Kinetic and product studies of Cl atoms reactions with a series of branched Ketones

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The rate constants for the Cl atom reaction with three branched ketones have been measured at 298 ± 2 K and 760 Torr using the relative rate method in the absence of NO. The rate constants values obtained (in units of 10^{-10} cm^3/(molecule·sec)) are: $k_{(2\text{-methyl-3-pentanone})}$ = 1.07 ± 0.26, $k_{(3\text{-methyl-2-pentanone})}$ = 1.21 ± 0.26, and $k_{(4\text{-methyl-2-pentanone})}$ = 1.35 ± 0.27. Combining the chemical kinetic data obtained by this study with those reported for other ketones, a revised Structure Activity Relationship (SAR) parameter and R group reactivity (k_R) of R(O)R′ and CHx (x = 1, 2, 3) group reactivity (k_{CHx}) toward Cl atoms were proposed. In addition, the products from the three reactions in the presence of NO were also identified and quantified by using PTR-ToF-MS and GC-FID, and the yields of the identified products are: acetone (39% ± 8%) + ethanal (78% ± 12%), 2-butanone (22% ± 2%) + ethanal (75% ± 10%) + propanal (14% ± 1%) and acetone (26% ± 3%) + 2-methylpropanal (24% ± 2%), for Cl atoms reaction with 2-methyl-3-pentanone, 3-methyl-2-pentanone and 4-methyl-2-pentanone, respectively. Based on the obtained results, the reaction mechanisms of Cl atoms with these three ketones are proposed.

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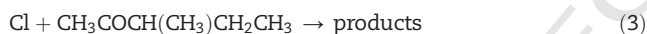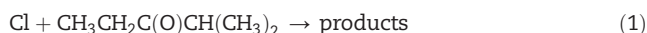
Introduction

Similar to other oxygenated volatile organic compounds (oVOCs), ketones play an important role in the atmospheric chemistry (Mellouki et al., 2015). Large amount of ketones are released into the atmosphere as primary pollutants from partial oxidation of hydrocarbons fuels, from industries where they are widely used (i.e., solvents and chemical intermediates) and from vegetation. Once in the atmosphere, they are decomposed through photolysis by sunlight radiations and/or by chemical reactions with the main atmospheric oxidants (OH radicals, Cl atoms, NO$_3$ radicals and O$_3$, the latter two reactions being important for the unsaturated compounds). The Cl atom reactions play an important role in the overall degradation processes of ketones in specific areas where Cl atom concentrations have been reported to be high enough to compete with photolysis and reaction with OH radicals (Thornton et al., 2010; Faxon and Allen, 2013). Although the global estimation of Cl atom concentration in the northern hemisphere is orders of magnitude lower than the ambient OH concentration (Arsene et al., 2007), Cl atoms may compete with OH radicals to initiate the oxidation of VOCs because the rate coefficients of the reactions of Cl atoms with VOCs are higher than those with OH radicals by one order of magnitude or more (Calvert et al., 2011). Hence, the reaction of Cl atoms could contribute significantly to the tropospheric degradation of ketones in areas with high concentration of Cl precursor, e.g., in the marine boundary layer (MBL).

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While the reactions of Cl atoms with small and straight-chain ketones have been already the subject of a number of kinetic studies, *e.g.*, acetone, 2-butanone (Calvert et al., 2011), only a limited number of investigations have been dedicated to large ketones (higher than C5) (Kaiser et al., 2010). Indeed, most of the high ketones studies are focused on the reactions with OH radical. Hence, the reactivity of OH with ketones is generally well reproduced by Structure-Activity-Relationships (SARs) whereas similar SAR for Cl reactivity is limited (Farrugia et al., 2015). Cuevas et al. (2004) have assumed that the reactivity of Cl with ketones takes place with a similar behavior to that of OH + ketone which is not confirmed experimentally so far. Furthermore, to our best knowledge, the product investigation from the reaction of larger branched ketones with Cl atoms is not well documented.

In light of the importance of ketones and Cl atoms in the troposphere, further considerable efforts are needed to better understand the reaction of branched ketones with Cl atoms. The present work deals with three high branched ketones: 2-methyl-3-pentanone (2M3P, $CH_3CH_2C(O)CH(CH_3)_2$), 4-methyl-2-pentanone (4M2P, $CH_3COCH_2CH(CH_3)_2$) and 3-methyl-2-pentanone (3M2P, $CH_3COCH(CH_3)CH_2CH_3$), which are widely used as solvents and intermediates for chemical synthesis. We have studied the reactions of Cl with 2M3P, 4M2P and 3M2P which enable us to recommend new rate constant values obtained using the relative method:

