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Trifluralin: Photolysis under sunlight conditions and reaction with HO[•] radicals

A. Le Person^a, A. Mellouki^{a,*}, A. Muñoz^b, E. Borras^b, M. Martin-Reviejo^b, K. Wirtz^b

^a LCSR-CNRS, 1C Avenue de la Recherche scientifique, 45071 Orléans cedex 02, France ^b Fundacion CEAM, Parque Tecnologico, E-46980 Paterna (Valencia), Spain

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Abstract

The gas phase atmospheric degradation of trifluralin (a widely used herbicide) has been investigated at the EUPHORE facility. Its photolysis has been studied under sunlight conditions and its reaction rate constant with HO[•] radicals was measured using the relative rate method. Using 1,3,5-trimethylbenzene as reference compound, the rate constant of HO[•] reaction with trifluralin was obtained to be $k_{\text{HO}} = (1.7 \pm 0.4) \times 10^{-11}$ cm³ molecule s⁻¹ at (300 ± 5) K and atmospheric pressure. The mean photolysis rate measured under solar radiation was $J_{\text{trifluralin}} = (1.2 \pm 0.5) \times 10^{-3} \text{ s}^{-1}$ ($J_{\text{NO}_2} = 8 \times 10^{-3} \text{ s}^{-1}$). The photolysis of trifluralin was found to generate organic aerosols with a yield of (20 ± 10) %. The data obtained enabled us to discuss the atmospheric fate of trifluralin in the gas phase.

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1. Introduction

The intensive use of pesticides has increased during the last decades resulting in a contamination of the environment. The presence of pesticides in food and water has been reported by different authors (DiCorcia and Marchetti, 1992). They are also present in the atmosphere as result of direct and indirect emission through dispersion during spraying operations, volatilisation from ground or leaf surfaces, and wind erosion (Sauret et al., 2000). A number of pesticides have been shown to have adverse health effects i.e., carcinogenic, mutagenic and reprotoxic properties (Konradsen et al., 2003; Gupta, 2004). Therefore, the persistence of these compounds in different media (soil, water and air) should be well under-

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stood in order to better evaluate their environmental impacts.

In the atmosphere, pesticides are distributed between the gas, particle and aqueous phases. The partitioning between different phases depends on their physicochemical properties (such as equilibrium vapour pressure, Henry's law constant) as well as on the environmental conditions (temperature, wind direction, cloud) (Tsal and Cohen, 1991). After their entry into the atmosphere, their main removal routes are wet and dry deposition (Bidlemann, 1988) and chemical reactions (Klöpffer et al., 1985; Atkinson et al., 1999). In the gas phase, pesticides may be degraded by solar light photolysis and chemical reaction with HO, NO₃ radicals and ozone. Reaction with HO radicals appears to be the major loss process for a large number of pesticides (Atkinson, 1989, 1994). While a number of studies have been conducted so far on the degradation of pesticides in soils and water, there is only a limited number of data on their atmospheric fate in the gas phase.

^{*} Corresponding author. Tel.: +33 238257612; fax: +33 238696004. *E-mail address:* mellouki@cnrs-orleans.fr (A. Mellouki).

Therefore, kinetic and mechanistic information on the gas phase degradation processes of pesticides are needed in order to assess the complete atmospheric fate, hence, their possible impact on air quality and human health.

In this work, we present a laboratory study of the atmospheric degradation in the gas phase of trifluralin, $C_{13}H_{16}F_3N_3O_4$, (α,α,α -trifluoro-2,6-dinitro-*N*,*N*-dipropyl*p*-toluidine):



Trifluralin was first registered in the USA in 1963, its use is increasing in some countries while it is banned in others. It is a selective pre-sowing or pre-emergence herbicide used to control many annual grasses and broadleaf weeds in a large variety of arable and horticultural crops and it is widely used on cotton and other crops in Africa and other developing countries.

