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# Photochemistry of chloropicrin in cryogenic matrices

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#### Abstract

The photolysis of chloropicrin (CCl<sub>3</sub>NO<sub>2</sub>) was investigated in Ar and N<sub>2</sub> cryogenic matrices. The extent of reaction was monitored using FT-IR spectroscopy. Phosgene and nitrosyl chloride were the observed photoproducts at all wavelengths investigated (220, 251, 313, 365, and 405 nm). When the photolysis was performed with 220, 251, or 313 nm light, two additional bands were also observed. These bands have been assigned to CCl<sub>3</sub>ONO. Chloropicrin was also photolyzed in the presence of O<sub>2</sub> and <sup>18</sup>O<sub>2</sub>. <sup>18</sup>O-labeled photoproducts were not detected in cryogenic matrices. © 2002 Elsevier Science B.V. All rights reserved.

#### 1. Introduction

Chloropicrin (trichloronitromethane,  $CCl_3NO_2$ ) is commonly used in agriculture as a soil fumigant, either alone or in conjunction with other fumigants such as methyl bromide. In 1990, 1610 metric tons of chloropicrin were used in California alone, particularly in the strawberry industry [1]. In the future, chloropicrin is likely to become more widely used as methyl bromide, the most widely used soil fumigant, is to be phased out by 2005 [2].

Chloropicrin has a high-vapor pressure, 23.8 torr at 298 K, and can therefore enter the troposphere, either during application or through sub-

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sequent evaporation from the soil [3,4]. Once in the troposphere, chemicals are removed by some combination of photodissociation, chemical removal (e.g., reaction with trace species such as OH, O<sub>3</sub>, or NO<sub>3</sub>), and physical removal through dry deposition or rainout [5,6]. For most volatile organic compounds, chemical removal is the most important pathway [7]. Chloropicrin is unusual in that direct photolysis appears to be the only significant atmospheric removal pathway [8–10].

The ultraviolet absorption spectrum of chloropicrin has two bands, a weak band centered at 275 nm and a strong band centered at 200 nm [11]. Only the weak band is of interest to photochemistry in the troposphere, since the actinic solar spectrum has little intensity below 295 nm. The spectrum of chloropicrin is very similar to that of

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its unchlorinated equivalent, nitromethane, so, as in nitromethane, the weak band should be a  $\pi^* \leftarrow$  n transition, involving promotion of a nonbonding electron of one of the O atoms [12].

Moilanen et al. photolyzed chloropicrin in the gas phase using a 275-W RS Sunlamp, and found that nitrosyl chloride (NOCl) and phosgene (Cl<sub>2</sub>CO) were produced when chloropicrin was photolyzed in air [13]. They observed no reaction in nitrogen. Additionally, when the reaction was performed with <sup>18</sup>O<sub>2</sub>, all of the photoproducts were found to be labeled [13]. Based on these results, they proposed that chloropicrin reacts with oxygen to form a trioxalone intermediate that then dissociates to produce NOCl and Cl<sub>2</sub>CO. They further suggested that O<sub>2</sub> catalyzes this process [13].



More recently, Carter et al. [10] have studied the reaction of chloropicrin with various organic pollutants, in order to determine if it is a significant generator of tropospheric ozone. They found that the quantum yield for production of NO<sub>x</sub> and Cl atoms from chloropicrin in the 300–360 nm region was  $87 \pm 13\%$  [10]. They used their data to test kinetic models of several mechanisms for chloropicrin photolysis, and found that their results were more consistent with the first step of the photodissociation being cleavage of the C–N bond [10]:

## $CCl_3NO_2 \rightarrow CCl_3 + NO_2$

The mechanism suggested by Carter et al. would be consistent with the primary dissociation pathway of nitromethane photolyzed via the  $\pi^* \leftarrow n$ transition. The major photodissociation pathway for nitromethane is also cleavage of the C–N bond, although two minor competing channels, molecular elimination and oxygen atom elimination, have been observed [14–16]:  $CH_3NO_2 \rightarrow CH_2O + HNO$ 

$$CH_3NO_2 \rightarrow CH_3NO + O$$

Since, the spectroscopy of chloropicrin is comparable to that of nitromethane, it is reasonable to assume that its photochemistry may be comparable as well.

This study focuses on the photodissociation of chloropicrin, with and without oxygen present. In cryogenic matrices, the primary photoproducts can be detected, since these primary photoproducts will not be able to travel and undergo secondary reactions. In addition, intermediates, which are too short lived to be detected in the gas phase, may be trapped in cryogenic matrices. In particular, we hoped to be able to trap the trioxolane intermediate suggested by Moilanen et al. [13].

