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Kinetic of the gas-phase reactions of OH radicals and Cl atoms with Diethyl Ethylphosphonate and Triethyl Phosphate.

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Abstract

In this paper, the relative-rate technique has been used to obtain rate coefficients for the reaction of two organophosphorus compounds: Triethyl phosphate (TEP) and Diethyl ethylphosphonate (DEEP) with OH radicals and Cl atoms at atmospheric pressure and at different temperatures. The calculated rate constants were fitted to the Arrhenius expression over the temperature range 298 – 352 K. The following expressions (in $\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$) were obtained for the reactions of OH and CL with DEEP and TEP: $k_{\text{OH}+\text{DEEP}} = (7.84 \pm 0.65) \times 10^{-14} \exp((1866 \pm 824)/T)$, $k_{\text{OH}+\text{TEP}} = (6.54 \pm 0.42) \times 10^{-14} \exp((1897 \pm 626)/T)$, $k_{\text{Cl}+\text{DEEP}} = (5.27 \pm 0.80) \times 10^{-11} \exp(765 \pm 140/T)$ and $k_{\text{Cl}+\text{TEP}} = (5.23 \pm 0.80) \times 10^{-11} \exp(736 \pm 110/T)$. These results show that the reaction of the studied compounds with Cl atoms proceeds more rapidly than that with OH radicals. The related tropospheric lifetimes suggest that once emitted into the atmosphere, TEP and DEEP can be removed within a few hours in areas close to their emission sources. TEP and DEEP are principally removed by OH radicals. However, in coastal areas where the Cl atoms' concentration is higher, TEP and DEEP removal by reaction with Cl atoms could be a competitive process.

Keywords: Organophosphorus; Hydroxyl radical; Chlorine atoms; rate coefficient; Kinetics; Atmospheric Chemistry.

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1 Introduction

Light organophosphate species are semi-volatile organic compounds. They are characterized by an active center formed by a phosphorus atom surrounded by oxygen atoms and/or alkyl organic groups. They are considered as potential toxicological agents due to the presence of the phosphorylate functional group (P=O) (Miles et al., 1998). They are used in several industrial sectors, particularly those involved in chemical, pharmaceutical and pesticide synthesis (Worthing et al., 1999). They are also used to manufacture plasticizers, flame inhibitors and retardants, (Toy et al., 1987; Hastie et al., 1980; Van der Venn et al., 2012). In addition to these industrial primary sources, the atmospheric degradation of organophosphorothioates constitutes a secondary source of organophosphates species (Aschmann et al., 2006b; Atkinson et al., 1989; Tuazon et al., 2007) the degradation process involves the conversion of a P=S bond to a P=O bond. Once in the atmosphere, organophosphate species can undergo chemical transformations mainly reactions with oxidizing radicals (OH, Cl, NO₃ ...), ultimately contributing to the formation of photochemical air pollution. Contrary to other VOCs, little information exists concerning the gas-phase reactions of organophosphates in the troposphere. Tuazon et al. (1986), Aschmann et al. (2005b; 2006a; 2008) and Atkinson et al. (1988) studied the kinetics of the reaction of alkyl/aryl organophosphates with OH radicals (alkyl= CH₃, C₂H₅; Aryl = OCH₃, OC₂H₅) in gas phase using the relative rate technique. The results obtained from these studies show a slight negative dependence of the rate coefficients on temperature. To our knowledge, the reaction of organophosphorus compounds with Cl has never been reported. Therefore, further laboratory studies are required in order to provide a more profound understating of organophosphorus compounds' atmospheric fate.

The purpose of this work is to investigate the degradation kinetics of two organophosphorus compounds with OH radicals and chlorine atoms as a function of temperature. The studied compounds are Triethyl phosphate (TEP) and Diethyl ethylphosphonate (DEEP). Their chemical structures are given bellow.

Triethyl phosphate TEP

Diethyl ethylphosphonate DEEP

Experiments were conducted using the relative rate method, over the temperature range 298 - 354 K and at a pressure of 760 Torr of purified air. The present work provides the first kinetic data for the reaction of Triethyl phosphate and Diethyl ethylphosphonate with Cl atoms as a function of temperature. Moreover, this study provides additional kinetic parameters for the reaction of these species with OH to be compared to those reported in the literature. Kinetic data determined in this work are used to estimate the effective tropospheric lifetimes of the studied compounds and to assess the importance of the investigated reactions in their atmospheric loss processes.