Trifluralin is a relatively immobile herbicide in soils so that there is little hazard for groundwater contamination. But it has a tendency to volatilize (vapour pressure $\approx 1.5 \times 10^{-2}$ Pa (Wauchope et al., 1992) and Henry Constant H = 16.8 Pa m³ mol⁻¹ at 25 °C), hence it can relatively easily enter the atmosphere. It has been detected in the air at concentrations of the order of ng m⁻³ (Sanusi et al., 2000).

The environmental fate of trifluralin has been partly studied. Grover et al. (1997) and Atkinson et al. (1999) have reviewed the existing data on its degradation, mobility, and persistence in soils as well as its potential concentrations in water and air and its transformation rates and products in the atmosphere. The photolysis of trifluralin has been studied in air, water and soils which enabled to estimate its lifetime and identify a number of products (Soderquist et al., 1975; Golab et al., 1979; Golab and Occolowitz, 1979; Mabury and Crosby, 1995; Burrows et al., 2002). However, in the gas phase, the only study conducted so far under sunlight and "controlled" conditions was performed under experimental conditions were the loss of trifluralin could have been affected by reaction with radicals such as HO[•] (Mongar and Miller, 1988). To our knowledge, no data are available on the HO' reaction with trifluralin in the gas phase.

In this work, we have conducted a study on the photolysis of trifluralin under sunlight conditions and a "controlled atmosphere" where all its loss processes were accounted for. In addition, the reaction rate constants of HO and ozone with trifluralin were determined. The photolysis of trifluralin was found to generate organic aerosols. The data obtained enabled us to discuss the atmospheric fate of trifluralin in the gas phase. The experiments have been performed at the large outdoor European Photoreactor (EUPHORE).

2. Experimental

The experiments have been conducted under sunlight conditions at the outdoor European Photoreactor (EUPHORE) in Valencia-Spain using the same procedures as those described in a recent paper from our group on the atmospheric fate of another pesticide (dichlorvos) (Feigenbrugel et al., 2006). The EUPHORE facility has been described in detail elsewhere (Becker, 1996; Volkammer et al., 2001) and only information directly related to the present work is given in the following section.

EUPHORE consists of two identical half-spherical FEP (fluorine–ethene–propene) foil chambers mounted on aluminium floor covered with FEP foil which transmits $\approx 90\%$ sunlight at wavelengths higher than 320 nm dropping to 75% transmission at the atmospheric threshold of 290 nm. The floor panels are water cooled in order to avoid excessive heating (<305 K). The chamber used for the experiments described here has a volume of approximately 204 m³ and two mixing fans to ensure homogeneity of the reaction mixtures within less than 2 min. A number of ports situated on the floor of the chamber are available for the introduction and sampling of reaction mixtures. A retractable steel housing surrounds the chamber is used to control the time of exposure to sunlight.

An air drying and purification system supplies the chamber with oil vapor, hydrocarbon and NO_x free dry air. Temperature and humidity inside the chamber were measured continuously using PT-100 thermocouples and a dew-point mirror system (Walz TS-2), respectively. The actinic flux was measured by using a calibrated filter radiometer specific to the photolysis frequency of NO₂.

A Fourier Transform InfraRed (FTIR) spectrometer coupled to a White-type mirror system (optical path length of 553.5 m) was used to monitor reactants and products. Infrared spectra were derived from the co-addition of 150-270 scans, collected over a 5 min period, and recorded using 1 cm⁻¹ resolution. The IR absorption cross sections used to analyze the FTIR data were determined in separate calibration experiments. Complex infrared spectra were analyzed by successively subtracting the absorption features of the compounds using the calibrated spectra. The gas mixture was also analyzed during the experiments by GC/MS (Gas Chromatography/Mass Spectrometry) and by TGA (Trace Gas Analyser): the first technique consists on a GC/MS Varian 3400 interfaced to an ultratrace ion trap mass spectrometer, a MS Saturn 2000, which incorporates a cryogenic sample pre-concentration. For GC/MS (electron impact ionization) analysis a GC-MS Varian 3400 interfaced to a MS (ion trap) Saturn 2000 was used. The samples were collected in a preconcentration trap made of glass beads at -196 °C for 5 min using a flow of 40 ml min⁻¹ then desorbed at 270 °C and injected onto the 30 m HP INNOWAX polyethylene glycol fused silica capillary column (thickness of 0.25 mm and i.d. of 0.25 mm) which temperature was programmed from 70 to 260 °C at 10 °C/min and held at