## 2. Experimental

Chloropicrin (98%) was obtained from Fluka Chemika, and purified by several freeze-pumpthaw cycles. The primary contaminant is believed to be dissolved Cl<sub>2</sub>, due to photodissociation of chloropicrin [11]. This Cl<sub>2</sub> appears as a yellow tint that disappears after freezing and pumping out the sample. O2 (99.99%) was obtained from Matheson Gas Products, and <sup>18</sup>O<sub>2</sub> (99.2% <sup>18</sup>O) was obtained from Isotech Incorporated. Mixtures of chloropicrin/Ar (1/200), chloropicrin/N<sub>2</sub> (1/200), chloropicrin/O<sub>2</sub>/Ar (1/2/200), and chloropicrin/ $^{18}$ O<sub>2</sub>/Ar (1/2/200 and 1/50/150) were deposited at a flow rate of 1.0-2.0 mmol/h onto a cold CsI window. The window was cooled to 11 K by an Air Products two stage closed cycle helium refrigerator (APD Cryogenics HC-2). Deposition and photolysis were carried out at 11 K. A medium pressure mercury arc lamp (Bausch and Lomb 200 W Hg or Oriel 66033 200 W Hg) was used as the photolysis source. Assorted Oriel and Corning filters were used to limit the lamp photolysis wavelengths. Infrared spectra were recorded from 400 to 4000 cm<sup>-1</sup> at 11 K by an FT-IR spectrometer (Mattson Nova Cygni II) at a resolution of  $0.50 \text{ cm}^{-1}$  (200 scans) with a frequency accuracy of  $\pm 0.1 \, \text{cm}^{-1}$ .

## 3. Results

Chloropicrin has a moderately complex infrared spectrum, as shown in Fig. 1. In a N<sub>2</sub> matrix, its ten strongest bands, in order of decreasing integrated area, are observed at 1619, 903, 865, 1314, 674, 712, 1354, 845, 3726, and 2917 cm<sup>-1</sup>.

Chloropicrin/Ar was photolyzed at several different wavelengths. Interference filters were used at 220 (Oriel 53320), 251 (53340), 313 (Oriel 56410), 365(Oriel 56430), and 405 nm (Oriel 56440). Additionally, a long-pass filter ( $\lambda \ge 300$  nm, Corning) was used. Table 1 summarizes the observed bands. In all cases, the same photoproducts were detected: phosgene ( $Cl_2CO$ ), which has major bands at 1837 and 849 cm<sup>-1</sup> and minor bands at 1673 and  $1020 \text{ cm}^{-1}$  [17], and NOCl, which has major bands at 1805 and 577 cm<sup>-1</sup> [18]. A typical difference spectrum is shown in Fig. 2. In this spectrum, the negative peaks are due to the loss of chloropicrin and the positive peaks are due to photolysis products. The strong band at 1828 cm<sup>-1</sup> is due to the overlap of the bands of phosgene and NOCl. Production of phosgene and NOCl, and consumption of chloropicrin, follow nearly first order kinetics, as shown in Fig. 3. However, at very short times, there is a deviation from first order kinetics, which suggests that phosgene and NOCl are not the primary photoproducts of this reaction.



Fig. 1. Matrix isolation spectrum of chloropicrin in N<sub>2</sub> (1:200).

Table 1						
Summary	of	Absorbance	bands	for	chloropicrin/Ar	matrix
following	pho	otolysis				

Wavenumber (cm <sup>-1</sup> )	Identification
577	NOCl
674	Chloropicrin
711	Chloropicrin
772	Cl <sub>3</sub> CONO
843	Chloropicrin
849	Phosgene
861	Chloropicrin
903	Chloropicrin
1020	Phosgene
1088	Cl <sub>3</sub> CONO
1310	Chloropicrin
1352	Chloropicrin
1614, 1617	Chloropicrin
1673, 1685	Phosgene
1805, 1820	NOCl
1827, 1837	Phosgene
2142	CO
2644	Chloropicrin
2906	Chloropicrin



Fig. 2. Difference spectrum of chloropicrin/Ar matrix following photolysis for 150 min at 313 nm.

An intermediate, which absorbs at 1088 and 772 cm<sup>-1</sup>, was also detected. The kinetic behavior of the 1088 cm<sup>-1</sup> band is shown in Fig. 4. The band at 1088 cm<sup>-1</sup> is in the spectral region typical for a C–O or N–O stretch and the band at 772 cm<sup>-1</sup> is



Fig. 3. Kinetic behavior of chloropicrin, phosgene, and NOCI following 313 nm photolysis of cryogenic matrix. Closed circles are chloropicrin, closed diamonds are phosgene, and open squares are NOCI. The lines are provided to guide the eye.