$$Cl + CH_3CH_2C(O)CH(CH_3)_2 \rightarrow products \quad (1)$$

$$Cl + CH_3COCH_2CH(CH_3)_2 \rightarrow products \quad (2)$$

$$Cl + CH_3COCH(CH_3)CH_2CH_3 \rightarrow products \quad (3)$$

In addition, we have conducted the products studies for the title reactions which allowed us to report some products we observed by a gas chromatograph equipped with flame ionization detector (GC-FID) and PTR-ToF-MS and their formation yields. To our knowledge, this work provides the first determination of the rate constant for Reaction (1), and the second one for that of Reaction (3). In addition, we report the first product investigation of reaction of 2M3P, 4M2P and 3M2P with Cl atoms in the presence of NO. Furthermore, this work aimed also at optimizing the SAR for ketone reaction with Cl atoms. The reported data from this work enable to better understand the atmospheric fate of ketones.

1. Experimental and material

1.1. Kinetic measurement

The experiments were performed in a 200 L Teflon chamber at 298 ± 2 K and 760 Torr total pressure of purified air with a relative humidity <2%. The chamber was surrounded by fluorescent black lamps, providing suitable UV radiation with a maximum around 360 nm and positioned in a wooden box with the internal faces covered with aluminum foil. Measured amounts of reagents were flushed from a calibrated bulb into the chamber through a stream of ultra pure air. It was then filled to its full capacity at atmospheric pressure with ultra pure air. Chlorine atoms were produced by the photolysis of molecular chlorine (Cl_2). A GC-FID (CP-3800 Varian) was used for the quantitative analysis of the reactants. Chromatographic separation was achieved by using a DB-1 capillary column (J&W Scientific. 30 m. 0.32 nm id. 5 μm Film). The column was operated at 120°C and helium was used as carrier gas. A series of tests were conducted before starting the reaction rate constant determinations. First ketone-air gas mixtures were left in the chamber for 1 hr to check for the possible loss of the reactant on the wall followed by another test consisting of irradiating the same mixture for 1 hr to check the photolysis of ketones under our experimental conditions. Chlorine was then added to the mixture and left in the dark for 1 hr to check for any dark reaction between Cl_2 and the investigated ketones. The same tests were made with the reference compounds. No significant wall losses, dark reactions or photolysis with 365 nm lamps have been observed for the ketones and reference compounds employed.

Rate constants for the reactions of Cl atoms with the investigated ketones were determined using the relative rate method in which the relative disappearance rates of the ketones and the reference compounds, whose rate constants with Cl atoms is well known, are monitored in the presence of Cl atoms without NO (no other additional losses were observed):

$$Cl + ketones \rightarrow products \qquad k_{ketone}$$

$$Cl + references \rightarrow products \qquad k_{ref}$$
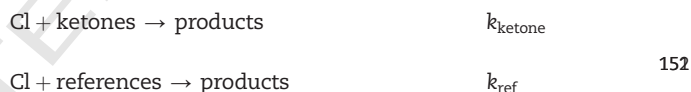
k_{ketone} (k_{2M3P}, k_{4M2P}, k_{3M2P}) and k_{ref} are the rate constants for the reaction of Cl atoms with ketones (2M3P, 4M2P, 3M2P) and reference compounds, respectively. Under these conditions, it can be shown that:

$$\ln\left(\frac{[ketone]_0}{[ketone]_t}\right) = \frac{k_{ketone}}{k_{ref}} \times \ln\frac{[reference]_0}{[reference]_t} \quad (4)$$

where $[ketone]_0$ and $[reference]_0$, represent the concentrations of the ketone and reference compound at reaction time t_0; $[ketone]_t$ and $[reference]_t$ represent the concentrations of the ketone and reference compound at reaction time t. Plotting $\ln\left(\frac{[ketone]_0}{[ketone]_t}\right)$ against $\ln\frac{[reference]_0}{[reference]_t}$ gives the slope $\left(\frac{k_{ketone}}{k_{ref}}\right)$, and zero intercept if no complex chemistry occurred.

1.2. Reaction products analysis

The reaction products were investigated for the reactions of studied ketones (2M3P, 3M2P and 4M2P) with Cl atoms in the presence of NO using the same experimental set-up as the one used in the kinetic studies. Both GC-FID and PTR-ToF-MS (8000, IONICON, Australia) were employed to monitor the reactants and products. PTR-ToF-MS spectra were analyzed using the PTR-ToF-MS Data Analyzer (Müller et al., 2013).

Calibrations have been conducted using pure samples of each expected product in GCFID and PTR-ToF-MS at different concentrations enabling to draw the calibration curves as shown in Fig. S2. In PTR-ToF-MS, m/z 59.045, 73.065, 45.035, 59.049, 73.065 were used to identify $CH_3COCH_3 \cdot H^+$ (acetone proton cluster), $CH_3CH_2COCH_3 \cdot H^+$ (2-butanone proton cluster),