2 Materials and methods

2.1 Experimental device and conditions

The reactions of TEP and DEEP with OH radicals and Cl atoms were carried out using an atmospheric simulation chamber coupled to an FTIR spectrometer. The experimental setup and the procedures used for data analysis have been previously described (Messaadia et al., 2013; Al Rashidi et al., 2014), and thus, will only be briefly discussed here. The chamber is composed of a triple-jacket Pyrex cell (length 2 m, internal diameter 20 cm) equipped with a multiple reflection system. This system is located in the inner chamber and consists of a White cell equipped with three gold mirrors located at both ends of the cell. These mirrors were used to regulate the path length of the probe beam between 8 and 80 m. The cell was connected to a primary pump that can achieve a pressure of 10^{-3} mbar. The chamber temperature was regulated through the circulation of a thermostatic fluid (water or ethanol) between the inner wall and the second jacket. A Julabo FPW 90 thermostat commands the fluid circulation and regulates its temperature (working temperature range is 280–355 K). The temperature and the pressure in the cell were respectively measured by a thermocouple and MKS Baratron manometer with a 0–1000 Torr full scale. 24 UV lamps emitting in the 300–400 nm range were symmetrically disposed around the reactor cell to ensure homogeneous photolysis of the reactants. An FTIR spectrometer (Equinox 55 from Bruker ©) which operates in the spectral range of 600–4000 cm^{-1} with a spectral resolution of 2–0.5 cm^{-1} was used to analyse the gaseous mixture in the reactor. OH radicals were generated by the photolysis of nitrous acid which was produced via the drop-wise addition of 5% sulfuric acid solution to a 0.5 M sodium nitrite solution. A small flow of purified air was used to carry the generated nitrous acid into the reactor. Meanwhile, Cl atoms were generated by the photolysis of Cl_2 at 300–400 nm. Before starting kinetic studies, concentration stability tests of DEEP

and TEP in the absence of photolysis were carried out and show that wall losses were negligible. Experimental conditions are summarized in Tables 1 and 2.

The measurements were performed in purified air provided by Air Liquide (> 99.9999%). The reagents used had the following purities as given by the manufacturer and were further purified before use: Triethyl phosphate (99.8%, Sigma-Aldrich), Diethyl ethyl phosphonate (99.8%, Interchim), benzaldehyde (99.5%, Sigma-Aldrich), dioxane (99.8%, Sigma-Aldrich), ethanol (99.8%, Sigma-Aldrich), n-heptane (99.5%, Across).

2.2 Methods

Rate constants of the reactions of OH radicals and Cl atoms with organophosphorus compounds (OPC) were determined using the relative rate method; i.e. the rate coefficients of the investigated reactions were determined relative to those of selected reference compounds. The reactions involved were as follows:

Since no reaction with cell walls or photolysis occurred, the organophosphorus and the reference compounds reacted only with OH radicals or Cl atoms. Therefore, the rate constants are determined according to the following equation (1):

$$\ln \left(\frac{[\text{OPC}]_0}{[\text{OPC}]_t} \right) = \frac{k_{\text{OPC}}}{k_{\text{ref}}} \left[\ln \frac{[\text{ref}]_0}{[\text{ref}]_t} \right] \quad (1)$$

where $[\text{OPC}]_0$ and $[\text{ref}]_0$ are the DEEP or TEP and the reference concentrations at time t_0 , respectively, $[\text{OPC}]_t$ and $[\text{ref}]_t$ are the corresponding concentrations at time t . k_{OPC} and k_{ref} are the second order rate coefficients of the OH-oxidation or Cl-oxidation reactions of organophosphorus and the reference compounds. The plot of $\frac{[\text{OPC}]_0}{[\text{OPC}]_t}$ as a function of $\frac{[\text{ref}]_0}{[\text{ref}]_t}$ should correspond to a linear curve, passing through the origin, the slope of which is equal to $k_{\text{OPC}}/k_{\text{ref}}$. Knowing k_{ref} , it is possible to determine k_{OPC} , the rate constant of the oxidation of the organophosphorus species by OH radicals or Cl atoms. During an experiment, spectra were recorded every 3 minutes. Each spectrum constitutes the average of 20 accumulated spectra resulting in a signal to noise ratio of ~15. The OPC and the reference degradation kinetics were measured by monitoring the evolution of the absorption band areas of both

