

Revised structure activity parameters derived from new rate coefficient determinations for the reactions of chlorine atoms with a series of seven saturated ketones at 290 K and 1 atm

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Oxygenated volatile organic compounds (OVOCs) represent the most abundant class of organic compounds within the atmosphere [1]. From the class of OVOCs, carbonyls are most abundant compounds [2].

Chlorine chemistry is predominantly active in the marine boundary layer,[3] and has received greater attention over the past decade since sources of chlorine atoms have been discovered over continental areas [4].

Rate coefficients of the reaction of chlorine atoms with a series of saturated ketones have been investigated at 298 K and 1 atm using relative rate method. This work on the reaction of saturated ketones with Cl atoms helps to reconcile the discrepancies between the existing rate coefficients in the literature data.

The following rate coefficients have been obtained in this study:

$k(2\text{-pentanone} + \text{Cl})$	$= (1.08 \pm 0.05) \times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
$k(3\text{-pentanone} + \text{Cl})$	$= (0.89 \pm 0.06) \times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
$k(3\text{-methyl-2-butanone} + \text{Cl})$	$= (0.68 \pm 0.06) \times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
$k(4\text{-methyl-2-pentanone} + \text{Cl})$	$= (1.10 \pm 0.05) \times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
$k(5\text{-methyl-2-hexanone} + \text{Cl})$	$= (1.65 \pm 0.14) \times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
$k(3\text{-methyl-2-pentanone} + \text{Cl})$	$= (0.94 \pm 0.10) \times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
$k(3,3\text{-dimethyl-2-butanone} + \text{Cl})$	$= (0.48 \pm 0.05) \times 10^{10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

The results are discussed in terms of Cl reactivity trends and compared with existing literature values. A revised room temperature SAR calculation for the series of ketones is therefore suggested based on IUPAC evaluation of $k(\text{butanone} + \text{Cl})$.

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