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Photolysis of Trichloronitromethane (Chloropicrin) under Atmospheric Conditions

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Dedicated to Prof. Dr. Reinhard Zellner on the occasion of his 65th birthday

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An experimental investigation on the photolysis of the pesticide chloropicrin, (trichloronitromethane, CCl_3NO_2), under atmospheric conditions was carried out at the outdoor European Photoreactor, (EUPHORE), in Valencia, Spain. The photodissociation rate coefficient, $J_{obs}(CCl_3NO_2)$, was determined directly under sunlight conditions during spring and summer months. Values in the range $J_{obs}(CCl_3NO_2) = (3.9–5.1)\times10^{-5}\ s^{-1}$ were obtained, corresponding to photolysis lifetimes of 7.1–5.4 hours. Absorption cross-sections for chloropicrin were determined over the wavelength range 260–370 nm, and together with the measured solar flux intensity, were used to calculate the maximum photolysis rate for chloropicrin, J_{max}. Comparison of the observed photolysis rate with the calculated maximum photolysis rate showed that the effective quantum yield of photodissociation, $\Phi = J_{obs}(CCl_3NO_2)/J_{max}$, was 0.94 ± 0.08. Photolysis of chloropicrin in air or nitrogen gave phosgene as the major carbon-containing product with a yield close to unity based on the loss of chloropicrin. The product yield data were shown to be consistent with a mechanism in which the photolysis channel produces a CCl_3 radical and NO_2. Kinetic studies on the reactions of hydroxyl radicals and ozone with chloropicrin suggest that, as expected, loss of CCl_3NO_2 by reaction with these species will be negligible under atmospheric conditions compared to photolysis. Photolysis of chloropicrin in air in the presence of isopropanol gave significant yields of ozone and is consistent with the generation of Cl atoms and NO_x following the photodissociation of CCl_3NO_2. The atmospheric implications of the use of chloropicrin as a pesticide are discussed.

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1. Introduction

The wide use of pesticides in agricultural applications is of some concern since they may have a significant environmental impact. Once a pesticide is applied in the field, it can be partitioned into the soil, water and atmosphere. Knowledge of the environmental fate of pesticides is important in order to assess the potential risks to human and animal health. The major fates of pesticides following their application are wet and/or dry deposition, or evaporation into the atmosphere. Pesticides can enter the atmosphere through spray drift, post-application volatilisation and wind erosion of treated soil, and is a function of their physical properties, and the manner of application. In the atmosphere these compounds can be distributed between the gas, particle and aqueous phases depending on their physicochemical properties and on environmental conditions. Chloropicrin, (trichloronitromethane, CCl_3NO_2, also known as "PS"), is a pesticide that is extensively used in agriculture as a pre-plant soil fumigant, and is used alone or in combination with methyl bromide. It is employed to control soil borne pathogens, parasitic nematodes, fungi and weeds [1]. Chloropicrin has a relatively high vapour pressure (24 mm Hg at 25 °C), and hence significant amounts may be expected to be emitted into the atmosphere during application or through evaporation from the soil.

The major pathways for the degradation of volatile organic compounds in the troposphere involve reactions with hydroxyl and nitrate radicals, ozone, or by photolysis [2]. Reactions of OH radicals with fully halogenated saturated organic compounds have been shown to be extremely slow and reaction with the nitro group unimportant under atmospheric conditions [3]. Similarly, reactions of NO_3 [4,5] and O_3 [6] with CCl_3NO_2 are not expected to be of importance under tropospheric conditions. Thus, it appears likely that the only significant loss process for chloropicrin in the troposphere is photolysis. The absorption spectrum of chloropicrin shows two broad bands centred at around 200 and 275 nm [7–9]. The strong absorption at 200 nm is due to a $\pi^* \leftarrow \pi$ transition, while the weaker band at 275 nm arises from a $\pi^* \leftarrow n$ transition. Since the actinic spectrum has little intensity below 290 nm, only the $\pi^* \leftarrow n$ absorption band is of relevance to the atmospheric chemistry of chloropicrin.

Moilanen *et al.* [10] photolysed chloropicrin with sunlamps in air and found phosgene and nitrosyl chloride as the major products. Under the reaction conditions employed, the lifetime for photolytic decomposition was estimated to be around 20 days. Rather surprisingly, photolysis in nitrogen did not appear to lead to decomposition of chloropicrin. The authors suggested that photolysis of chloropicrin in the presence of molecular oxygen gives rise to the direct formation of a trioxalone intermediate, that subsequently decomposes to form phosgene and nitrosyl chloride. Carter *et al.* [8] carried out an experimental and modelling study on the photolysis of chloropicrin in order to assess the possible atmospheric impact of its emissions. Decay of chloropicrin due to photolysis in air under the reaction conditions used was found to correspond to a half-life of approximately 18 hours. This value is much shorter than the estimate provided by Moilanen *et al.* [10], and it was suggested that the light source employed by these workers had significantly lower intensities in the chloropicrin absorption wavelength region than the one used by Carter *et al.* [8]. Carter *et al.* [8] also measured chloropicrin absorption cross-sections and found that the ratio of the observed photolysis rate in simulated solar conditions to the calculated maximum photolysis rate, gave an effective quantum yield for dissociation of 0.87±0.26. The spectral distribution of the light source employed by Carter *et al.* [8] was slightly different to that of natural sunlight with lower intensities in the chloropicrin absorption region. Assuming that the effective quantum yield for photodissociation of chloropicrin in solar radiation is essentially the same as that determined in the simulated solar photolysis conditions used by Carter *et al.* [8], then the atmospheric chloropicrin half-life was estimated to range from 3.4 hours for direct overhead sun to 7.6 hours for a solar zenith angle of 60°. Carter *et al.* [8] also carried out environmental chamber experiments on the photolysis of chloropicrin in air in the presence of a number of volatile organic compounds and NO_x. The results showed that chloropicrin significantly enhanced the rates of NO oxidation, O_3 formation and the consumption of the organic compounds. The results were used in kinetic models to test the possible mechanisms for the primary step in the photolysis of chloropicrin, and it was concluded that the data were consistent with formation of CCl_3 radicals and NO_2 by cleavage of the C-N bond as the predominant photolytic process. In addition, the photolysis of chloropicrin has been studied in argon and nitrogen cryogenic matrices and the reactions monitored by infrared absorption spectroscopy [11]. The reactions were investigated at several wavelengths from 220–405 nm and it was found that phosgene and nitrosyl chloride were the final products of the reactions. The reaction products were unchanged when the photolysis were carried out in the presence of O_2. It was evident from the concentration-time profiles for loss of chloropicrin, and the formation of phosgene and nitrosyl chloride that these compounds were not the major primary photolytic degradation products. An intermediate, whose infrared absorptions were consistent with CCl_3ONO, was detected following photolysis of chloropicrin. It was proposed that chloropicrin initially undergoes cleavage of the C-N bond to generate CCl_3 radicals and NO_2. In the matrix these species can recombine to give CCl_3ONO, which on photolysis generates CCl_2O and ClNO. Wade *et al.* [9] have reported an investigation on the photolysis of chloropicrin vapour at 193, 248 and 266 nm in which the initial products of the reaction were observed by time-dependent FTIR emission spectroscopy. For excitation at 248 and 266 nm, the major emission features following photodissociation were found to be consistent with cleavage of the C-N bond to produce CCl_3 radicals and electronically excited NO_2.

