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Photolysis of chloropicrin by simulated sunlight

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HIGHLIGHTS

- Chloropicrin is photolyzed to produce phosgene and nitrosyl chloride.
- Oxygen changes the reaction mechanism of chloropicrin's photoproducts.
- The environmental half-life of chloropicrin is 5.9 ± 1.5 h.

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ABSTRACT

The rate of chloropicrin removal and product formation when chloropicrin is exposed to simulated sunlight were determined in the absence and presence of oxygen. We observed phosgene and nitrosyl chloride as the products, which are produced after chloropicrin undergoes cleavage of the C–N bond to form carbon trichloride and nitrogen dioxide radicals. The observed rates are not strongly dependent on chloropicrin pressure but do vary with oxygen pressure, and the presence of oxygen clearly changed the mechanism of the reaction of the radical products. Under near-environmental pressures of oxygen, we estimate the environmental half-life of chloropicrin at 5.9 ± 1.5 h.

1. Introduction

Chloropicrin (CCl_3NO_2, trichloronitromethane) is a common broad spectrum pesticide, which is applied to fields as a pure liquid or in conjunction with methyl bromide to sterilize the soil before planting (Ware, 1992). In 2010, 2.6 million kg of chloropicrin were applied in California alone, which was a 12% increase over the prior five years (CA Dept. of Pesticide Regulation, 2010). The California value is useful here, as that state has the most stringent reporting requirements and publishes the total amount of each pesticide applied each year (typically with a 3–4 year lag in publishing the data). The U.S. Environmental Protection Agency, on the other hand, does not publish comparable information annually, and tends to only publish comparable information for a single type of crop. The most recent estimates available are that 2-4 million kg of chloropicrin were applied in the United States in 2001 (Kiely et al., 2004). In the European Union, agricultural use of chloropicrin has been phased out, and as of 2012, it is no longer in use (Hillocks, 2012).

Chloropicrin has a relatively high vapor pressure, 18 torr at 20 °C, (Ware, 1992) and can be found in the ambient atmosphere (Baker et al. 1996). Chloropicrin is also highly photosensitive, and photolysis provides the major atmospheric removal pathway. (Carter et al. 1997; Wade et al. 2006) The rate of removal of chloropicrin from the atmosphere, however, has not been well-established. In 1978, Allston et al. estimated a lifetime of ~4.8 h at the earth's surface, based on the absorbance spectrum, solar flux, and assuming unity quantum yield. That same year, Moilanen et al. measured a lifetime of 20 days in a smog chamber. However, these results are not consistent with later studies, as Moilanen et al. (1978) also observed no reaction when chloropicrin was photolyzed in the absence of oxygen, while several other studies (including this work) have observed that chloropicrin alone will undergo photolysis to form CCl_3 and NO_2 (Carter et al. 1997; Wade

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et al. 2006). These radicals then react together to form the final, stable products: Cl_2CO (phosgene) and NOCl. Wade et al. observed the infrared emission a few microseconds after photolysis, and were able to demonstrate that the immediate products of this photolysis, without oxygen present, were:

$$CCl_3NO_2 \rightarrow CCl_3 + NO_2$$

$$CCl_3 + NO_2 \rightarrow Cl_2CO + NOCl$$

In 1997, Carter et al. studied the reactions of chloropicrin with other organic pollutants, and estimated the environmental half-life of chloropicrin to be ~18 h, with a quantum yield of 87 ± 13%. Most recently, in 2010, Vera et al. observed chloropicrin photolysis under atmospheric conditions in the outdoor European Photoreactor, and measured its lifetime at 5.4–7.1 h, equivalent to a half-life of 3.8–4.9 h, as well as an effective quantum yield of 94 ± 8%. They reported an observed rate constant of (3.9–5.1) × 10^{-5} 1/sec. Interestingly, this most recent result is quite close to Allston's original estimate (Allston et al. 1978). Carter et al.'s and Vera et al.'s observations were best modeled assuming that chloropicrin photolysis proceeded via cleavage of the C–N bond, consistent with the observations of Wade et al.

Cl_2CO and NOCl are secondary products, it is possible that the rate constants of product formation differ from the rate constants for chloropicrin photolysis, and that their production rates are sensitive to the presence of oxygen even if the removal rate of chloropicrin is not. We have directly measured the rate constants for chloropicrin photolysis at a range of pressures of chloropicrin and oxygen, to determine whether the process is pressure-sensitive and whether the presence of oxygen changes either the rate of photolysis of chloropicrin or the rate of production of final products.