this temperature for 4 min. The temperature of the transfer line was set at 170 °C and the mass range was 46-450 m/z (scan time of 0.42 s). The trace gas analyzer (TGA, Fisons) incorporates a cryogenic enrichment trap. 200 ml of air were collected in a sampling loop at 120 °C and then passed during 4 min into a micro trap with Tenax cooled to -120 °C. The injection onto the chromatographic silica capillary column (30 m DB-1, J&W Scientific, 100% Dimethylpolysiloxane, 0.25 mm id., 1.0 mm film) was achieved by a rapid heating of the micro trap to 240 °C. The GC was held at 40 °C for 7 min and then raised to 160 °C at 20 °C min⁻¹ and held at this temperature for 10 min, and then the temperature is raised until 200 °C and held at this temperature for 5 min. The detector used is a FID (Flame Ionization Detector) and the acquisition time was 30 min.

Other gases such as O_3 , CO, and NO_x were measured using specific analyzers, Monitor Labs 9810, Thermo Environment 48C, Monitor Labs 9841A and ECO-Physics CLD770 AL ppt with PLC 760 photolytic converter, respectively.

The particle phase was physically characterized by a Scanning Mobility Particle Sizer (SMPS) which consists of a differential mobility analyzer TSI 3081DMA and a particle counter TSI 3022A CPC. Calculations were conducted using the geometric mean of the minimum and maximum diameters, based on the assumption of a log normal distribution of spherical particles within each size bin. For all aerosol mass calculations, an aerosol density of 1 g $\rm cm^{-3}$ was assumed on the expected condensed-phase products and they were corrected for wall loss processes. The total aerosol mass was also measured by a Tapered Oscillating Element Microbalance (TEOM, series 1400a). In addition, the particles were sampled with a quartz filter and immediately after sampling, the filters were put into glass vials with 5 ml $CH_2Cl_2/acetonitrile$, sealed and store in a freezer to -4 °C for future analysis by mass spectrometry (GC–MS).

Known amounts of trifluralin (99.5%, Cil Cluzeau), TMB (99%, Fluka), 2,3-dimethyl, 2-butene (98 %, Fluka) were introduced into the chamber *via* a stream of purified air. Due to their relative low vapour pressures, trifluralin and TMB were gently heated to accelerate their introduction into the chamber. The temperature inside the chamber varied slightly during experiments but was always within the range 293–303 K. The dilution rate of the chamber due to small leaks was determined by measuring the decay of SF₆ (\approx 20 ppbv) added at the start of the experiments. The decay of SF₆ was monitored using its IR absorption at 935–956 cm⁻¹.

3. Results and discussion

The results obtained in the photolysis of trifluralin as well as its reaction with HO[•] radicals are presented and discussed below.

3.1. Photolysis of trifluralin under sunlight conditions

Two experiments were carried out in July 2003. The initial concentrations of trifluralin were 32.7 and 68.7 ppbv for the runs of 100703 and 110703, respectively. In the second run (110703), 168 ppbv of 1,3,5-trimethyl benzene (TMB) were added to the gas mixture to trace the HO[•] radicals concentrations that could be produced in the chamber. In these conditions, trifluralin is lost by photolysis, by reaction with HO[•] (if present), and by dilution while the disappearance of TMB is only due to its dilution and reaction with HO[•] radicals:

Trifluralin + $hv \rightarrow$ products J

Trifluralin + HO \rightarrow products k_{HO} .

