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Kinetics of the photolysis and OH reaction of 4-hydroxy-4-methyl-2-pentanone: Atmospheric implications

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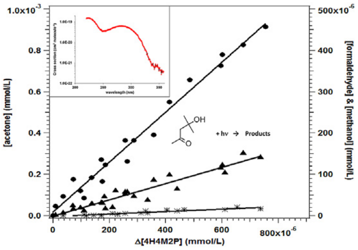
HIGHLIGHTS

- This work provides the kinetic of the photolysis and OH reaction of 4H4M2P.
- Slight negative temperature dependence in the OH + 4H4M2P reaction kinetics.
- Results are compared to those found in literature.
- The tropospheric lifetimes of this compound is estimated.

GRAPHICAL ABSTRACT



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ABSTRACT

This study provides the first kinetic and mechanistic study of the photolysis of 4-hydroxy-4-methyl-2-pentanone (4H4M2P) and the determination of the temperature dependence of the relative rate coefficient for the reaction of OH radicals with 4H4M2P. The UV absorption spectrum of 4H4M2P was determined in the spectral range 200–360 nm. The photolysis frequency of this compound in the atmosphere was evaluated relative to actinometers and found to be $J^{atm}_{4H4M2P} = 4.2 \times 10^{-3}\ h^{-1}$, corresponding to a lifetime of about 10 days. Using 4H4M2P cross section measurements, an atmospheric effective quantum yield of 0.15 was calculated. The main primary photolysis products were acetone (121 ± 4) % and formaldehyde (20 ± 1) %. A low methanol yield of (3.0 ± 0.3) % was also determined. These results enabled us to propose a mechanistic scheme for the photolysis. Rate coefficients for the reaction of 4H4M2P with OH radicals were determined over the temperature range 298–354 K and the following Arrhenius expression was obtained: $k_{OH+4M4H2P} = (1.12 \pm 0.40) \times 10^{-12} \exp(461.5 \pm 60/T)$ $cm^3\ molecule^{-1}\ s^{-1}$. The lifetimes of 4H4M2P due to reaction with OH radicals has been estimated to ~2.5 days and indicates that the gas-phase reaction with the OH could be the main loss process for this compound.

1. Introduction

Hydroxyketones constitute a sub-family of carbonyl compounds. They can be emitted as primary pollutants into the atmosphere by the use of paints, solvents and disinfectants. They are also formed *in situ* as secondary pollutants from the oxidation of

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alkanes, alkenes, and other oxygenated compounds (Calvert et al., 2011). Their subsequent atmospheric fate is elimination by dry and/or wet deposition (Finlayson-Pitts and Pitts, 2000) and oxidation through chemical reactions largely initiated by reaction with the OH radical (Atkinson, 1989). Besides oxidation by OH radicals, direct solar photolysis of hydroxyketones may represent a significant degradation pathway and source of free radicals in the atmosphere. It should be noted that several studies have underlined the difficulties to satisfactorily model radical levels in the atmosphere, invoking possible lacking sources of radicals (Wolfe et al., 2014; Stone et al., 2012; Kanaya et al., 2012). In addition, OH reactivity measurements often disagree with models, the reasons invoked being unmeasured secondary oxygenated reaction products (Yang et al., 2016).

In their study of 3-hydroxy-3-methyl-2-butanone (3H3M2B), Bouzidi et al. (2014) compared the kinetics of OH reaction and photolysis and concluded that photolysis may be the major gas-phase degradation loss of 3H3M2B in the atmosphere, producing acetone and formaldehyde as main products. Conversely, for 4-hydroxy-2-butanone (4H2B), photolysis is negligible and OH initiated oxidation represents the main fate (Bouzidi et al., 2015), due to both a higher OH reactivity and a lower photo-activity compared to 3H3M2B. In their analysis of summertime photochemistry during the measurement campaign CAREBeijing in 2007, Liu et al. (2012) reported that the photolysis of oxygenated volatile organic compounds is the largest primary peroxy radical source in Beijing urban atmosphere. Thus, further evaluation of the importance of hydroxyketone photolysis in the atmosphere is required.