$$CCl_3NO_2 + h\nu \rightarrow CCl_3 + NO_2(\tilde{A}\,^2B_2) \tag{1}$$

These results indicate that the formation of phosgene and nitrosyl chloride previously reported in the studies of the photolysis of chloropicrin in both the gas phase [8,10] and in matrices [11] arise from secondary reactions involving CCl_3 radicals and NO_2.

The present series of experiments were carried out in order to determine the photolytic lifetime, quantum yield and mechanism for chloropicrin degradation under atmospheric conditions. Since quantum yield data was not available over the whole wavelength range relevant to the troposphere, photolysis experiments were performed using natural sunlight at the European Photoreactor (EUPHORE) in Valencia, Spain. The measured photodissociation rate coefficient was combined with the chloropicrin absorption cross-sections determined over the wavelength region of atmospheric relevance together with the measured solar flux intensity to calculate the effective quantum efficiency of chloropicrin photolysis under atmospheric conditions. The products of photolysis in air were also determined and mechanisms for their formation are proposed. These results are discussed in terms of the impact on the environment of emissions of chloropicrin to the atmosphere.

2. Experimental

2.1 Photolysis under laboratory conditions

Photolysis of chloropicrin was carried out in a T-shaped Pyrex reaction vessel of volume 171 cm^3 at 298±2 K. The reaction vessel was housed in the sample compartment of a Mattson Research Series Fourier Transform infrared (FTIR) spectrometer fitted with a mercury cadmium telluride detector. Infrared spectra were recorded using sodium chloride windows (5 cm diameter) with a pathlength of 10.5 cm. The photolytic light source entered through a quartz window (5 cm diameter) at right angles to the IR beam. The light source was a Hanovia medium pressure mercury lamp (500 W) powered with an intensity-stabilized supply. Quartz optics were used to produce an approximately parallel beam of light, and a narrow band interference filter was employed to isolate light of wavelength centred around 300 nm. At the beginning of each experiment the reaction vessel was evacuated and an IR spectrum recorded as the background spectrum. Chloropicrin was handled on a Pyrex vacuum line and pressures measured with MKS capacitance manometers. Following addition of chloropicrin to the reaction vessel, zero-grade nitrogen (BOC Gases) was expanded into the vessel until the desired pressure was achieved. Infrared spectra of the reaction mixtures were recorded during the course of the photolysis over the wavelength range 600–2500 cm^{-1} with a resolution of 2 cm^{-1}. The spectra were derived from the co-addition of 120 scans and analysed using Mattson WINFIRST software. Prior to analysis, calibrations were carried out for reactants and products. Reference spectra and calibration curves were obtained by expanding measured pressures of the pure compounds into the reaction vessel and recording their spectra. Reactant and product concentrations were determined through a process of spectral stripping in which small fractions of calibrated reference spectra were incrementally subtracted from the sample spectra.

2.2 Photolysis under sunlight conditions

Photolyses of chloropicrin by natural sunlight were performed at the European Photoreactor, (EUPHORE), during 2006 and 2007. EUPHORE consists of two large outdoor simulation chambers integrated into the Centro de Estudios Ambientales del Mediterraneo (CEAM) in Valencia, Spain, (longitude = −0.5°, latitude = 39.5°N). Technical information concerning the installation has previously been reported in the literature [12–15] and only details related to the present work are given here.

The experiments were performed in a hemispherical chamber made of FEP (fluorinated ethylene propylene) foil with a volume of approximately 200 m^3. The FEP foil is highly transparent to sunlight, with a transmission of greater than 75% of the solar radiation in the wavelength range 290 to 500 nm. A retractable steel housing surrounds the chamber and is used to control the time of exposure to sunlight. The floor of the simulation chamber consists of aluminium panels covered with FEP foil, and has a specially designed cooling system to compensate for heating of the chamber caused by solar radiation. Several ports situated in the floor of the chamber are available for the introduction and sampling of reaction mixtures. The reactor is filled to atmospheric pressure with purified dry air generated from ambient air using an air purification system. Homogenous gas mixtures were obtained by the use of two mixing fans located inside the chamber. At the end of each experiment the chamber was cleaned by flushing with clean air.

EUPHORE is equipped with a variety of instruments for physical and chemical analysis. The temperature inside the chamber was continuously measured using PT-100 thermocouples and humidity was monitored with a dew-point mirror system (Walz TS-2). A calibrated spectroradiometer (Bentham DM300) was used to measure the solar flux intensity and consists of a double monochromator, photomultiplier and silicon diode detector. Specially designed measurement heads with uniform sensitivity to the incident angles of the solar light were located inside the chamber to measure the incident and reflected radiation. The heads were coupled through a quartz fibre bundle to the entrance optics of the monochromator such that the direct and reflected light beams passed geometrically separated through the double monochromator simultaneously. The solar flux intensity was recorded over the range 290–520 nm with a spectral resolution of 1nm FWHM. A full spectral scan took 420–430 s. The calibration of the spectroradiometer is based on a certified standard Wolf tungsten lamp with a quoted precision of better than 5% in the relevant spectral range. Comparison of $J(NO_2)$ values calculated from the spectroradiometer data with those obtained from an independently calibrated $J(NO_2)$ filter radiometer (Schmitt Glashütten, Germany) showed that the values from these two instruments were within 10%

of each other. Hence, the uncertainty in measurement of the absolute light intensity is expected to be less than 10%.