compounds as a function of time. The absorption bands whose areas were monitored are indicated in tables 1 and 2. The reference compounds were chosen so that their rate coefficients are well documented in the literature and are of the same order of magnitude as those of the investigated compounds. In addition, the reference compound should have an FTIR spectrum exhibiting at least one spectral band that does not interfere with the studied compound's spectrum. Benzaldehyde was chosen as a reference compound for the study of OH-oxidation of TEP and DEEP; whereas dioxane, ethanol and heptane were used as references in the case of Cl-oxidation. The rate expressions of the reference reactions used in this study are (in $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$): $k(\text{benzaldehyde}+\text{OH}) = 5.33 \times 10^{-12} \exp(243/T)$ (Semadeni et al., 1995) ; $k(\text{dioxane}+\text{Cl}) = (1.91 \pm 0.20) \times 10^{-10}$ (Li et al., 2006) ; $k(\text{ethanol}+\text{Cl}) = (1.09 \pm 0.12) \times 10^{-10}$ (Taatjes et al., 1999,) ; $k(\text{heptane}+\text{Cl}) = (3.50 \pm 0.13) \times 10^{-10}$ (Anderson et al., 2007).

3. Results

3.1 Degradation kinetics of DEEP and TEP with OH

The following reactions were studied and the corresponding rate coefficients were measured:

Figures 1a and 1b show the plots of $\frac{[\text{OPC}]_0}{[\text{OPC}]_t}$ vs $\frac{[\text{ref}]_0}{[\text{ref}]_t}$ at different temperatures for the reaction of OH radicals with DEEP and TEP, respectively. Good linearity is observed with a correlation coefficient greater than 95%. The rate coefficients obtained are reported in table 3. The values presented in table 3 are derived from the average of 2 to 4 independent kinetic experiments. The average rate coefficients of OH-oxidation are $k_{\text{DEEP}+\text{OH}} = (3.6 \pm 1.1) \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ and $k_{\text{TEP}+\text{OH}} = (3.4 \pm 1.0) \times 10^{-11} \text{ cm}^3\text{molecule}^{-1}\text{s}^{-1}$ at 305 K. The Arrhenius plots derived from the experimental rate coefficients are represented in Figures 2a and 2b. As can be seen, the rate constants of these reactions decrease significantly when the temperature increases (Table 3). Least-square analysis of the rate coefficients obtained at different temperatures leads to the following Arrhenius equations (in $\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$):

$$k_{\text{DEEP}+\text{OH}} = (7.84 \pm 0.65) \times 10^{-14} \exp(1866 \pm 824/T)$$

$$k_{\text{TEP}+\text{OH}} = (6.54 \pm 0.42) \times 10^{-14} \exp(1897 \pm 626/T).$$

3.2 Degradation kinetics of DEEP and TEP with Cl

DEEP and TEP degradations with Cl atoms were also studied at different temperatures:

Since this study provides the first kinetic data for the reaction of DEEP and TEP with Cl atoms; more than one reference was used for each reactant, thus ensuring the precision of the obtained results. As can be seen in Figures 3a and 3b good linear plots were obtained for the reaction of Cl atoms with OPC. The TEP versus ethanol plot is relatively noisy in comparison with other plots. This could be due to the integration of IR band of ethanol, whose reactivity is low, regarding Cl atoms, compared to TEP. Although, if there is some fluctuation in the TEP versus ethanol plots, the linearity of TEP versus all references plot in Figure 3a were obtained with a correlation coefficients greater than 90 %. In addition as can be seen in Table2, the obtained rate coefficients, with different references, present a difference of 20%. The origin of the discrepancy may be due to experimental errors coming from the treatment of experimental measurements especially IR bands integration. Although, these differences are acceptable since there is an overlap of the error bars of the determinations. At room temperature (298 K), the average rate coefficients for the reactions with Cl atoms were as follows (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): $k_{\text{DEEP}+\text{Cl}} = (6.60 \pm 0.30) \times 10^{-10}$ and $k_{\text{TEP}+\text{Cl}} = (6.40 \pm 0.40) \times 10^{-10}$. The rate coefficients obtained at different temperatures are summarized in Table 3. As in the case of OH-oxidation, each value is derived from the average of 2 to 4 independent kinetic experiments. The Arrhenius plots are displayed in Figure 4 and the related Arrhenius equations obtained by least-square analysis for the reactions of Cl atoms with DEEP and TEP (in $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) are given below:

$$k_{\text{DEEP}+\text{Cl}}(T) = (5.27 \pm 0.80) \times 10^{-11} \exp(765 \pm 140/T)$$

$$k_{\text{TEP}+\text{Cl}}(T) = (5.23 \pm 0.80) \times 10^{-11} \exp(736 \pm 110/T).$$