Trifluralin \rightarrow loss by dilution k_1

Trifluralin \rightarrow Wall loss k_{wl}

TMB + HO \rightarrow products k_{TMB}

TMB \rightarrow loss by dilution k_1

Under the assumption that the HO radical concentration remains constant during the photolysis experiment, it can be shown that:

$$\ln \left(\frac{[\text{trifluralin}]_0}{[\text{trifluralin}]_t} \right) = (J + k_{\text{HO}} [\text{HO'}] + k_1 + k_{\text{wl}}) \times t$$
$$= k_{\text{tot}} \times t \tag{1}$$

The residual concentration of HO[•] radicals was estimated to be $[\text{HO}^{-}] \approx 4 \times 10^5$ molecule cm⁻³ from the first order decay of the TMB.

Gas phase analysis of trifluralin was made by FTIR using the $1129-1200 \text{ cm}^{-1}$ range since the GCMS data showed some memory effects.

The photolysis rate constant, J, was derived from the slope of $\ln([trifluralin]_0/[trifluralin]_t)$ versus photolysis time t. The obtained slope, k_{tot} , represents the sum of all trifluralin loss, reaction with HO[•], k_{HO} ·[HO[•]], wall loss, k_{wl} , dilution rate, k_1 , and photolysis, J:

$$k_{\text{tot}} = J + k_{\text{HO}}[\text{HO'}] + k_1 + k_{\text{wl}}$$
⁽²⁾

The contribution of the HO[•] reaction was estimated using $[\text{HO}^{-}] = 4 \times 10^5$ molecule cm⁻³ and the rate constant of the HO[•] reaction with trifluralin ($k_{\text{HO}^{-}} = 1.7 \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹) obtained in this work and presented below, leading to $k_{\text{HO}^{-}}[\text{HO}^{-}] = 6.8 \times 10^{-6} \text{ s}^{-1}$. The other losses (dilution and wall) were derived from the consumption of trifluralin before exposing the mixture to sunlight (typically $k_1 + k_{wl} = 3 \times 10^{-5} \text{ s}^{-1}$). Fig. 1 shows the plots of ln([trifluralin]₀/[trifluralin]_t) versus photolysis time obtained for the two runs.

The photolysis rates obtained under our experimental conditions are $(1.3 \pm 0.4) \times 10^{-3} \text{ s}^{-1}$ and $(1.1 \pm 0.4) \times 10^{-3} \text{ s}^{-1}$, for the runs of 10th July and 11th July, respectively. The quoted errors correspond to 2σ obtained from the least-square analysis and the estimated systematic error



Fig. 1. Plots of $ln([trifluralin]_0/[trifluralin]_t)$ versus photolysis time. The loss of trifluralin due to dilution and wall was accounted for (see text).

20% due mainly to the difficulties in data analysis using FTIR. The recommended value for the photolysis rate under our experiment conditions is: $J_{\text{trifluralin}} = (1.2 \pm 0.5) \times 10^{-3} \text{ s}^{-1}$. For both experiments, the photolysis rate of NO₂ was $J_{\text{NO}_2} \approx 8 \times 10^{-3} \text{ s}^{-1}$.

To the best of our knowledge, no UV–Vis absorption spectrum has been reported so far in the gas phase. However, in solution (acetonitrile) the spectrum shows a large absorption in the UV–Vis region (the measured absorption cross sections are $\approx 10^{-17}$ and $\approx 10^{-18}$ cm² molecule⁻¹ at 300 and 450 nm, respectively) (Tagle et al., 2005).

