Reaction mechanism of the Cl-atom initiated oxidation of 3-methyl-2-butanone and 2,4-dimethyl-3-pentanone

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Carbonyls are important intermediates formed in the atmospheric photo-oxidation of virtually all hydrocarbons. Their subsequent reactions may impact HOx levels and their reaction products may contribute to secondary organic aerosol (SOA) loadings. Reaction with Cl-atoms is an important chemical sink for organics under some conditions, and is widely used in laboratory studies to initiate photochemistry. The atmospheric chemistry of smaller aldehydes and ketones has been well studied, but the dataset for larger (> C4) carbonyls is sparse.

In this work, the mechanisms of the reactions of Cl-atoms with two structurally-related ketones (3-methyl-2-butanone and 2,4-dimethyl-3-pentanone) were investigated. Mixtures containing the ketone, chlorine and air were photolyzed in a reaction chamber at 298 K and 1 atm, and changes in the chemical composition were monitored by long path FTIR spectroscopy and GC-FID. Product yields of formaldehyde, acetone, carbon dioxide and peroxy acyl nitrates (PANs) for both compounds were measured in the presence and absence of NOx or an HO_2 source (methanol). Additional product yield experiments were carried out for the Cl + 3-methyl-2-butanone reaction as a function of O_2 partial pressure.

A partial mechanism for the reactions is shown in Figure 1. Chlorine atoms may abstract a hydrogen atom from either a primary or tertiary carbon center (Reactions R1a and R1b, respectively). The product yields measured imply branching ratios of $Y_{R1a} = Y_{R1b} = 0.5$ for both reactions. The resultant organic peroxy radicals may react to form a hydroperoxide (Reactions R2a and R3a) or an alkoxy radical and OH (Reactions R2b and R3b) in the presence of HO_2. Product yields measured in experiments with an HO_2 source are consistent with a significant fraction of radical recycling via Reactions R2b and R3b. Implications of these measurements will be discussed.

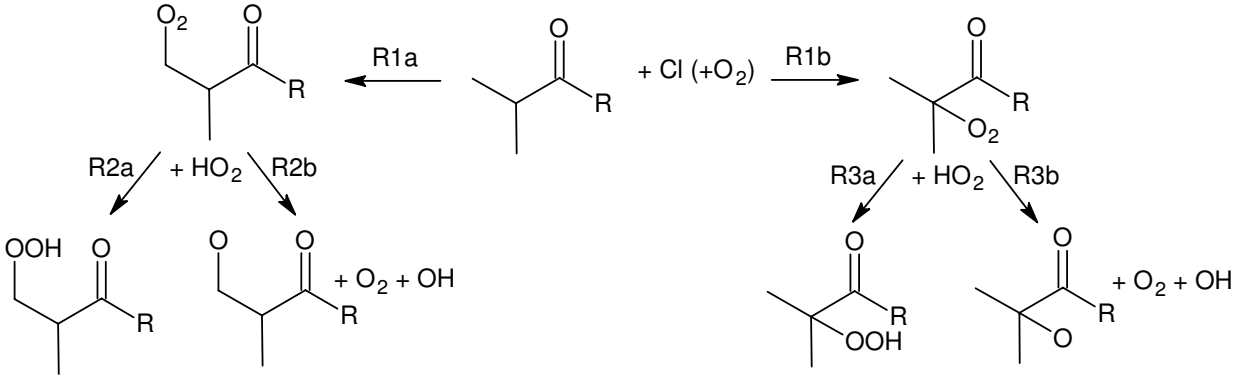

Figure 1. Partial mechanism of the reaction of 3-methyl-2-butanone (R = CH_3) and 2,4-dimethyl-3-pentanone (R = $CH(CH_3)_2$) with Cl atoms in air.