## Short Communication

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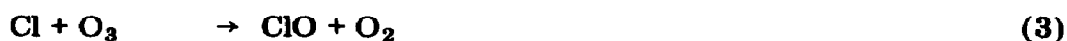## Photochemical stability of atmospheric $CF_2ClNO$ and $CFCl_2NO$

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### 1. Introduction

Chlorine atoms produced by photolysis of $CFCl_3$ and $CF_2Cl_2$ in the stratosphere cause a series of chemical reactions which includes the ozone-depleting chain reactions (3) and (4) [1].

$$CFCl_3 + h\nu \quad \rightarrow \quad CFCl_2 + Cl \tag{1}$$

$$CF_2Cl_2 + h\nu \quad \rightarrow \quad CF_2Cl + Cl \tag{2}$$

$$Cl + O_3 \quad \rightarrow \quad ClO + O_2 \tag{3}$$

$$ClO + O \quad \rightarrow \quad Cl + O_2 \tag{4}$$

The search for chain-terminating steps involving the chain centers Cl and ClO has led to investigations of coupling reactions between the chlorine cycle and the $NO_x$ cycle, and therefore the photoabsorption spectra of the chlorine nitrogen oxides ClNO [2], $ClNO_2$ [2], ClONO [3] and $ClONO_2$ [4, 5] have been studied.

The halogenated methyl radicals produced in reactions (1) and (2) mainly react with oxygen to produce the phosgene-like compounds CClFO and $CF_2O$ with the release of a second chlorine atom as either Cl or ClO [1]. Photoabsorption measurements of CClFO have been made to estimate the release rate of the third chlorine atom from $CFCl_3$ [6].

Trace amounts of the nitrogen oxides of halogen-substituted methane may be formed in the atmosphere and, if stable, they may prevent release of the chlorine from the halogenated methyl radicals [7]. The reactions between $CF_2Cl$ [8, 9] and $CFCl_2$ [9, 10] with NO have been observed in the laboratory to produce halogen-substituted nitrosomethanes by the reactions

$$CF_2Cl + NO + M \rightarrow CF_2ClNO + M \tag{5}$$

$$CFCl_2 + NO + M \rightarrow CFCl_2NO + M \tag{6}$$

The photoabsorption spectra of $CF_2ClNO$ and $CFCl_2NO$ were studied in order to estimate their photochemical stability in the atmosphere.

## 2. Experimental procedure

$CF_2ClNO$ was prepared by bubbling $ClNO$ gas (Matheson, greater than 97% purity) through a well-stirred slurry of $CF_2ClCO_2Na$ (Pfaltz and Bauer) and diglyme at 148 °C [11, 12].

$$CF_2ClCO_2Na + ClNO \rightarrow NaCl + CO_2 + CF_2ClNO \qquad (7)$$

The resultant gases were collected at −196 °C and separation was attempted by bulb-to-bulb distillations on a greaseless vacuum line. However, as observed by IR absorption, it was difficult to separate the $CF_2ClNO$ from the large amounts of unreacted $ClNO$.

A modification of this procedure was therefore used to obtain pure $CF_2ClNO$. 10 g of finely crushed $CF_2ClCO_2Na$ and approximately 0.5 atm $ClNO$ were placed in a 1 l flask fitted with a Teflon greaseless stopcock. The flask and its contents were heated in an oil bath at 145 °C for 1 - 2 days. Bulb-to-bulb distillations of the product gases were performed at dry ice-acetone slush temperature (−86 °C) to remove the more volatile $CO_2$ and NO gases, and at methanol slush temperature (−98 °C) to separate the more volatile $CF_2ClNO$ from the bulk of unreacted $ClNO$. The gases were then passed through a column of dried granular LiOH to remove traces of $CO_2$ and $ClNO$ [13] and collected at −196 °C. Final purification was achieved by redistilling at −86 °C and collecting the volatile blue fraction.

Reaction (5) has previously been used to prepare $CF_2ClNO$ from the gas phase photolysis of $ClNO$ in a mixture of $CF_2ClH$ and NO [9]. The $CF_2ClNO$ that is produced is difficult to separate from $ClNO$ [9]. To avoid this separation problem, $CF_2ClNO$ was made by photolyzing $CF_2ClBr$ (PCR Research Chemicals) in NO at 253.7 nm. Photodissociation of $CF_2ClBr$ occurs predominantly by breakage of the weakest bond, the C—Br bond [14]. Thus the separation of BrNO, instead of $ClNO$, from $CF_2ClNO$ was easier because of the larger vapor pressure difference between $CF_2ClNO$ and BrNO. This photolysis method gave smaller amounts of $CF_2ClNO$ than that formed by the decarboxylation method but the IR and UV−visible spectra of the purified $CF_2ClNO$ produced by the two techniques were consistent with each other.