A White mirror system installed inside the chamber and aligned with an optical path length of 553.5 m was used for *in situ* measurements by FTIR spectroscopy. The FTIR spectrometer (NICOLET Magna 550) was positioned on a platform beneath the chamber and operated using a MCT-B detector. Infrared spectra were derived from the co-addition of 240–270 scans, collected over a 5 minute period, with a resolution of 1 cm^{-1}. Ozone was analysed using a Monitor Labs 9810 instrument incorporating a non-dispersive UV photometer monitor.

Photolysis of chloropicrin was studied in purified dry air at ambient temperature and pressure. Chloropicrin was introduced into the chamber using a specially designed heated system *via* a stream of purified air. The large volume of the chamber minimizes the effects of wall reactions. In order to avoid contamination of the reaction mixtures from diffusion of outside air into the chamber due to leaks in the system, the chamber was kept at a slight overpressure relative to that of the outside air. This was achieved by continuously passing a flow of clean air into the chamber at 1 L s^{-1} using a thermal mass–flow controller. This procedure led to minor losses of the reactants and products by leakage from the chamber during the photolysis experiments. The overall dilution rate was determined by adding around 20 ppbv (1 ppbv = 2.46×10^{10} molecule cm^{-3}, at 760 Torr and 298 K) of the unreactive tracer gas SF_6 to the chamber in a stream of dry air along with the chloropicrin. The loss of SF_6 during the photolysis reactions was continuously monitored by FTIR spectroscopy. The derived correction factors for dilution were used to calculate the amounts of reactants consumed and products formed in the photolysis. In a number of experiments isopropanol was also added to the system using purified air. Following addition of the reactants to the chamber, they were allowed to mix for approximately 30 minutes to ensure homogenous gas samples. Photolysis by natural sunlight was initiated by opening the chamber's protective housing. The temperature inside the chamber increased slightly as the reaction progressed, but was always within the range 292–312 K. Similarly the humidity varied from 0.32 to 0.46 Torr. Chemical analyses were performed throughout the photolysis. The reactants and products were quantified using calibrated reference infrared spectra obtained by introducing measured volumes of pure materials into the chamber. Complex infrared spectra were analysed by successively subtracting the absorption features of the compounds using their calibration spectra. Ozone was continuously monitored during the photolysis.

Under the present experimental conditions chloropicrin is lost predominantly by photolysis with smaller amounts by dilution through the following reactions:

$$CCl_3NO_2 + h\nu \rightarrow \text{Products} \qquad J_{obs}(CCl_3NO_2) \tag{2}$$

$$CCl_3NO_2 \rightarrow \text{Dilution} \qquad k_{dil} \tag{3}$$

It is also possible that chloropicrin may be removed by dark reactions at the chamber wall:

$$CCl_3NO_2 \quad \rightarrow \quad \text{Wall loss} \quad k_{wall} \tag{4}$$

The overall dilution rate coefficient was obtained from the SF_6 decay data:

$$SF_6 \quad \rightarrow \quad \text{Dilution} \quad k_{dil}. \tag{5}$$

Thus, the measured rate coefficient for chloropicrin loss is given by:

$$\ln([CCl_3NO_2]_0/[CCl_3NO_2]_t) = (J_{meas})t \tag{I}$$

where $J_{meas} = J_{obs}(CCl_3NO_2) + k_{dil} + k_{wall}$, and $[CCl_3NO_2]_0$ and $[CCl_3NO_2]_t$ represent the concentrations of chloropicrin at the start of the photolysis and at time t, respectively.

The temporal concentration-time profile for SF_6 is given by:

$$\ln([SF_6]_0/[SF_6]_t) = k_{dil}t \tag{II}$$

where $[SF_6]_0$ and$[SF_6]_t$ are the concentrations of SF_6 initially and at time t, respectively.

The possibility of dark reactions was examined by starting the analytical sampling at least 30 minutes before opening the chamber to sunlight, and hence the onset of photolysis.

2.3 UV absorption cross-section measurements

The UV absorption spectrum of chloropicrin was determined with a DOAS system using a White multi-reflection cell of 8 m base path-length, which was contained in the chamber. The optical system employed a xenon high pressure short-arc lamp (PLI-500W) as the light source. The beam was focused by means of a Newton telescope onto a 1 cm pinhole and directed into the White type f/53.3 cell. The multi-reflection cell consists of three quartz prisms and three UV-enhanced aluminium coated mirrors, and was operated with a path-length of 386 m. Two laser diodes were used to adjust the path-length of the system. The exit beam from the White cell was focussed with a second Newton telescope onto an optical fibre (NA = 0.12, ϕ = 200 μm; BTO) leading to the entrance slit of the f/6.9 Czerny-Turner spectrograph (ACTON Pro-500; focal length 0.5 m). Homogeneous illumination of the spectrograph/detector system was achieved with a quartz fibre mode mixer. The 300 grooves/mm grating (blaze 300 nm) gave a dispersion of 0.16 nm/pixel. The spectral resolution was 0.72 nm FWHM. The spectrograph was thermostated at a temperature of 30ºC to reduce temperature drifts. The photodiode array detector (1024 diodes; Hamamatsu) was cooled to a temperature of −20 °C to reduce the dark current.

2.4 Materials

Chloropicrin (BDH Chemicals, 97%) and phosgene (BDH Chemicals, 99%) used in the laboratory photolysis experiments were purified by bulb to bulb distillation on the vacuum system prior to use. Chloropicrin (Riedel de Haën, 97.5%) and isopropanol (Scharlab, 99.8%) used in the EUPHORE chamber experiments were degassed by freeze-pump-thaw cycles. Calibrations for phosgene in the chamber photolysis were performed with an approximately 20% v/v solution of phosgene in toluene (Fluka). The exact proportion of toluene present in the solution was determined by gas chromatography and FTIR spectroscopy, and the balance assumed to be phosgene. Acetone (Aldrich, >99.9%), the product of the oxidation of isopropanol and SF_6 (Aldrich, 99.9%) were used as received.

