



Ozonation of isoproturon adsorbed on silica particles under atmospheric conditions

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HIGHLIGHTS

- ▶ Little is known about the atmospheric heterogeneous processes of pesticides.
- ▶ Heterogeneous ozonation kinetics is faster for lower surface coverage.
- ▶ Isoproturon very likely adsorbs on the solid support in isolated aggregates.
- ▶ Trifluralin is about 20–25-times less reactive to ozone than isoproturon.
- ▶ The lifetime of isoproturon in particulate phase is ca. one week regarding ozone.

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ABSTRACT

The results on heterogeneous ozonation of a phenylurea pesticide, isoproturon, under atmospheric conditions are presented for the first time in the present study. The study was carried out using an experimental device previously adopted and validated for the heterogeneous reactivity of organics toward ozone (Pflieger et al., 2011). Isoproturon was adsorbed on silica particles via a liquid-to-solid equilibrium with a load far below a monolayer (0.02% by weight/surface coverage of 0.5%). The rate constants were estimated by measuring the consumption of the organic (dark, $T = 26\text{ }^{\circ}\text{C}$, $\text{RH} < 1\%$). The experimental data were fitted by both the modified Langmuir–Hinshelwood and the Eley–Rideal patterns, resulting in atmospheric lifetimes of heterogeneous ozonation of 4 and 6 days, respectively (for 40 ppb of O_3). Parameters, such as the number and the quantity of pesticides adsorbed on the solid support, which can significantly influence the heterogeneous kinetics, were investigated as well. The results obtained suggest that the organic compound is adsorbed in multilayer aggregates on the aerosol even though submonolayer coverage is assumed. The presence of a second herbicide, trifluralin, together with isoproturon on the aerosol surface does not affect the kinetics of ozonation, indicating that both compounds are adsorbed on different surface sites of silica particles.

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1. Introduction

As a significant fraction (up to 50% or more) of applied pesticides transfers into the troposphere (Guicherit et al., 1999), comprehensive knowledge of the atmospheric behaviour of these compounds is required to understand their environmental fate. Thus, pesticides can undergo an important atmospheric dissemination from local to global scale (Bidleman, 1988). Because of their usually low or intermediate volatility, these organic compounds predominantly

partition into the gaseous and particulate atmospheric phases. Such partitioning indirectly influences their atmospheric fate by affecting processes such as (photo)chemical degradation (Bidleman, 1999). Although pesticides can be associated with particles, their atmospheric lifetimes are usually estimated from their reactivity in the gaseous phase due to the very limited kinetic data currently available regarding their heterogeneous chemistry (Atkinson et al., 1999). However, it has been shown that the heterogeneous kinetics can differ significantly from that in the gaseous phase (Esteve et al., 2006; Pflieger et al., 2009a). As a result, non-consideration of the reactivity in the particulate phase can lead to a poor estimation of the atmospheric lifetimes of pesticides. In order to understand their atmospheric behaviour, the heterogeneous degradation mechanisms of pesticides should be further investigated.

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During the past years, there has been a surge of interest regarding heterogeneous ozone and OH radicals processing on atmospheric aerosol surfaces (Gäß and Korte, 1978; Parlar et al., 1981; Alebić-Juretić et al., 1990; Palm et al., 1998; Mmereki et al., 2004; Kwamena et al., 2004, 2006; Kahan et al., 2006; Perraudin et al., 2007; Vlasenko et al., 2008; Jammoul et al., 2008; Miet et al., 2009; Pflieger et al., 2009a, 2009b, 2011; Net et al., 2010), but only a few studies have been focused on ozonation of pesticides in the particulate phase (Segal-Rosenheimer and Dubowski, 2007, 2011; Meng et al., 2009, 2010; Pflieger et al., 2009b, 2011; Gan et al., 2010; Yang et al., 2010). Since these studies were performed under various experimental conditions (e.g. nature of the solid support, load of pesticides on the particles, relative humidity, etc.) and with the use of several kinds of experimental devices, a comparison of the kinetic results is quite difficult. For instance, Vlasenko et al. (2008), Jammoul et al. (2008) and Pflieger et al. (2009a,b) carried out their investigations in coated-wall flow tubes, whereas Gäß and Korte (1978), Parlar et al. (1981) and Pflieger et al. (2011) performed the experiments in a rotary evaporator. Similarly, various supports were used as model of atmospheric aerosol: solid organic and salt aerosol (Kwamena et al., 2004), highly disperse silicon dioxide (Palm et al., 1998), silica and graphite particles (Miet et al., 2009) or hydrocarbon soot film (Vlasenko et al., 2008). Thus, since no general conclusions can be derived from these studies, the atmospheric behaviour of pesticides adsorbed on a particulate phase remains poorly understood.