Fig. 4. Kinetic behavior of cryogenic matrix intermediate at  $1088 \text{ cm}^{-1}$  when photolyzed at 313 nm. The line is given to guide the eye.

consistent with a C–Cl stretch. Other strong bands of the intermediate species could easily be obscured by chloropicrin or other product bands, and could not be isolated. This intermediate was detected when chloropicrin was photolyzed with 220, 251 and 313 nm light. Somewhat less of the intermediate was observed at shorter wavelengths, which may indicate that the intermediate is also photoactive. The intermediate was not detected when the photolysis was performed at 365, 405 nm, or with the long-pass filter. However, with these filters, photodissociation was less efficient, either because less UV was absorbed by chloropicrin (at 365 or 405 nm, where chloropicrin does not absorb strongly) or because more UV was absorbed by the filter (with the long-pass filter).

Chloropicrin/O<sub>2</sub>/Ar and chloropicrin/<sup>18</sup>O<sub>2</sub>/Ar were photolyzed using the 313 nm filter and the long-pass filter. The infrared bands observed were identical to those observed in the chloropicrin/Ar matrices, including the intermediate at 1088 cm<sup>-1</sup>. Even when the concentration of <sup>18</sup>O<sub>2</sub> was extremely high (chloropicrin/18O2/Ar:1/50/150), no labeled product bands were observed. At very high  $^{18}O_2$  concentrations, the intermediate was not observed. However, this is probably because, in that matrix, all of the bands were broadened so that the intermediate band, which is very small, was washed out. The kinetics of the chloropicrin/ $O_2$ /Ar matrices are consistent with the kinetics of the chloropicrin/Ar matrices, given the limits of uncertainty. Based on these experiments, there is no experimental evidence of a trioxolane intermediate, as suggested by Moilanen et al. [13], in these cryogenic matrices.

In the chloropicrin/N<sub>2</sub> matrix, the same bands were observed as in chloropicrin/Ar, although, as expected, they are somewhat shifted in frequency when compared to the chloropicrin/Ar matrices. For example, the major band of phosgene is observed at 1847 cm<sup>-1</sup> rather than 1840 cm<sup>-1</sup>, and the intermediate bands are observed at 766 and 1097 cm<sup>-1</sup>. It was thought that the chloropicrin/ N<sub>2</sub> matrix might allow for better observation of the intermediate bands by stabilizing vibrationally excited species. However, the increase in the absorbance of the intermediate was no more than 10%, which is within the uncertainty of experiments performed with lamp/filter combinations. The kinetics were also the same as in the chloropicrin/Ar matrices, within this uncertainty.

### 4. Discussion

It is clear that there is some mechanism by which chloropicrin can photolyze in the absence of oxygen, contrary to the observations reported by Moilanen et al. [13]. Chemistry could occur via a one-step molecular elimination process, as in nitromethane [14–16], which in the case of chloropicrin would directly give the final products:

# $CCl_3NO_2 \rightarrow Cl_2CO + NOCl$

However, such a one-step process would not account for the observed intermediates in the cryogenic matrices. Thus, such a one-step mechanism cannot account for all of the photolyzed chloropicrin.

Another likely mechanism for chloropicrin photolysis is cleavage of the C–N bond, as suggested by Carter et al. [10].

 $CCl_3NO_2 \rightarrow CCl_3 + NO_2$ 

The fragments can then react to produce phosgene and NOCl.

 $CCl_3 + NO_2 \rightarrow Cl_2CO + NOCl$ 

It is reasonable that the NO<sub>2</sub> and CCl<sub>3</sub> radicals themselves would not be observed, since their vibrational bands overlap with strong bands in chloropicrin. The strongest vibrational band of CCl<sub>3</sub> is at 898 cm<sup>-1</sup> [21], in a region where chloropicrin has several very strong bands. Two vibrational bands of NO<sub>2</sub>, at 2900 and 1610 cm<sup>-1</sup> [22,23], are similarly overlapped with the nitrogroup bands of chloropicrin at 2917 and 1619 cm<sup>-1</sup>. The other vibrational band, at 749 cm<sup>-1</sup> [22,23], is weaker than the other two, and is in the congested 700–900 cm<sup>-1</sup> region.

The intermediate observed in the cryogenic matrices cannot be absolutely identified, but the two observed bands are consistent with a C–Cl stretch and either a C–O or N–O stretch. Based on these two bands, it is likely that the intermediate is CCl<sub>3</sub>ONO. This could be produced as a primary photoproduct through rearrangement, but is more likely produced following the cleavage of the C–N bond to produce CCl<sub>3</sub> and NO<sub>2</sub>.