3. Results and discussion

3.1 Absorption cross-sections

UV absorption cross-sections for chloropicrin were determined in several independent experiments at 298±5 K over the wavelength range 260–370 nm in the reaction chamber with a resolution of 0.72 nm. A background spectrum was measured in the chamber after it was flushed with purified air prior to the addition of chloropicrin to the chamber. All the spectra were corrected for dark current, stray light and the electronic offset of the detector. The spectrum of chloropicrin obtained in this work is shown in Figure 1 together with the spectra reported by Allston *et al.* [7], Carter *et al.* [8] and Wade *et al.* [9]. The maximum absorption occurs at approximately 275 nm and corresponds to the weak $\pi^* \leftarrow n$ transition involving promotion of a non-bonding electron of one of the oxygen atoms. At the wavelength of maximum absorption the standard deviation in the measured absorption cross-section is around 2%. Uncertainties in concentration measurements of chloropicrin, temperature and instrumental drift probably add a further 5% to the errors in the reported absorption cross-sections (base e), which are given in intervals of 5 nm in Table 1.

The maximum value determined in this work for the absorption cross-section of CCl_3NO_2 is $\sigma = (1.67\pm0.20)\times10^{-19}$ cm^2 molecule^{-1} at 275 nm. This value is in good agreement with the maximum values of the cross-sections reported by Allston *et al.* [7], 1.64×10^{-19} cm^2 molecule^{-1}, and Carter *et al.* [8], 1.73×10^{-19} cm^2 molecule^{-1}, however, it is somewhat higher than the measurement of Wade *et al.* [9], 1.40×10^{-19} cm^2 molecule^{-1}. The spectrum of chloropicrin is similar to that of the analogous non-chlorinated compound nitromethane, which consists of two broad bands at 270 and 198 nm [9]. The band at 198 nm in nitromethane is considerably stronger than the corresponding absorption in chloropicrin, while the $\pi^* \leftarrow n$ transition is significantly weaker. In a similar manner to chloropicrin, photolysis of nitromethane in the $\pi^* \leftarrow n$ band appears to result mainly in cleavage of the C-N bond to form CH_3 radicals and electronically excited NO_2 [9].

$$CH_3NO_2 + h\nu \rightarrow CH_3 + NO_2(\tilde{A}\,^2B_2) \tag{6}$$

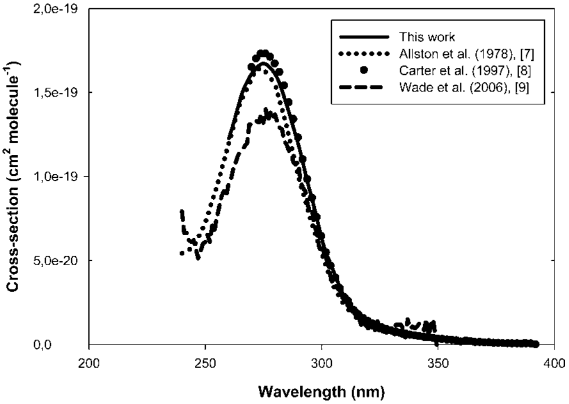

Fig. 1. UV absorption cross-sections of chloropicrin from this work and from Allston *et al.* [7], Carter *et al.* [8] and Wade *et al.* [9] at 298±5 K.

Table 1. Absorption cross-sections in cm^2 molecule^{-1} (base e) for chloropicrin determined in this work at 298±5 K.

Wavelength (nm)	σ (cm^2 molecule^{-1})	Wavelength (nm)	σ (cm^2 molecule^{-1})
260	1.22×10^{-19}	320	1.06×10^{-20}
265	1.46×10^{-19}	325	8.79×10^{-21}
270	1.61×10^{-19}	330	7.40×10^{-21}
275	1.67×10^{-19}	335	5.21×10^{-21}
280	1.61×10^{-19}	340	5.03×10^{-21}
285	1.43×10^{-19}	345	3.75×10^{-21}
290	1.19×10^{-19}	350	3.74×10^{-21}
295	9.14×10^{-20}	355	3.24×10^{-21}
300	6.30×10^{-20}	360	2.50×10^{-21}
305	4.43×10^{-20}	365	1.11×10^{-21}
310	2.76×10^{-20}	370	9.67×10^{-22}
315	1.70×10^{-20}		

The atmospheric photolysis rate coefficient for chloropicrin, J_{calc}, can be calculated from the measured absorption cross-sections from the expression:

$$J_{\mathrm{calc}} = \int \sigma_{\mathrm{T}}(\lambda)\Phi(\lambda)\mathrm{I}(\lambda)d\lambda \qquad (\lambda = 290 \text{ to } 370 \text{ nm}) \tag{III}$$

where, $\sigma_{\mathrm{T}}(\lambda)$, $\Phi(\lambda)$ and $\mathrm{I}(\lambda)$ are the absorption cross-section at temperature T, the quantum yield of dissociation and the actinic flux over the absorption wavelength range respectively. The integration was carried out from 290 to 370 nm. The actinic flux during the photolysis of chloropicrin during spring and summer was calculated from the measured photolysis rate coefficient of NO_2, $J(NO_2)$, the photolytic rate coefficient for the production of $O(^1D)$, $J(O(^1D)$, and the reported

Table 2. Experimental conditions and results for the photolysis of chloropicrin in air with natural sunlight at 298±5 K and atmospheric pressure ^{a}.

Date	11th July 2006	12th June 2007	13th July 2007
Initial mixing ratio of CCl_3NO_2 (ppbv)	373	164	137
Irradiation period (h)	~6	~5	~4
k_{dil} $(s^{-1})^{b}$	$(2.84±0.14)\times10^{-5}$	$(7.88±0.39)\times10^{-6}$	$(5.99±0.30)\times10^{-6}$
J_{meas} $(s^{-1})^{c}$	$(7.29±0.36)\times10^{-5}$	$(5.92±0.30)\times10^{-5}$	$(5.07±0.25)\times10^{-5}$
$J_{obs}(CCl_3NO_2)$ $(s^{-1})^{d}$	$(4.45±0.39)\times10^{-5}$	$(5.13±0.33)\times10^{-5}$	$(4.47±0.26)\times10^{-5}$
$J(NO_2)$ (s^{-1})	$(8.07±0.81)\times10^{-3}$	$(9.45±0.95)\times10^{-3}$	$(8.84±0.88)\times10^{-3}$
$J_{obs}(CCl_3NO_2)/J(NO_2)$	$(5.51±0.72)\times10^{-3}$	$(5.43±0.65)\times10^{-3}$	$(5.06±0.60)\times10^{-3}$
J_{max} $(s^{-1})^{e}$	$(4.37±0.44)\times10^{-5}$	$(5.12±0.51)\times10^{-5}$	$(4.78±0.48)\times10^{-5}$
Effective quantum yield^{f}	1.02±0.14	1.00±0.12	0.94±0.11
Molar yield of CCl_2O^{g}	0.94±0.10	1.10±0.10	1.11±0.10
Molar yield of O_3^{g}	0.53±0.04	1.12±0.08	1.67±0.12