Due to the chemical diversity among the different classes of pesticides, their degradation kinetics might cover a wide range of reaction rates. Thus, in our previous work, we developed an experimental setup adapted for the investigation of both low and high reactive organic compounds towards gaseous ozone (Pflieger et al., 2011). This simple device yields comparable results to those obtained with flow tubes, which are usually used for investigating heterogeneous reactivity (Pflieger et al., 2009b). Consequently, this alternative experimental setup allows us to increase the number of investigations on ozonation of semi-volatile organic compounds such as pesticides, and hence it is possible to better determine the

mechanisms involved as well as atmospheric fate of these compounds.

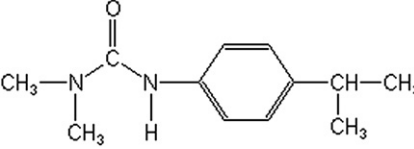
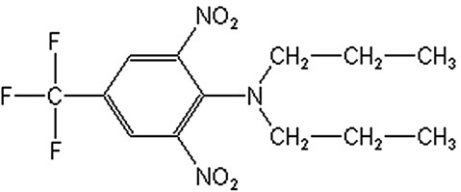
Isoproturon (ISO) is a phenylurea herbicide widely used in agriculture to control broadleaf and grassy weeds in cereals and other crops (Tomlin, 1997). It is usually applied on culture as a concentrate suspension diluted in water. According to Council Directive 91/414/EEC, the use of this pesticide as phytochemical has been approved for 12 years (from 1/1/2003 to 12/31/2015) (European Pesticides Database, 2012). ISO was detected in the atmosphere at urban, rural and remote sites with maximal concentrations of 1.3, 33.0 and 0.7 ng m⁻³, respectively (Sanusi et al., 2000; Baraud et al., 2003; Yusà et al., 2009). Unfortunately, the procedures used in these studies did not allow separate measurements of the gaseous and particulate phases, which is why the herbicide levels correspond to the total concentration of both phases. However, according to Bidleman (1988), organic compounds with a vapour pressure lower than 10⁻⁵ Pa are mainly present in the atmospheric particulate phase, as is the case of ISO (Table 1). The investigation of its atmospheric heterogeneous ozonation is important and therefore all the more justified because its reactivity has not been studied so far.

The aim of the present work was to estimate the ozonation kinetic constant of isoproturon adsorbed on silica particles. The influence of the load of organic compounds on the solid support surface was studied by working with two different amounts of ISO adsorbed on the aerosols. Moreover, the silica particles were covered with a second pesticide, trifluralin (TRIF), in order to observe its possible effect on the degradation rate of ISO. TRIF, a dinitroaniline herbicide, was chosen as the reference compound since its heterogeneous ozonation has already been studied elsewhere (Pflieger et al., 2009b, 2011).

2. Material and methods

The experimental protocol and setup were presented in detail in a previous paper (Pflieger et al., 2011) therefore only a brief description is given here.

Table 1
Structure and physico-chemical characteristics of isoproturon and trifluralin.

Compound	Nature	Chemical class	Vapour pressure at 25 °C (Pa)	Molecular surface area (Å ²) ^c
Isoproturon  (≥99.9%, Fluka analytical, Pestanal)	Herbicide	Phenylurea	3.29 × 10 ⁻⁶ ^a	227
Trifluralin  (≥99.2%, Fluka analytical, Pestanal)	Herbicide	Dinitroaniline	6.11 × 10 ⁻³ ^b	276

^a Tomlin, 1994.

^b Tomlin, 1997.

^c Estimated from the molar volume determined by the "Sparc on-line calculator" (<http://archemcalc.com/sparc/>).

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