In addition to the photolysis rate, these experiments enabled us to identify some of the photolysis products. HPLC-DAD and TGA analysis indicated the formation of small amounts of formaldehyde, acetaldehyde and propanaldehyde while the IR spectra showed the formation of a product with absorption features close to those of trifluralin indicating that it has similar structure. In the absence of authentic sample, this photolysis product could not be identified (Fig. 2). However, a small peak was detected by GC/MS at trace level in the experiment of 11th July 2003 (where the initial concentration of trifluralin was twice that of the 10th) and its retention time corresponds to α, α, α -trifluoro-2,6-dinitro-*N*-propyl-*p*-toluidine (molecular weight 293).

Fig. 3 shows the concentration-time profiles of trifluralin, 1,3,5-trimethylbenzene and the resulting products (aerosols, aldehydes and unknown product). It shows that the primary photolysis product is also rapidly photolysed by sunlight. Its photolysis rate is estimated from its first order decay: $J \approx 2 \times 10^{-4} \text{ s}^{-1}$. It is not excluded that α, α, α -trifluoro-2,6-dinitro-*N*-propyl-*p*-toluidine and/



Fig. 2. IR spectra obtained during a photolysis experiment of the trifluralin (100703): (a) spectrum of trifluralin; (b) spectrum of the mixture after 5 min of irradiation; (c) spectrum after 20 min of irradiation and (d) spectrum after 1 h 40 min of irradiation.

or α, α, α -trifluoro-2,6-dinitro-*p*-toluidine which were reported in previous studies (Soderquist et al., 1975) could be among the products formed:



 α, α, α -trifluoro-2,6-dinitro-N-propyl-p-toluidine α, α, α -trifluoro-2,6-dinitro-p-toluidine

A number of other compounds have been detected in studies conducted in the laboratory or in the field in different phases (gas, solution or on dust) (Soderquist et al., 1975; Golab et al., 1979; Golab and Occolowitz, 1979; Mabury and Crosby, 1995; Burrows et al., 2002) but not positively identified here.

In addition to the gas phase degradation products reported above, aerosol formation was observed during these photolysis experiments. Particle formation occurred as soon as the trifluralin was exposed to sunlight irradiation. The particle formation – photolysis time profiles showed a rapid increase in the particle concentration (Fig. 3). The initial particles observed had a diameter of about 20 nm followed by a rapid growth leading to particles with a final mean diameter of around 100 nm. A time series of aerosol size distribution measured during the experiment on 110703 is shown in Fig. 4. Aerosol yields on a mass basis were derived of the slope of the linear regression of the corrected aerosol mass against the



Fig. 3. Time-concentrations profiles of trifluralin, 1,3,5-trimethylbenzene (TMB), aerosols and the product formed during a photolysis experiment (110703) of trifluralin.



Fig. 4. Aerosol distribution observed during the photolysis experiment of trifluralin (110703).

amounts of trifluralin reacted. The values of the calculated aerosols yields are $(20 \pm 10)\%$. These yields were obtained after taking into account different loss processes of particles in the chamber such as dilution and wall deposition which were obtained directly after closing the chamber by observing the decay of the aerosols.

Particles were collected on quartz filters when all trifluralin was consumed and analyzed by GCMS. The main product detected in the particle phase is suspected to be 2-ethyl-4-nitro-6-(trifluoromethyl)-1H-benzimidazole since the fragments observed have masses m/z such as 259, corresponding to the molecular ion M, 258 $(M-H)^+$, 244 $(M-CH_3)^+$, 240 $(M-F)^+$, 213 $(M-NO_2)^+$, 212 $((C_8H_4-N_3O_2F_2)^+$ or $(C_{10}H_7N_2F_3))$, 198 $(C_{10}H_7F_3N)^+$ and 185 $((C_7H_3N_2F_2O_2)^+$ or $(C_8H_4N_2F_3)^+)$. Trifluralin was not detected in these filters.