(a) Except for $J(NO_2)$, quoted errors are twice the standard deviation arising from the least-squares analysis of the data and include the uncertainty in calibration and response factors. For $J(NO_2)$, the estimated error is 10% (see text).
(b) Estimated from $\ln([SF_6]_0/[SF_6]_t) = k_{dil}t$, Eqn.(II).
(c) Estimated from $\ln([CCl_3NO_2]_0/[CCl_3NO_2]_t) = (J_{meas})t$, Eqn.(I).
(d) $J_{obs}(CCl_3NO_2)$ derived from $J_{meas} = J_{obs}(CCl_3NO_2) + k_{dil}$.
(e) $J_{max} = J_{calc}$ for $\Phi = 1$ (see text).
(f) Effective quantum yield derived from $\Phi = J_{obs}(CCl_3NO_2)/J_{max}$.
(g) Based on the molar loss of CCl_3NO_2.

data for the absorption cross-section and quantum yield for the photolysis of NO_2 by sunlight [16]. Assuming the quantum yield for photodissociation is unity across the complete solar absorption region for chloropicrin, then the maximum photolytic rate coefficient, ($J_{max} = J_{calc}$ for $\Phi = 1$), for chloropicrin can be calculated from Eqn. (III). The maximum photolysis rate coefficients averaged across the irradiation periods employed in the present studies were calculated under the conditions in which the photolysis experiments were carried out and varied from $(4.37–5.12)\times10^{-5}$ s^{-1}, Tables 2 and 3.

3.2 Determination of the photodissociation rate coefficient and effective quantum efficiency of chloropicrin under atmospheric conditions

The photolysis of chloropicrin in air was investigated at EUPHORE under spring and summer conditions in 2006 and 2007. A summary of the initial conditions and results from experiments performed on five different days are given in Tables 2 and 3. The experiments were conducted over 4 to 7 hours during the middle of the day. The decay of chloropicrin and the formation of phosgene were monitored by FTIR spectroscopy and the ozone yield was determined from the ozone UV absorption monitor. The sunlight intensity was measured from the

Table 3. Experimental conditions and results for the photolysis of chloropicrin in air with natural sunlight at 298±5 K and atmospheric pressurein the presence of isopropanol[a].

Date	28th March 2006	5th April 2006
Initial mixing ratio of		
CCl_3NO_2 (ppbv)	353	177
$(CH_3)_2CHOH$ (ppbv)	8264	14480
Irradiation period (h)	~6	~7
k_{dil} (s^{-1})[b]	$(1.51\pm0.08)\times10^{-5}$	$(7.63\pm0.38)\times10^{-6}$
J_{meas} (s^{-1})[c]	$(5.62\pm0.28)\times10^{-5}$	$(4.03\pm0.20)\times10^{-5}$
$J_{obs}(CCl_3NO_2)$ (s^{-1})[d]	$(4.11\pm0.29)\times10^{-5}$	$(3.90\pm0.27)\times10^{-5}$
$J(NO_2)$ (s^{-1})	$(8.73\pm0.87)\times10^{-3}$	$(8.25\pm0.83)\times10^{-3}$
$J_{obs}(CCl_3NO_2)/J(NO_2)$	$(4.71\pm0.57)\times10^{-3}$	$(4.73\pm0.57)\times10^{-3}$
J_{max} (s^{-1})[e]	$(4.73\pm0.47)\times10^{-5}$	$(4.47\pm0.45)\times10^{-5}$
Effective quantum yield[f]	0.87±0.10	0.87±0.10
Molar yield of CCl_2O[g]	1.27±0.11	1.16±0.10
Molar yield of CH_3COCH_3[g]	6.03±0.54	7.24±0.65
Molar yield of O_3[g]	6.06±0.55	6.18±0.56

(a) Except for $J(NO_2)$, quoted errors are twice the standard deviation arising from the least-squares analysis of the data and include the uncertainty in calibration and response factors. For $J(NO_2)$, the estimated error is 10% (see text).
(b) Estimated from $\ln([SF_6]_0/[SF_6]_t) = k_{dil}t$, Eqn.(II).
(c) Estimated from $\ln([CCl_3NO_2]_0/[CCl_3NO_2]_t) = (J_{meas})t$, Eqn.(I).
(d) $J_{obs}(CCl_3NO_2)$ derived from $J_{meas} = J_{obs}(CCl_3NO_2) + k_{dil}$.
(e) $J_{max} = J_{calc}$ for $\Phi = 1$ (see text).
(f) Effective quantum yield derived from $\Phi = J_{obs}(CCl_3NO_2)/J_{max}$.
(g) Based on the molar loss of CCl_3NO_2.

photolysis frequency of NO_2, $J(NO_2)$. The loss of reactants by dilution in the chamber was determined from the decay of the inert tracer SF_6, which was measured by FTIR spectroscopy. Loss of chloropicrin at the chamber walls was shown to be negligible in dark reactions carried out prior to sunlight irradiation. The experiments gave essentially similar results, and only the data from the run carried out on 12th June 2007 are graphically presented. Concentration-time profiles for chloropicrin and the major reaction product phosgene are shown in Figure 2. Also given in Figure 2 is the photolysis rate of NO_2, $J(NO_2)$, which provides a measure of the solar light intensity during the experiment.