4 Discussion

4.1 Error analysis

The error bars, shown in figures 2 and 4, vary from 9 to 19%. These values represent the systematic errors associated with uncertainties in the experimental results, particularly those related to the integration of the spectral absorption bands. The overall uncertainties on the rate coefficient are calculated using error propagation method according to the relation:

$$\Delta k_{OPC} = k_{OPC} \sqrt{\left(\frac{\Delta k_{ref}}{k_{ref}}\right)^2 + \left(\frac{\Delta R}{R}\right)^2} \quad (6)$$

Where k_{ref} , Δk_{ref} are the reference rate coefficient and its uncertainty, respectively, $R=k_{OPC}/k_{ref}$ is the slope of the linear data fit and ΔR its uncertainty. the sources of error in this work are mostly related to:

- i) the determination of k_{ref} : this error is taken from the literature and varies from 4 to 30% depending on the reference compound,
- ii) the determination of the slope $R=k_{OPC}/k_{ref}$, which is directly related to experimental data. This error was minimized by the repetition of experiments, the use of different references and the choice of spectral bands. In this work, the slope uncertainty varies between 3% and 11%.

4.2 Effect of the temperature

The rate coefficient values obtained at different temperatures show that the reactivity between the organophosphorus compounds (DEEP and TEP) and OH radicals or Cl-atoms exhibits negative temperature dependence. This trend is in good agreement with the observations of Aschmman et al (2006a) who suggest that the initiation step involved in OH-oxidation does not have an activation energy barrier and that the mechanism proceeds via the formation of an organophosphorus-OH adduct. The temperature dependence of the rate coefficients corresponding to oxidation by Cl-atoms is also highly negative, indicating that reaction with Cl proceeds via a mechanism similar to that of OH-oxidation. Furthermore, the effect of the temperature is more pronounced in the case of the OH reaction with DEEP or TEP than in the case of Cl-atoms reaction. Indeed a temperature increase of 50 K leads to a 60% decrease in the rate coefficient of OH-oxidation, compared to a 30% decrease in the rate coefficient of oxidation by Cl-atoms.

4.3 Comparison with previous study

The room temperature rate coefficient for the reaction of TEP with OH radicals has been reported in four previous studies carried out at atmospheric pressure in purified air using a relative method (Aschmann et al. 2008, Aschmann et al. 2006a, Aschmann et al. 2005b, Atkinson et al. 1988). The rate coefficient obtained in these studies varies from 5.0 to $5.5 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$. The difference between our value and those reported in the literature is around 35% (Figure 2). Concerning the reaction of DEEP with OH radicals, the room temperature rate coefficient reported in the literature using the relative method varies between 5.4 and $6.5 \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (Aschmann et al. (2005a, 2006a, 2008)). The value measured in this work is about 40% lower than those reported in the literature (Figure 2).

Figures 2a and 2b show the Arrhenius plots and the related error bars of the kinetic constants determined in this study compared to those obtained by Aschmann et al. (2008). The differences observed between our values and those referenced and cited above are usually included in the domain of error. However, this difference increases up to 44 - 48% when the temperature increases. Still, both sets of values are of the same order of magnitude (Aschmann et al. (2008 and 2006a)).

To the best of our knowledge, no data currently exists in the literature regarding the kinetics of oxidation of TEP and DEEP by Cl-atoms.

4.4 Reactivity trend

In accordance with previous studies (Aschmann 2005a), it has been shown that, at room temperature, DEEP is slightly more reactive towards OH radicals than TEP. Moreover, the OH-reactivity of TEP at 296 K is five times greater than that of trimethyl phosphate (TMP), a compound of similar structure (Tuazon et al. 1986). This comparison shows that, as expected, the OH-reactivity increases when the methyl groups in TMP are replaced by ethyl groups in TEP. Similarly, the rate constants of OH-oxidation of DEEP are compared to those of the structurally similar diethyl methylphosphonate compound (DEMP). Two values of $k_{\text{DEMP}+\text{OH}}$ are reported in the literature: $(3.23 \pm 0.11) \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (Kleindienst and Smith 1996) and $(5.53 \pm 0.66) \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$ (Aschmann et al., 2006a). When compared to Kleindienst and Smith's value, the rate constant measured herein ($k_{\text{DEEP}+\text{OH}} = (3.6 \pm 1.1) \times 10^{-11} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$) is slightly greater (10%), which suggests that, as reported previously by Aschmann et al. (2005b), the substitution of an ethyl group by a methyl group might favor reactivity. However, this behavior is not observed when we compare our value

with the rate constant of DEMP determined by Aschmann et al. (2006a). This can be explained by the difference observed between our determinations and those of Aschmann et al. (2006a). Indeed, our rate constant value for the reaction of OH radicals with DEEP is about 40% lower than those of Aschmann et al. (2006a).