In this work, we report on the reactivity of 4-hydroxy-4-methyl-2-pentanone (4H4M2P, also called diacetone alcohol) towards OH radicals and direct photolysis. This colorless compound is used in many industrial applications such as paints and glues, and is an intermediate in organic synthesis. 4H4M2P was also shown to be produced in the gas-phase OH radical-initiated reactions of methyl-alcohols with yields around 0.2 (Atkinson and Aschmann, 1995). The OH radical kinetics has been investigated only at ambient temperature using relative (Atkinson and Aschmann, 1995; Magneron et al., 2003) and absolute rate methods (Sleiman et al., 2013) and displayed good agreement with an average rate coefficient of 4.2×10^{-12} cm^3 $molecule^{-1}$ s^{-1}. Magneron et al. (2003) measured the absorption spectrum from 234 nm up to 330 nm and found a maximum at 282 nm ($\sigma = 8.91 \times 10^{-20}$ cm^2 $molecule^{-1}$), indicating that 4H4M2P may be photolyzed in the atmosphere. The only experiment was performed under natural sunlight at the Euphore atmospheric simulation chamber and allowed only to estimate an upper limit of the photolysis rate ($<5 \times 10^{-6}$ s^{-1}, Magneron et al. (2003)). Therefore, the objective of this work is to bring relevant information on the atmospheric fate of 4H4M2P and enrich databases on the kinetic of oxygenated species. The experiments were carried out using two different experimental setups. The reaction with OH was investigated at GSMA-Reims at 760 Torr of purified air and in the temperature range of 298–354 K. The photolysis study was conducted at SAGE-Douai at 298 K and 760 Torr of purified air. This work provides the first kinetic data for the reaction of 4H4M2P with OH as a function of temperature, using relative method, and the first data concerning the product yields of the photolysis reaction of 4M4H2P. The kinetic data obtained in this work were used to estimate the effective lifetimes in the troposphere of the studied compound. In addition, based on the identified photolysis products, we propose a photolysis mechanism.

2. Experimental section

Photolysis experiments were carried out at SAGE in a Teflon environmental simulation chamber while OH reaction experiments were performed at GSMA in a Pyrex reactor. Both setups were described in details in previous publications (Bouzidi et al., 2014; Szabo et al., 2011) and thus, only essential features are recalled in the next paragraphs.

2.1. UV-absorption experiments (GSMA)

The technique used for the measurements of cross-sections has been described in a previous paper (Messaadia et al., 2012). It will be briefly reviewed here.

Cross sections were measured using a double-jacket multiple path cell made of stainless steel, 100 cm in length and 10 cm in diameter, equipped with quartz windows. The light source consists of a 30 W deuterium lamp providing a continuum extending from 200 to 400 nm. To obtain a monochromatic light, the light is focused through a lens into a Jobin-Yvon monochromator (focal length: 245.76 mm, aperture: F/4.1, blazed grating: 1200 lines/mm, dispersion: 3 nm/mm, resolution: 0.1 nm). The exiting beam multipassed through the absorption cell and the light intensity was measured by a Hamamatsu R 955 photomultiplier tube. The temperature inside the cell was regulated by the circulation of thermostated water and was measured by several Pt sensors. The pressure inside the cell was measured by a (0–10) Torr MKS Baratron manometer. All experiments were carried out under static conditions. Before each experiment, the residual background dark current $I_n(\lambda)$ and the light intensity $I_0(\lambda)$ were measured at each wavelength in the absence of the studied compounds, i.e. with vacuum in the absorption cell. The transmitted intensity $I(\lambda)$ is then measured at each wavelength in the presence of the studied compound. The absorption cross-sections were calculated according to Beer Lambert's law, assuming the gas is perfect. Thus, the cross-section $\sigma(\lambda)$ at wavelength (λ) in (cm^2 $molecule^{-1}$) is given by:

$$\sigma_\lambda = \ln\left(\frac{I_0(\lambda) - I_n(\lambda)}{I(\lambda) - I_n(\lambda)}\right) \times \frac{R \times T}{P \times l \times N_A} \tag{1}$$

where l is the optical path, R the perfect gas constant, T the temperature, P the pressure and N_A the Avogadro's constant.

Several experiments were carried out between 200 and 350 nm and the pressure range of 0.1–0.7 Torr. Experiments were carried out at 348 K to avoid condensation. The optical path can be varied between 4 and 12 m. To get an optical density between 1.5 and 0.05, pressure and absorption length are adjusted for each scanning region. Following each run, the cell was evacuated and purged with N_2 and $I_0(\lambda)$ was recorded to check the stability of the light source during a sequence of measurements.

2.2. Photolysis experiments (SAGE)

The 300 L Teflon reactor is surrounded by 9 actinic tubes (T-20M Vilber-Lourmat) emitting between 275 nm and 330 nm with a maximum at 312 nm (Fig. S1). All experiments were performed at 298 K and atmospheric pressure. In a typical experiment, an aliquot of 4H4M2P is evaporated in a low pressure, slightly heated Pyrex line and directly flushed to the reactor. After completion by zero air, the chamber is left in the dark for about one hour to stabilize. Then, three samples are taken to determine the initial concentration of 4H4M2P. Photolysis experiments lasted about 8 h and the concentration of 4H4M2P was measured every hour by Fourier Transform Infrared (FTIR) spectroscopy using a 2 L White-type multireflection cell with 10 m optical pathlength. Carbonyl products were analyzed by sampling every hour on DNPH cartridges followed by liquid chromatography. Five experiments were carried out in the presence and eight experiments in absence of a