The rate coefficient for the photolytic loss of chloropicrin, $J_{obs}(CCl_3NO_2)$, in this experiment was obtained from the expression $\ln([CCl_3NO_2]_0/[CCl_3NO_2]_t) = (J_{obs}(CCl_3NO_2))t$, in which the loss of chloropicrin has been corrected for dilution using the SF_6 decay data. The data plotted in the above form are shown in Figure 3, and provide a value of the rate coefficient for loss of chloropicrin due to photolysis, $J_{obs}(CCl_3NO_2) = (5.13\pm0.33)\times10^{-5}\ s^{-1}$. The values of $J_{obs}(CCl_3NO_2)$ for the experiments shown in Tables 2 and 3 differ slightly, since the sunlight intensity during each day was variable as reflected by the $J(NO_2)$ values.

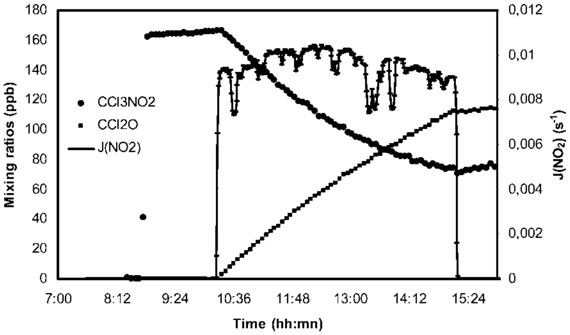

Fig. 2. Concentration-time profiles of the reactant and product during the photolysis of chloropicrin (164 ppbv) in air at EUPHORE. The photolysis rate $J(NO_2)$ during the course of the experiment is also shown.

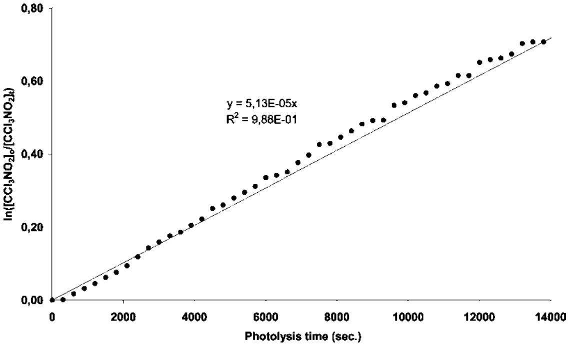

Fig. 3. Plot of the concentration-time data for the loss of chloropicrin plotted in the form $\ln([CCl_3NO_2]_t)$ against time.

The atmospheric lifetime of chloropicrin due to photolysis was calculated from $1/J_{obs}(CCl_3NO_2)$. In the experiments performed in this study, values of $J_{obs}(CCl_3NO_2)$ were in the range $(3.90\text{–}5.13)\times10^{-5}\ s^{-1}$, corresponding to photolysis lifetimes of 7.1–5.4 hours. Obviously, the photolysis rate depends on the intensity and spectral distribution of the sunlight, consequently it is more useful to quote the photolysis rate relative to a conventional measure of solar light intensity, such as $J(NO_2)$. For the experiments carried out in this work, the average value of $J_{obs}(CCl_3NO_2)/J(NO_2)$ was 5.1×10^{-3}. The photolysis performed at EUPHORE (latitude 39.5° N) measured the photolysis rate during the middle of the day in spring and summer months under relatively clear sky conditions. The maximum photolysis rate occurs at solar noon in the summer months, where $J(NO_2)$ is typically about $1\times10^{-2}\ s^{-1}$ [12–15]. Thus, under these conditions, the average value of $J_{obs}(CCl_3NO_2) = 5.1\times10^{-5}\ s^{-1}$, which gives a lifetime due to photolysis of around 5.4 hours. This is in good agreement with the values calculated by Carter *et al.* [8] of 3.4–7.6 hours for direct overhead sun and a solar zenith angle of 60°, respectively. The atmospheric lifetimes estimated by Carter *et al.* [8] were based on a quantum yield for photolysis of 0.87 determined from the experimental photodissociation rate determined in simulated solar conditions and the measured absorption cross-sections of chloropicrin. It was assumed that the measured quantum yield for photolysis determined under simulated solar conditions was the same as that for natural sunlight. The results from the present work enable the effective quantum yield for dissociation to be determined directly by calculating the ratio of the measured photolysis rate, $J_{obs}(CCl_3NO_2)$, to the maximum theoretical photolysis rate, J_{max}, The value of J_{max} was calculated from the solar flux intensity measurements of the spectroradiometer, the measured absorption cross-sections and assuming a quantum yield of unity across the atmospheric absorption wavelength range of chloropicrin using Eqn. (III). The maximum photolysis rate coefficients averaged over the irradiation periods were calculated under the sunlight conditions in which the experiments were performed in spring and summer and were found to lie in the range $(4.37–5.12)\times10^{-5}\ s^{-1}$. The corresponding measured rate coefficients determined in the experiments were $(3.90–5.13)\times10^{-5}s^{-1}$ and provide estimates for the effective quantum yields for photodissociation of chloropicrin, $J_{obs}(CCl_3NO_2)/J_{max}$, of 0.87–1.02, Tables 2 and 3. The average value of 0.94±0.08 is in broad agreement with the value of 0.87±0.26 estimated by Carter *et al.* [8].

3.3 Photolysis products

The major carbon-containing product from the photolysis of chloropicrin carried out in the simulation chamber in air was phosgene (CCl_2O). Yield plots of phosgene, based on the loss of chloropicrin in the experiments, were linear indicating that phosgene was a primary reaction product from the photolysis. Figure 4 shows the yield plot of phosgene derived from the photolysis experiment performed on 12th June 2007, and gives a molar yield of 1.10±0.10.

There are various possible pathways for the photolysis of chloropicrin under atmospheric conditions, (λ>290 nm), which may lead to the generation of CCl_2O.