$CFCl_2NO$ was prepared by reacting 16 g $CFCl_2SCl$ and 85 ml 33% $HNO_3$ with vigorous stirring for 4 h below 25 °C [15]. A flow of nitrogen gas carried the product gases through (1) a water trap to remove $ClNO$ that is formed in the reaction [15] and (2) through a $P_2O_5$ drying tube. The product was collected at −86 °C and purified on a vacuum line by bulb-to-bulb distillations at −98 °C. The middle fraction was saved and used. $CF_2ClSCl$ was made from the reaction between 90 g $CCl_3SCl$ and 100 g $HgF_2$ (Ozark Mahoning) and distilled from the reaction mixture at 97 - 98 °C [16].

The purified $CF_2ClNO$ and $CFCl_2NO$ were deep blue in color and were stored in the dark to prevent photodecomposition. Their IR spectra were in agreement with those reported in the literature [17]. The vapor pressures of $CF_2ClNO$ and $CFCl_2NO$ were measured over the temperatures $-63$ to $-111$ °C and $-23$ to $-80$ °C respectively and the respective least-squares linear expressions were obtained ($T$ in kelvins):

$$\ln p \text{ (Torr)} = -\frac{2620}{T} + 17.62$$

$$\ln p \text{ (Torr)} = -\frac{2923}{T} + 16.75$$

Extrapolation of the vapor pressure curves gave $-34.5$ °C and $16$ °C for the boiling points of $CF_2ClNO$ and $CFCl_2NO$ respectively which are in good agreement with previously reported values [8, 15]. Using the Clausius–Clapeyron equation, the heats of vaporization of $CF_2ClNO$ and $CFCl_2NO$ were calculated to be 5.2 kcal mol$^{-1}$ and 5.8 kcal mol$^{-1}$ respectively.

UV−visible measurements were made at 298 K using a Varian Cary 219 spectrophotometer at a constant spectral bandwidth of either 0.5 or 1 nm. The spectrophotometer was interfaced with an IMSAI 8080 microcomputer for data handling and storage. Cells with 10 cm path lengths were filled on a greaseless vacuum line with pressures of $CF_2ClNO$ and $CFCl_2NO$ from 0.5 to 215 Torr and from 0.3 to 400 Torr respectively. Pressures were determined with MKS Baratron gauges while temperatures were measured with an iron−constantan thermocouple.

## 3. Results and discussion

Figures 1 and 2 show the computer-averaged plots for the absorption spectra of $CF_2ClNO$ and $CFCl_2NO$. The fine structure in the visible region is analogous to that observed in absorption by $CH_3NO$ [18 - 20], $CD_3NO$ [20], $CCl_3NO$ [7] and $CF_3NO$ [7, 21] and is due to excited vibrational modes of the $n_N,\pi^*$ transition of nitrogen non-bonding electrons. The largest absorption maxima occur at 642.5 nm and 633 nm for gaseous $CF_2ClNO$ and $CFCl_2NO$ respectively and compare favorably with the reported values of 650 nm for $CF_2ClNO$ in liquid acetic acid, ethanol and dimethyl formamide and 630 nm for $CFCl_2NO$ in liquid ethanol [22].