Regarding the reactions of Cl atoms with the OPCs investigated in this study, the rate constants are approximately one order of magnitude higher than those of the corresponding reactions with OH radicals. This enhancement can be explained by the strong electronegativity of Cl atoms which facilitates H-abstraction. Moreover, it appears that the reactivities of DEEP and TEP towards Cl atoms are similar in the temperature range 298-353 K and it seems that no significant effect is observed when C₂H₅O is replaced by a C₂H₅ group. Considering, that (i) the chemical structure effect on the reactivity of the OP toward Cl atoms is negligible, (ii) the estimation of the gas kinetic limit of the reaction of OP studied in this work toward chlorine atoms is around 7.0×10^{-10} , the reaction between OP compounds and chlorine atoms occurs with a high probability close to gas kinetic limit collision. As high rate coefficients toward Cl atoms have been determined for other organic compounds, particularly larger biogenic compounds (Finlayson-Pitts et al., 1999).

5. Atmospheric implications

The tropospheric lifetimes of TEP and DEEP relative to reactions with OH and Cl can be estimated from the kinetic constants obtained in this work according to the equation:

$$\tau_{Ox} = \frac{1}{k_{Ox}[Ox]} \quad (7)$$

where k_{Ox} is the second order rate constant of the oxidation of organophosphorus compounds by OH or Cl radicals and [Ox] is the concentration of the oxidant. Using a global daytime average tropospheric OH concentration (molecule per cm³) of 10^6 (Finlayson-Pitts et al. 2000) the calculated lifetimes of DEEP and TEP relative to OH-radicals are 6.7 and 7.3 hours, respectively (Table 4). Atmospheric lifetimes of 18 and 21 days for DEEP and TEP, respectively were estimated using a 24 h daytime average global tropospheric Cl[•] concentration of 1×10^3 molecule cm⁻³ (Singh et al., 1996) (Table 4). These values indicate that reaction with OH is the main loss process of these species in the troposphere. However, in coastal areas where the concentration of Cl atoms reaches 1×10^5 molecule cm⁻³ (Spicer et al., 1998), the tropospheric lifetimes incurred by Cl-oxidation are less than 1 day (4.3 hours for TEP and 5.1 hours for DEEP) (Table 4). In these areas, the contribution of Cl atoms to the

removal of OPCs seems to be important. According to the calculated lifetimes of TEP and DEEP, these species can be considered non-persistent in the atmosphere. Thus their atmospheric impact is significant in areas near to their emission sources.

6. Conclusion

The degradation kinetics of organophosphorus compounds namely TEP and DEEP relative to OH radicals and Cl atoms has been investigated as a function of temperature, using the relative method. This work represents the first reported kinetic study of the reaction of Cl atoms with TEP and DEEP.

The data measured here shows that the reaction of the studied compounds with Cl atoms proceeds more rapidly than that with OH radicals. The kinetic reactions of these compounds with OH radicals were found to be more sensitive to the structure than those with Cl atoms. The rate coefficients measured herein show negative temperature dependence, which is more pronounced in the case of OH-oxidation.

The atmospheric lifetimes of the investigated compounds were estimated relative to OH and Cl using the kinetic data obtained in this work. The calculated tropospheric lifetimes suggest that once emitted into the atmosphere, TEP and DEEP can be removed quite rapidly in areas close to their emission sources.

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Table 1 : Experimental conditions used for the reactions of DEEP and TEP with OH radicals in the Pyrex simulation chamber coupled to a FTIR spectrometer.

	DEEP + OH → products	TEP + OH → products
Temperature (K)	305-354	296-352
Pressure (Torr)	760	760
Reference compound	benzaldehyde	benzaldehyde
Optical path (m)	56-64	56-64
[compound] (ppm)	10-50	10-50
[reference] (ppm)	10-50	10-50
Spectral range: product (cm ⁻¹)	910-990	940-980
Spectral range (cm ⁻¹): benzaldehyde	2700-2850	2700-2850

Table 2 : Experimental conditions used for the reactions of DEEP and TEP with Cl atoms in the Pyrex simulation chamber coupled to a FTIR spectrometer (*only at room temperature).