Fig. 5 summarizes the possible photolysis channels based on the literature data (Leitis and Crosby, 1974; Soderquist et al., 1975; Golab et al., 1979) and the finding of this work. The first step of the photolysis of trifluralin may go through a photo-excitation leading to an energetic complex followed by a mechanism that may involve de-alkylation, nitro-reduction and cyclization (Soderquist et al., 1975; Golab et al., 1979; Leitis and Crosby, 1974). The direct observation of formaldehyde, acetaldehyde and propanaldehyde in our experiments confirms the de-alkylation while the suggested detection of 2-ethyl-4-nitro-6-(trifluoromethyl)-1H-benzimidazole (detected in the particle phase) supports the cyclization processes. The mechanism presented in Fig. 5 shows also a number of photolysis channels suggested by previous studies in solution and/or on surface of different materials as well as in the gas phase. However, it has to be noticed that we are not able to confirm the formation of these products in our experimental conditions.



Fig. 5. Possible channels for trifluralin photolysis.

3.2. Reaction of trifluralin with HO[•] radicals

Since it was found that the photolysis of trifluralin was a very fast process under sunlight conditions, HO[•] radicals were generated in the dark using the ozonolysis of 2,3-dimethyl, 2-butene ($(CH_3)_2C=C(CH_3)_2$) as the OH radicals source (Siese et al., 2001).

First, checks were made to find out about the reactivity of ozone with trifluralin. Independent runs were made where known amounts of both reactants (typically 50 ppbv of trifluralin and 150 ppbv of ozone) were introduced into the chamber and their concentrations monitored versus reaction time. The loss of trifluralin in the presence of ozone was found not discernible from that in its absence which enabled us to estimate an upper limit for the rate constant of the reaction of ozone with trifluralin of $k(O_3 + \text{trifluralin}) < 1 \times 10^{-17} \text{ cm}^3$ molecule⁻¹ s⁻¹. This low value indicated that, in our experimental conditions, the presence of ozone will not interfere in the k_{HO} measurement while using the reaction $O_3 + (\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$ as HO' source.

The rate constant for the HO reaction with trifluralin was determined using the conventional relative rate method where 1,3,5-Trimethylbenzene (TMB) was the reference compound:

HO' + trifluralin \rightarrow products (k_{HO}) HO' + TMB \rightarrow products (k_{TMB})

 $k_{\rm HO}$ and $k_{\rm TMB}$ are the rate coefficients of HO[•] reaction with trifluralin and TMB, respectively. Assuming that the reaction with OH is the only significant loss process for both trifluralin and reference, it can be shown that:

$$\ln\left(\frac{[\text{trifluralin}]_0}{[\text{trifluralin}]_t}\right) = \left(\frac{k_{\text{HO}}}{k_{\text{TMB}}}\right) \times \ln\left(\frac{[\text{TMB}]_0}{[\text{TMB}]_t}\right)$$
(3)

where the subscripts 0 and t indicate concentrations at the start of the experiment and at reaction time t, respectively. Taking into account the leak rate, k_1 , and the wall loss rate, k_{wl} , of trifluralin (no significant wall loss of TMB could be observed in our experimental conditions), we have then:

$$\ln \left(\frac{[\text{trifluralin}]_{0}}{[\text{trifluralin}]_{t}} \right) - (k_{1} + k_{\text{wl}}) \times t$$
$$= \left(\frac{k_{\text{HO}}}{k_{\text{TMB}}} \right) \times \ln \left(\frac{[\text{TMB}]_{0}}{[\text{TMB}]_{t}} \right) - k_{1} \times t$$
(4)

The initial concentrations of trifluralin, TMB and ozone were (42.6–56.9), (71.8–75) and (255–300) ppbv, respectively. The loss of trifluralin and TMB were monitored using FTIR spectroscopy at 1125-1160 and 828-840 cm⁻¹, respectively.