 $CCl_3NO_2 \rightarrow CCl_3 + NO_2$ 

$$CCl_3 + NO_2 \rightarrow CCl_3ONO$$

In the matrix, these two radicals would be trapped close to one another, and could rearrange slightly in order to form CCl<sub>3</sub>ONO. This explains why no reaction with oxygen was observed in the matrix, even though there was a reaction with oxygen in the gas phase. The CCl<sub>3</sub>ONO would then either thermally dissociate or photolyze to give either the same radicals or phosgene and NOCl. It is likely that the intermediate is photochemically active, because it was not stabilized by the N<sub>2</sub> matrix and its detection was strongly dependent on the photolysis wavelength. This mechanism is consistent with the photolysis of nitromethane in Ar matrices [19,20], where nitromethane initially photolyzes to produce NO<sub>2</sub> and CH<sub>3</sub>, which then undergo cage recombination to produce CH<sub>3</sub>ONO. CH<sub>3</sub>ONO then photolyzes to produce HNO and H<sub>2</sub>CO [19,20].

In order to further support the identity of this intermediate, ab initio calculations were performed using GAUSSIAN 98 at B3LYP/6-31g [24]. The predicted vibrational frequencies and infrared intensities are consistent with the observed intermediate spectrum and are summarized in Table 2. Only five bands, at 617, 691, 791, 1096, and 1829 cm<sup>-1</sup>, are predicted to have significant infrared intensity and to be in the detection region of our instrument. Two of these bands, at 791 and 1096 cm<sup>-1</sup>, are consistent with the observed intermediate bands at 772 and 1088 cm<sup>-1</sup>. The band at 1096 cm<sup>-1</sup> is predicted to be the strongest infrared band. A band at 1829 cm<sup>-1</sup> is predicted to have nearly the same infrared intensity as the 1096 cm<sup>-1</sup> band, but would overlap with and be

Table 2

Calculated ab initio (B3LYP/6-31g) [24] spectrum of Cl<sub>3</sub>CONO

Frequency (cm <sup>-1</sup> )	Intensity (arb. units <sup>a</sup> )	
57.09	0.003	
111.06	0.001	
116.22	0.005	
216.00	0.032	
223.80	0.001	
111.07	0.070	
328.15	0.084	
371.89	0.008	
398.72	0.034	
567.83	0.032	
617.21	0.321	
691.04	0.636	
791.92	0.674	
1096.08	1.000	
1828.76	0.910	

<sup>a</sup> Intensities normalized to intensity of 1096 cm<sup>-1</sup> band.

obscured by strong phosgene bands at 1827 and 1837 cm<sup>-1</sup>. Similarly, the 691 cm<sup>-1</sup> band is predicted to have nearly the same intensity as the 791 cm<sup>-1</sup> band, but is very close to a strong chloropicrin band at 674 cm<sup>-1</sup> and would likely not be observed. The fifth predicted band, at 617 cm<sup>-1</sup>, is not observed, but is predicted to be the weakest of these five bands with less than one-third the intensity of the 1096 cm<sup>-1</sup> band. Given the small observed signal in the most intense feature of the intermediate spectrum, our failure to observe this band is not sufficient to disprove our assignment of the intermediate as Cl<sub>3</sub>CONO.

## 5. Conclusion

Chloropicrin undergoes photolysis to produce phosgene and nitrosyl chloride in cryogenic matrices. These products are observed at a wide range of photolysis wavelengths, and whether or not oxygen is present. Furthermore, when  ${}^{18}O_2$  is present,  ${}^{18}O$ -labeled photoproducts are not observed in cryogenic matrices.

Based on these observations, the following mechanism is proposed. Chloropicrin initially undergoes cleavage of the C–N bond to produce  $NO_2$  and  $CCl_3$  radicals. In the matrix, these radicals are kept close to each other, and can recombine to form  $Cl_3CONO$ , which itself undergoes photolysis.  $CCl_3$  and  $NO_2$  eventually react with each other to form phosgene and NOCl. It is also possible that some fraction of the chloropicrin photolyzes to produce phosgene and NOCl directly.

This mechanism would be consistent with many, but not all, of the previous gas phase experiments [10,11,13]. In particular, we have observed that chloropicrin will dissociate in the absence of oxygen in cryogenic matrices, contrary to what was reported by Moilanen et al. [13]. Further, gas-phase studies will be required to completely explain these results and predict the atmospheric behavior of chloropicrin.

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