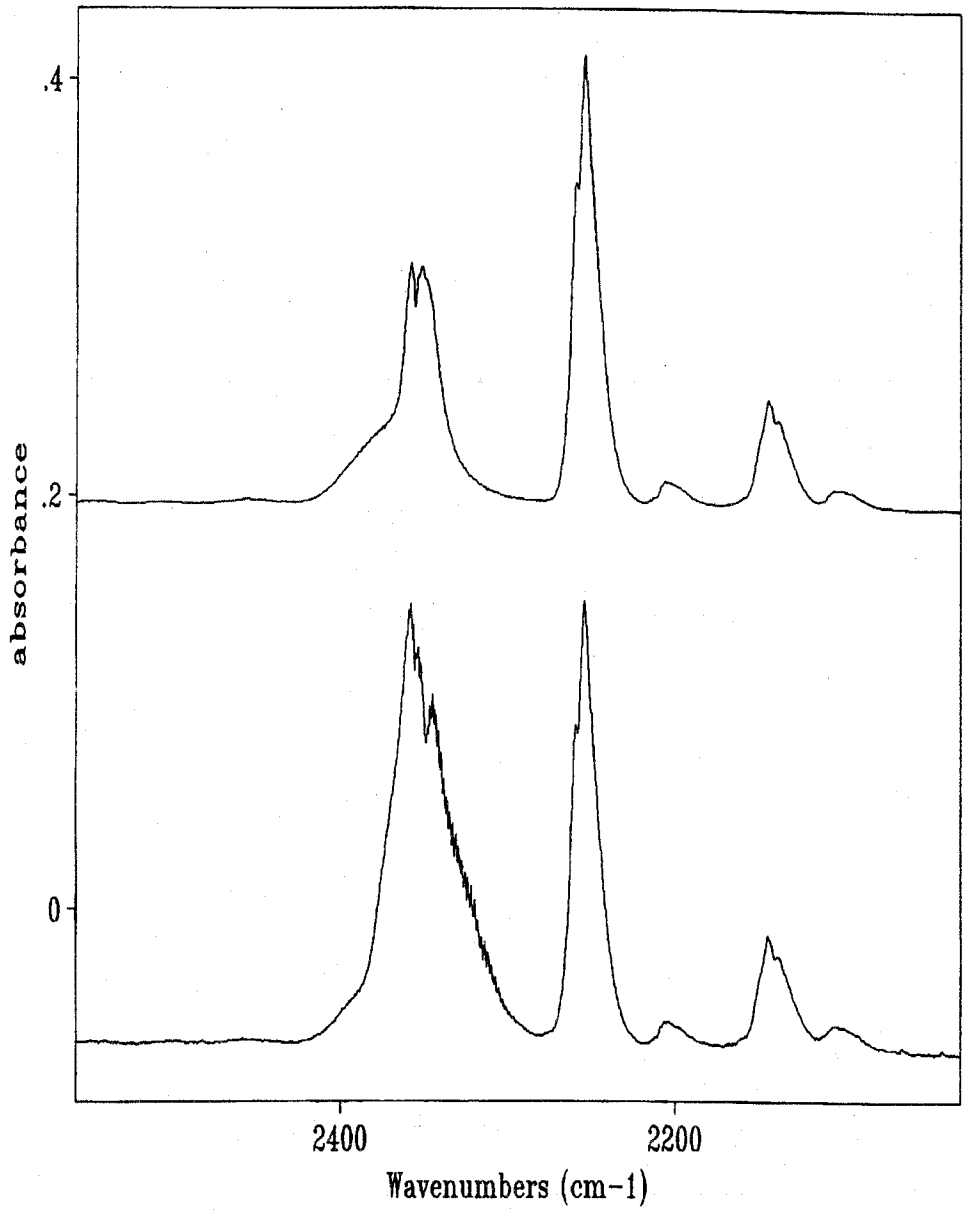

Figure 11. IR spectrum of a mixture of CF_3I and air after irradiation for 24 hours with a fluorescent lamp.

photodegradation given above, would then be only about 0.1 %. Even if all of the fluorine atoms were converted to HF (and none deposited on the walls), the concentration of HF would only be about 20 μL/L by volume. Alternatively, a COF_2 concentration of about 5 μL/L would be possible if all of the agent were to be converted to this compound (and none were to react further to form HF). Given the conservative assumptions used in this estimation, it seems unlikely that anyone who evacuated promptly would be seriously harmed by exposure to the degradation products. It would, however, be beneficial to assess the effect of exposure to low concentrations of HF on the integrity of sensitive electronic equipment in the vicinity of a release.

3.4 Conclusions

CF_3I photolyzes in the presence of radiation from common fluorescent lights with a rate constant which is comparable to that in photolysis in direct sunlight. The potential byproducts of this process include COF_2 and HF. The high level of toxicity associated with these compounds merits their inclusion when considering the impacts of accidental releases of CF_3I in well-lit, occupied spaces. However, the experiments performed as part of this study indicate that the indoor rate of photolytic decomposition is quite low, and a calculation based on conservative estimates further indicates that the resulting concentrations of the most hazardous degradation products (i.e., HF and COF_2) would also be expected to be quite low.

3.5 Acknowledgments

The GC/MS analyses were performed by Mr. Richard Harris of the Fire Science Division of NIST. The author also wishes to acknowledge the helpful advice and guidance offered Dr. Barna Laszlo and Dr. Robert Huie of the Chemical Kinetics and Thermodynamics Division of NIST.

3.6 References

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