2. Methods

A 5-cm gas cell (McCarthy Scientific) was evacuated and then filled with various pressures of chloropicrin vapor (Aldrich, 98+%) and oxygen gas (Matheson, 99.997%). In some experiments, nitrogen gas (Matheson, 99.98%) was also used. Before use, the chloropicrin was purified by at least three freeze–pump–thaw cycles to remove any dissolved gas. The gas cell was exposed to light from a Newport Model 96,000 150 W solar simulator with a 1.5 × Air Mass filter to match the lamp spectrum to the solar spectrum at the earth's surface at mid-latitudes (with a solar zenith angle of 48.2°). The solar simulator's intensity was calibrated using a Molectron Power Meter and found to be 0.18 ± 0.01 W/cm^2 or ~1.8× the solar radiation one would expect on a cloudless day at the earth's surface. The reaction mixture was monitored before and during irradiation via FTIR (Nicolet Avatar). Spectra were collected at 8 cm^{-1} resolution, every 10–60 min. Higher resolutions did not result in better peak resolution, as the P and R band structures of some observed peaks naturally overlap, but did lead to noisier spectra and more uncertainty in the extracted rate constants. For each set of pressures, experiments were repeated at least two times.

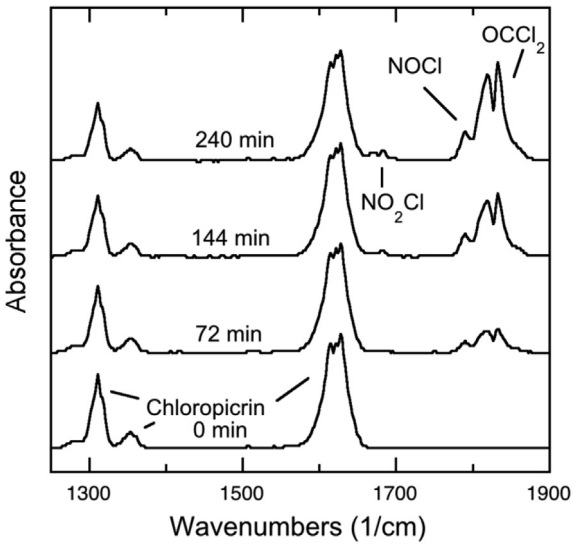

Fig. 1. Spectra of chloropicrin undergoing solar simulator photolysis in the absence of oxygen. The initial pressure of chloropicrin is 3.0 ± 0.1 torr. Spectral resolution is 8 cm^{-1}. Higher FTIR resolution did not improve peak separation due to underlying rotational structure.

3. Results

When chloropicrin is photolyzed alone, we observe the production of phosgene and NOCl, as expected. Typical time-dependent spectra are shown in Fig. 1. We also observe NO_2Cl as a minor product, which provides further support for the contention that the mechanism proceeds via cleavage of the C–N bond. We determined the rate constant (k) of the observed reaction by fitting the infrared absorbance (Abs) to the following pseudo-first order equations for chloropicrin

$$Abs = C_1 e^{-kt}$$

and for the products phosgene and NOCl.

$$Abs = C_2\left(1 - e^{-kt}\right)$$

where t is the time, and C_1 and C_2 are conversion terms that convert the fraction reacted or formed into absorbance data. Individual rate constants were determined for each product. In fact, because phosgene and NOCl are secondary photo-products, produced by reaction of the primary photoproducts CCl_3 and NO_2, they should not quite follow first order kinetics. However, at the times observed, we do observe pseudo-first order kinetics, as shown in Fig. 2.

The rate constants for chloropicrin photolysis and production of phosgene, nitrosyl chloride (NOCl), and NO_2Cl were measured as a function of chloropicrin pressure, with the pressure varied from 1 to 18.5 torr (where 18.5 torr was the vapor pressure of chloropicrin at laboratory temperatures). The observed rate constants are given in Table 1. The rate constants for NOCl production show large uncertainties because the IR absorption bands of NOCl overlap with the IR absorption of phosgene (as can be seen in Fig. 1) and as a result the weaker NOCl bands had more variation in observed production rate. This overlap is fundamental to the system (the R branch of NOCl overlaps with the P branch of phosgene) and could not be improved by changing the instrumental resolution. It is also likely that photolysis of NOCl, which is also photoactive with a cross-section ~200× that of chloropicrin, contributes to the uncertainty.

The observed rate constants for chloropicrin photolysis and product formation were consistent within uncertainty for a given chloropicrin pressure. Generally, we observed a decrease in rate as chloropicrin pressure increased. This decrease was modest, with the rate at 18.5 torr about half that at 5.0 torr, when the pressure increased by a factor of 3.7. There are two likely sources of this decrease in rate, which could be due to a pressure effect or to screening of the available ultraviolet by chloropicrin, which absorbs strongly in the ultraviolet.

To separate out these possible effects, we performed a series of experiments, where chloropicrin pressure was maintained at a