In Fig. 6 we present the plot $\ln[[trifluralin]_0/[trifluralin]_t] - (k_1 + k_{wl}) \times t$ versus $\ln[[TMB]_0/[TMB]_t] - k_1 \times t$ for the two experiments conducted. The ratios k_{HO}/k_{TMB} derived from the slopes are (0.33 ± 0.04) and (0.28 ± 0.09) for the first and the second run, respectively leading to a mean value of k/k_{TMB} of 0.30 ± 0.07 where the uncer-



Fig. 6. Plots of $\ln[[trifluralin]_0/[trifluralin]_t - (k_1 + k_{wl}) \times t$ versus $\ln[[TMB]_0/[TMB]_t) - k_t \times t$ during kinetic experiments of trifluralin reaction with HO (the slope of the straight lines corresponds to k_{HO}/k_{TMB}).

tainties correspond to 2σ obtained from the least-square analysis. Using a rate constant of 5.67×10^{-11} cm³ molecule⁻¹ s⁻¹ for the reaction HO[•] + TMB (Kramp and Paulson, 1998), the resulting value of k(OH + trifluralin) is $(1.7 \pm 0.4) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹. To our knowledge, this is the first experimental value reported for the rate coefficient of HO[•] reaction with trifluralin in the gas phase.

An additional experiment was performed to look for the reaction products using the following initial concentrations of the reactants: 51 ppbv of trifluralin, 157 ppbv of ozone and 174 ppbv of $(CH_3)_2C=C(CH_3)_2$. No products could be positively identified in the gas phase, however, a non negligible yield of aerosol was observed estimated to be $\approx 15\%$ on a mass basis. Analysis of the collected filters showed the presence of 2-ethyl-4-nitro-6-(trifluorom-ethyl)-1H-benzimidazole in the particle phase. We have also detected a compound with a MS spectrum containing the following main ions: m/z 293 (M⁺), m/z 274 (M-F)⁺, m/z 264 (M-C₂H₅)⁺, m/z 251 (M-C₃H₆), m/z 217 (C₈F₃N₂O₂H₄). This was tentatively attributed to α, α, α -trifluoro-2,6-dinitro-*N*-propyl-*p*-toluidine but could not be checked with a pure sample.

4. Atmospheric implications

The obtained data have been used to estimate the lifetime of trifluralin towards photolysis and reactions with HO[•] radicals and O₃ using the expressions: $\tau_J = 1/J$, $\tau_{\text{HO}} = 1/(k_{\text{HO}}[\text{HO}^{-}])$ and $\tau_{\text{O}_3} = 1/(k_{\text{O}_3}[\text{O}_3])$. Using an HO[•] reaction rate constant of 1.7×10^{-11} cm³ molecule⁻¹ s⁻¹ and an HO[•] concentration ([HO[•]]) of 2×10^6 cm⁻³ (Hein et al., 1997), the lifetime towards HO[•] reaction is calculated to

be 8.5 h. From the upper limit of the reaction with ozone $(k_{O_3} < 1 \times 10^{-17} \text{ cm}^3 \text{ molecule s}^{-1})$, and $[O_3] = 7 \times 10^{11}$ molecule cm⁻³ (Logan, 1985), we have estimated $\tau_{O_3} > 40$ h. Using the measured mean photolysis rate of $J_{\text{trifluralin}} = 1.2 \times 10^{-3} \text{ s}^{-1}$, the lifetime towards the photolysis is about 15 min at ground level (typically for conditions similar to those under which these experiments were conducted). Therefore, it has been concluded that the tropospheric degradation of trifluralin is mainly controled by photolysis with a non negligible contribution of HO reaction.

The atmospheric loss of trifluralin through wet chemistry in hydrometers and in soils are also significant as reported in earlier studies. Hence, it is important to consider all sinks of trifluralin as well as its oxidation products in assessing the tropospheric impact of this widely used pesticide. In addition, both degradation processes of trifluralin (photolysis under sunlight conditions and reaction with HO[•] radicals) have been found to generate organic aerosols with a non negligible yield. However, the mechanism leading to the formation of the observed aerosols is not clear. Therefore, further work is needed to complete the understanding of the chemical pathways of the degradation of trifluralin and similar compounds under atmospheric conditions.

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