A. Fission of the carbon-nitrogen bond in the photolysis step of chloropicrin.

$$\begin{aligned}&CCl_3NO_2 + h\nu \rightarrow CCl_3 + NO_2(\tilde{A}\,^2B_2)\\&\Delta H^0_{298} = 293\ \text{kJ mol}^{-1}[9],\ \lambda \leq 408\ \text{nm}\end{aligned} \tag{1}$$

Subsequent reactions of CCl_3 radicals yield phosgene.

$$CCl_3 + O_2 + M \rightarrow CCl_3O_2 + M \tag{7}$$

$$CCl_3O_2 + NO \rightarrow CCl_3O + NO_2 \tag{8}$$

$$CCl_3O \rightarrow Cl + CCl_2O \tag{9}$$

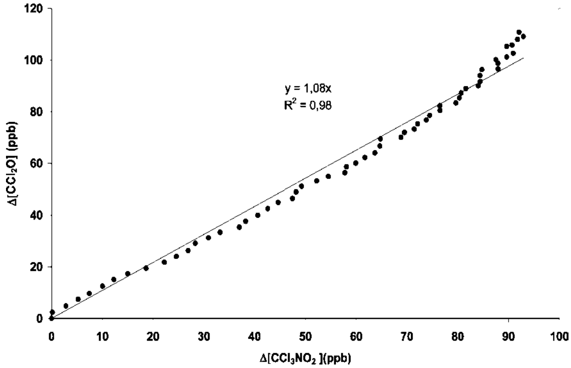

Fig. 4. Yield plot for phosgene from the photolysis of chloropicrin (164 ppbv) at EUPHORE.

B. Direct formation of phosgene in the photolysis process.

$$CCl_3NO_2 + h\nu \rightarrow CCl_2O + ClNO \quad \Delta H^0_{298} = -92\ \text{kJ mol}^{-1}\ [9] \qquad (10)$$

A number of studies have been reported that provide information on the mechanism for the primary step in the photolysis of chloropicrin under atmospheric conditions. Carter *et al.* [8] carried out a modelling study on the results from the photolysis of chloropicrin in the presence of a number of volatile organic compounds, and found that the product yields were consistent with C-N bond cleavage in the photolysis step, reaction (1), rather than the direct formation of CCl_2O in reaction (10). It has been shown that CCl_2O and ClNO were not the primary products when chloropicrin was photolysed in argon or nitrogen cryogenic matrices, but CCl_3ONO was detected as an intermediate in the reaction [11]. It was proposed that photolysis gave CCl_3 radicals and NO_2, which recombined in the matrix to form CCl_3ONO. Subsequent photolysis of CCl_3ONO was suggested as the source of CCl_2O and ClNO. Wade *et al.* [9] presented compelling evidence that CCl_3 radicals and NO_2 are formed in the photolysis of CCl_3NO_2, reaction (1), from a study in which the initial products from the photolysis in the vapour phase were detected by time-dependent FTIR emission spectroscopy. The data also showed that phosgene was not formed directly in the initial photolytic process. In the present investigation, the photolysis of chloropicrin in air using natural sunlight gave CCl_2O as a major product with a yield close to unity, Tables 2 and 3. Phosgene could be formed either from the production of CCl_3 in reaction (1), followed by reactions (7) to (9) (pathway A), or directly in the photolysis step, reaction (10) (pathway B). However, ozone was also a major product of the photolysis of chloropicrin in air, although the measured yields of O_3 were somewhat variable. Ozone can only be generated in this system from the photolysis of NO_2

$$NO_2 + h\nu \rightarrow O + NO \qquad (11)$$

and subsequent reaction of oxygen atoms with oxygen, reaction (12).

$$O + O_2 + M \rightarrow O_3 + M \tag{12}$$

The formation of ozone from pathway B is not possible if the photolysis of chloropicrin produces CCl_2O and ClNO directly in reaction (10), since NO_2 is not generated in the system.

Since two molecules of NO_2 are formed in reaction sequence A, photolysis of chloropicrin by reactions (1), (7), (8) and (9) can in principle give rise to the generation of two molecules of ozone. The product yield data from the photolysis of chloropicrin in air under sunlight conditions carried out in the absence of isopropanol in air given in Table 2 show that the ozone yield varies from 0.53 to 1.67 rather than the predicted value of 2. Presumably the lower than expected yields of O_3 are due to loss of NO_x from the system.

The photolysis of chloropicrin was also investigated in this work in the absence of oxygen in a small quartz reaction vessel. Photolysis were carried out over a range of chloropicrin pressures from 5 to 10 Torr in nitrogen, (100–400 Torr), as the diluent gas. In all the experiments phosgene was observed as the only carbon-containing product with a yield close to unity. Small amounts of nitrosyl chloride were also detected in the reaction products, however, under the reaction conditions employed ClNO was rapidly photolysed to form Cl and NO. Assuming that the primary photolytic process of chloropicrin produces CCl_3 radicals and NO_2, the CCl_3 radicals will react with NO_2. Addition of CCl_3 to NO_2 may occur at either the nitrogen or the oxygen atoms of NO_2.

$$CCl_3 + NO_2 \leftrightarrow [CCl_3NO_2]^* + M \rightarrow CCl_3NO_2 \tag{13}$$

$$CCl_3 + NO_2 \leftrightarrow [CCl_3ONO]^* + M \rightarrow CCl_3ONO \tag{14}$$

The CCl_3NO_2 and CCl_3ONO molecules initially formed in reactions (13) and (14) respectively, contain sufficient energy to decompose. Dissociation energies for the bonds in these compounds suggest that the values of D(CCl_3-NO_2) and D(CCl_3-ONO) are similar at around 250 kJ mol^{-1} [16,17]. In CCl_3NO_2 the C-N bond formed is the weakest in the molecule and dissociation into the original fragments is the only alternative pathway to stabilization by collision. For CCl_3ONO the weakest bond in the molecule is the CCl_3O-NO bond, D(CCl_3O-NO) $\approx$ 170 kJ mol^{-1} [16,17], and hence unless around 80 kJ mol^{-1} excess energy is removed on collision, the initially formed nitrite will dissociate to form CCl_3O radicals and NO, reaction (15).

$$[CCl_3ONO]^* \rightarrow CCl_3O + NO \tag{15}$$

In the gas phase formation of stable nitrites is unlikely and the net effect of addition of CCl_3 radicals to NO_2 through an oxygen atom will be formation of CCl_3O and NO. Decomposition of CCl_3O radicals forms phosgene and a chlorine atom. Reaction of Cl atoms with NO leads to the production of ClNO.

$$Cl + NO + M \rightarrow ClNO + M \quad (16)$$

These results are in line with the data reported from the photolysis of chloropicrin in argon and nitrogen cryogenic matrices, where CCl_3ONO was observed as a transient intermediate, which subsequently decomposed to generate phosgene and nitrosyl chloride [11].