The UV absorption spectra of $CF_2ClNO$ and $CFCl_2NO$ possess strong absorption bands together with a weak shoulder which appears between 260 and 320 nm. Similar absorptions have been reported for other geminal chloronitroso compounds [23]: 2-chloro-2-nitrosopropane; 2-chloro-2-nitrosobutane; 1-chloro-1-nitrosocyclohexane; 2,2-dimethyl-3-chloro-3-nitrosobutane. The shoulder becomes more prominent along the series $CCl_3NO$ [7], $CFCl_2NO$ (Fig. 2), $CF_2ClNO$ (Fig. 1) and $CF_3NO$ [7] and has been assigned to an $n_O,\pi^*$ transition of oxygen non-bonding electrons for $CF_3NO$ [24]. The more intense short wavelength band arises from a $\pi,\pi^*$ transition [24].
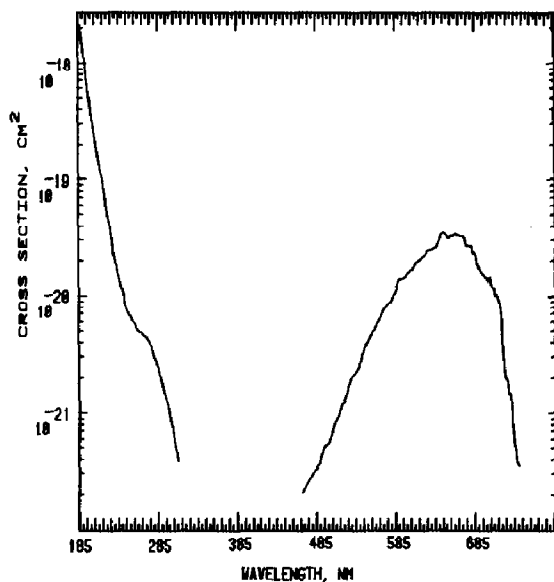
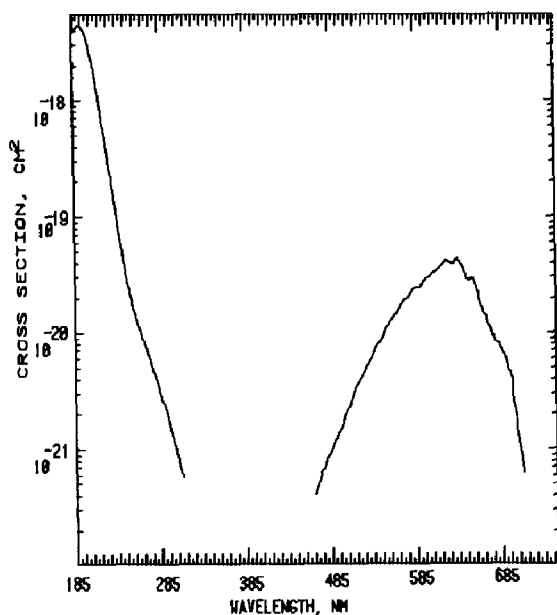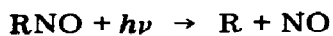Fig. 1. Photoabsorption spectrum of gaseous $CF_2ClNO$ at 298 K.



Fig. 2. Photoabsorption spectrum of gaseous $CFCl_2NO$ at 298 K.

The photolysis of *C*-nitrosoalkanes, on absorption of red light from 580 to 680 nm, causes C—N bond rupture [23], as demonstrated in the photodissociation of $CCl_3NO$ [25] and $CF_3NO$ [26].

$$RNO + h\nu \rightarrow R + NO \tag{8}$$

If the C—N bond strengths for $CF_2ClNO$ and $CFCl_2NO$ are assumed to be $31 \pm 3$ kcal $mol^{-1}$ and $32 \pm 3$ kcal $mol^{-1}$ respectively, as they are for $CF_3NO$ and $CCl_3NO$ respectively [27], reactions (8) are energetically possible below 922 nm and below 893 nm respectively*. Using these bond energies and the heats of formation for $CF_3$ [28], $CF_2Cl$ [29], $CFCl_2$ [29], $CCl_3$ [28, 30] and NO [28], the heats of formation of $CF_3NO$, $CF_2ClNO$, $CFCl_2NO$ and $CCl_3NO$ are calculated to be $-121.8 \pm 4.0$ kcal $mol^{-1}$, $-73.7 \pm 5.0$ kcal $mol^{-1}$, $-33.4 \pm 7.0$ kcal $mol^{-1}$ and $8.6 \pm 4.0$ kcal $mol^{-1}$ respectively at 298 K.)

Taking the quantum yield for photodissociation to be unity over the entire range of absorbing wavelengths, $1/e$ photodissociation lifetimes for $CF_2ClNO$ and $CFCl_2NO$ are estimated to be about 2 min and 1 min respectively from the solar flux intensities between 190 and 730 nm. The lifetimes are approximately independent of the altitude in the stratosphere because dissociation of $CF_2ClNO$ and $CFCl_2NO$ occurs mainly by absorption of the intense visible solar radiation. These short lifetimes indicate that $CF_2ClNO$ and $CFCl_2NO$ formed in the stratosphere by reactions (5) and (6) are not very stable and rapidly photodissociate by reaction (8) to regenerate the halogenated methyl free radicals.

## Acknowledgment

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*See note added in proof.

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*Note added in proof*

Johnson and Wright [31] have shown that photolysis of $CF_2ClNO$ at 147 nm occurs by C—N bond breakage to produce electronically excited $NO(B\,^2\pi)$ while photolysis at 123 nm proceeds according to $CF_2ClNO + h\nu \rightarrow CF_2(^1B_1) + Cl + NO$.

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