	DEEP + Cl → products	TEP + Cl → products
Temperature (K)	298-351	298-349
Pressure (Torr)	760	760
Reference compounds	Ethanol *	Ethanol *
	n-heptane *	n-heptane *
	1,4 dioxane	1,4 dioxane
Optical path (m)	56-64	56-64
[compound] (ppm)	10-50	10-50
[reference] (ppm)	10-50	10-50
Spectral range: product (cm ⁻¹)	910-860	920-1000
Spectral range (cm ⁻¹): Ethanol	845-910	845-910
n-heptane	1430-1502	1430-1486
1,4 dioxane	925-990	1342-1380

Table 3: The average rate coefficients for reaction of organophosphorus compounds with OH and Cl obtained in this work. (*) correspond to the weighted average values.

	Reference	Temperature (K)	k/kref	k ($10^{-10} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$)
DEEP + OH	benzaldehyde	305 ± 2	3.0 ± 0.3	0.36 ± 0.11
		319 ± 2	2.4 ± 0.1	0.28 ± 0.08
		330 ± 2	2.0 ± 0.2	0.22 ± 0.06
		335 ± 2	1.7 ± 0.1	0.19 ± 0.05
		352 ± 2	1.5 ± 0.1	0.16 ± 0.04
TEP + OH	benzaldehyde	296 ± 2	3.4 ± 0.1	0.41 ± 0.12
		305 ± 2	2.9 ± 0.3	0.34 ± 0.10
		321 ± 2	1.9 ± 0.1	0.22 ± 0.06
		336 ± 2	1.8 ± 0.1	0.19 ± 0.05
		352 ± 2	1.4 ± 0.1	0.15 ± 0.04
DEEP + Cl	ethanol	298 ± 2	5.9 ± 0.1	6.4 ± 0.7
	heptane	298 ± 2	1.9 ± 0.1	6.7 ± 0.4
	dioxane	298 ± 2	3.3 ± 0.1	6.4 ± 0.7
				6.6 ± 0.3 (*)
		313 ± 2	3.3 ± 0.4	6.4 ± 0.8
		338 ± 2	2.7 ± 0.4	5.2 ± 0.8
		351 ± 2	2.3 ± 0.3	4.5 ± 0.5
TEP + Cl	ethanol	298 ± 2	5.1 ± 0.1	5.6 ± 0.6
	heptane	298 ± 2	2.0 ± 0.1	7.0 ± 0.5
	dioxane	298 ± 2	3.0 ± 0.1	5.8 ± 0.6
				6.4 ± 0.4 (*)
		316 ± 2	2.6 ± 0.4	5.1 ± 0.9
		330 ± 2	2.5 ± 0.4	4.9 ± 0.9
		349 ± 2	2.3 ± 0.4	4.4 ± 0.8

Table 4: Lifetimes of DEEP and TEP at 298 K

	τ_{OH}^a	τ_{Cl}^b
DEEP	6.7 hours	4.3 hours to 18 days
TEP	7.3 hours	5.1 hours to 21 days

^a $[\text{OH}] = 10^6 \text{ molecule} \cdot \text{cm}^{-3}$; ^b $[\text{Cl}] = 10^3 \text{ to } 10^5 \text{ molecule} \cdot \text{cm}^{-3}$

Figure 1a : Relative rate plots for the reaction of OH radicals with DEEP at different temperatures.

Figure 1b : Relative rate plots for the reaction of OH radicals with TEP at different temperatures.

Figure 2a : Arrhenius plots for the reaction of OH radicals with TEP.

Figure 2b : Arrhenius plots for the reaction of OH radicals with DEEP.

Figure 3a : Relative rate plots for the reaction of Cl atoms with DEEP and several reference compounds at room temperature.

Figure 3b : Relative rate plots for the reaction of Cl atoms with TEP and several reference compounds at room temperature.

Figure 4: Arrhenius plots for reactions of Cl atoms with DEEP and TEP.

- This work provides the kinetic reaction of two organophosphorus compounds with Cl and OH radicals.
- Studies were carried out over the temperature ranges 298-333 K.
- Results are compared to those found in literature, reactivity trends are discussed
- Effects of temperature and structure and the atmospheric implications are discussed