Two experiments were carried out on the photolysis of chloropicrin in air in the simulation chamber in the presence of isopropanol as a scavenger of Cl atoms, and the results are given in Table 3. Comparison of the rate coefficients for photodissociation of chloropicrin determined in air, Table 2, and those measured when the photolysis were performed in the presence of isopropanol, Table 3, shows that the average value of $J_{obs}(CCl_3NO_2)$ for the three experiments carried out in the absence of isopropanol was $(4.7 \pm 0.3) \times 10^{-5}\ s^{-1}$, while the average value obtained for the two photolyses performed in the presence of isopropanol was $(4.0 \pm 0.2) \times 10^{-5}\ s^{-1}$. The results indicate that the photolysis rates for experiments carried out in air are slightly higher than those in which isopropanol was also present in the system. The data for photolysis with isopropanol present were from runs performed in spring, and hence were carried out with lower solar intensities than the experiments performed in summer months. In order to compare the data from the two sets of experiments, it is useful to calculate the photolysis rates relative to the photolysis of NO_2, $J_{obs}(CCl_3NO_2)/J(NO_2)$. The values of these ratios were $(5.3 \pm 0.4) \times 10^{-3}\ s^{-1}$ and $(4.7 \pm 0.3) \times 10^{-3}\ s^{-1}$ for photolysis carried out in air, and in air in the presence of isopropanol respectively.

These two ratios are within experimental error of each other and indicate that the Cl atoms formed in the photolysis of chloropicrin in air do not contribute to the decay of CCl_3NO_2. Photolysis of CCl_3NO_2 leads to the generation of CCl_3O radicals which decompose to produce Cl atoms. In the presence of excess isopropanol, Cl atoms are efficiently scavenged in the rapid reaction with $(CH_3)_2CHOH$, $k(Cl + (CH_3)_2CHOH) = (8.4 \pm 0.4) \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$ [18]. The molar yield of phosgene in both sets of photolysis were similar and close to unity, however for reactions performed in the presence of isopropanol, there was a significant increase in the yield of ozone compared to the yield observed in its absence. Reaction of Cl atoms generated in the photolysis of chloropicrin will react with isopropanol to form acetone.

$$Cl + (CH_3)_2CHOH \rightarrow (CH_3)_2COH + HCl \quad (17)$$

$$(CH_3)_2COH + O_2 \rightarrow HO_2 + CH_3C(O)CH_3 \quad (18)$$

The HO_2 radicals form OH radicals by conversion of the NO in the system to NO_2, and hence lead to the production of ozone.

$$HO_2 + NO \rightarrow OH + NO_2 \quad (19)$$

Hydroxyl radicals will also rapidly react with isopropanol.

$$OH + (CH_3)_2CHOH \rightarrow (CH_3)_2COH + H_2O \qquad (20)$$

Thus, isopropanol will be rapidly removed from the system in a chain reaction leading to the generation of ozone and acetone. As expected the yields of O_3 and CH_3COCH_3 were found to be similar, Table 3.

In a separate series of experiments the reactions of O_3 and OH radicals with chloropicrin were investigated in order to ascertain whether these reactions are important under atmospheric conditions. A mixture of O_3 (69 ppbv) and CCl_3NO_2 (344 ppbv) was left in the dark in the simulation chamber for around 5 hours. The loss of O_3, after correction for leakage from the chamber, was estimated to be less than 5% after 5 hours. The pseudo first-order rate coefficient for O_3 loss was estimated to be less than 3.0×10^{-6} s^{-1} giving a value of the rate coefficient for the reaction of O_3 with $CCl_3NO_2 < 3.5\times10^{-19}$ cm^3 molecule^{-1} s^{-1}. This rate coefficient gives an atmospheric lifetime for chloropicrin due to reaction with ozone of > 50 days, assuming the atmospheric concentration of O_3 is 7×10^{11} molecule cm^{-3} [19].

Photolysis in natural sunlight of a mixture of HONO (162 ppbv) and chloropicrin (166 ppbv) in the simulation chamber for 5 hours showed that the decay rate of CCl_3NO_2 was unchanged within experimental error of the decay due to photolysis observed in the absence of the OH radical source. The lifetime of toluene when photolysed with the same amount of HONO in the chamber was around 5 hours indicating that the concentration of OH radicals in the chamber was around 1×10^7 molecule cm^{-3} taking a value of $k(OH + C_6H_5CH_3) = 6.0\times10^{-12}$ cm^3 molecule^{-1} s^{-1} [3]. Assuming the concentration of OH radicals in the chloropicrin experiment was approximately the same as in the toluene experiment, and that loss of chloropicrin due to reaction with OH radicals was less than 5% during the course of the reaction, then the rate coefficient for reaction of OH radicals with CCl_3NO_2 is estimated to be $< 3\times10^{-13}$ cm^3 molecule^{-1} s^{-1}. With a concentration of OH radicals in the troposphere of 2×10^6 molecule cm^{-3} [20], the lifetime of chloropicrin in the atmosphere due to reaction with OH radicals is estimated > 20 days. Thus, the degradation of chloropicrin in the atmosphere by reaction with O_3 or OH radicals will be negligible compared to loss by photolysis.

4. Conclusions and atmospheric implications

Following its release into the atmosphere chloropicrin is readily photolysed by sunlight with an effective quantum yield close to unity. Under relatively clear sky conditions at ground level and a latitude of 39.5° N, the average photodissociation rate coefficient of chloropicrin, $J_{obs}(CCl_3NO_2)$, during the middle of the day in summer months was estimated to be approximately 5.1×10^{-5} s^{-1}, which corresponds to a lifetime of around 5.4 hours. Reaction of OH radicals and O_3 with chloropicrin was shown to be negligible, and hence photolysis is the major removal pathway for CCl_3NO_2 from the troposphere. Photodecomposition of CCl_3NO_2 occurs predominantly by C-N cleavage to give CCl_3 radicals and NO_2. Further reactions of CCl_3 radicals generate CCl_2O and Cl atoms. Modelling studies have shown that removal of phosgene occurs mainly by wet deposition with a lifetime of about 70 days [21]. Formation of chlorine atoms leads to enhanced loss of volatile organic compounds from the troposphere. Production of NO_x in the photolysis of CCl_3NO_2 suggests that the impact of emissions of chloropicrin on the formation of ozone under low tropospheric conditions of NO_x will be relatively high.

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