AN EXPERIMENTAL KINETIC STUDY OF THE GAS-PHASE REACTIONS OF OH RADICALS WITH UNSATURATED KETONES

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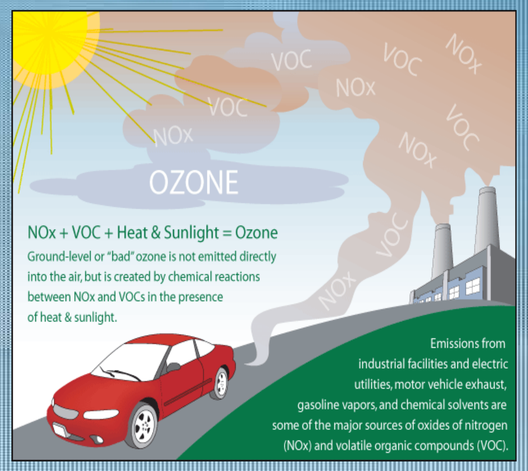
INTRODUCTION

Volatile Organic Compounds (VOC), such as 4-hexen-3-one, 5-hexen-2-one, and 3-penten-2-one, are emitted into the environment from different sources; from mechanical and biological treatment plants[1], as intermediate products resulting from the synthesis of perfume, insecticides and fungicides[2] and also from biomass burning in Europe[3]. Field and laboratory studies show that these compounds are also released into the atmosphere by the wounded leaves of variety of plants[4].

The release of these unsaturated ketones into the atmosphere is likely to contribute to the formation of ozone and other components of photochemical smog found in urban areas mainly through their reactions with OH radicals and but also with other oxidants such as NO_3 radicals, O_3 molecules and Cl atoms.

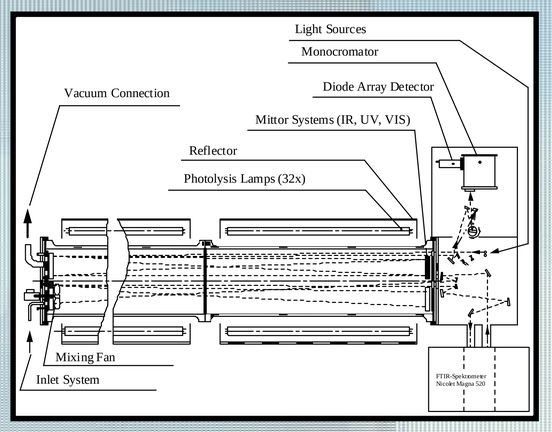


OBJECTIVES

Knowledge of the rate coefficients for the OH-radical initiated reactions of ketones is needed to better ascertain their role in the formation of tropospheric photooxidants. To help in this respect, a kinetic study of the reactions of OH radicals with 4-hexen-3-one, 5-hexen-2-one, and 3-penten-2-one has been performed.

$OH + CH_3CH=CHC(O)CH_2CH_3 \rightarrow$ products (k_1)
$OH + CH_3C(O)CH_2CH_2CH=CH_2 \rightarrow$ products (k_2)
$OH + CH_3CH=CHC(O)CH_3 \rightarrow$ products (k_3)

EXPERIMENTAL SETUP AND RESULTS



- 480 L quartz-glass photoreactor filled with synthetic air (298 ± 3 K and 1000 mbar).
- Optical path length of 48.11 m.
- IR spectra (resolution 1 $cm^{-1)}$ recorded with a Thermo Nicolet Magna 520 FTIR equipped with a MCT detector.
- The photolysis of CH_3ONO with 20 superactinic fluorescent lamps, Philips TLA 40W/05, with λ_{max} = 360 nm was used as the OH radical source.

The kinetic constants for the reactions of OH radicals with the unsaturated ketones were determined by relative rate method using 1-butene and isobutene as reference compounds.

Examples of the experimental data are plotted in Figures 1 and 2 according to an expression for the analysis of kinetic data obtained by the relative technique:

$$\ln([ketone]_0/[ketone]_t) = (k_{ketone}/k_{ref.})\ln([ref]_0/[ref]_t)$$

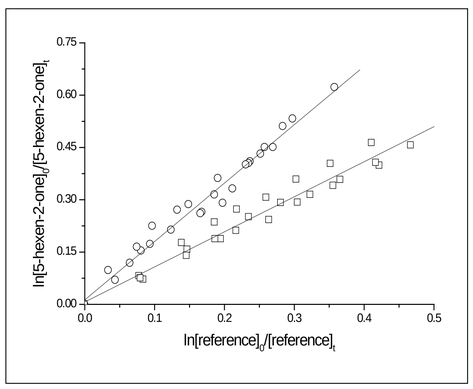


Fig. 1. Plots of the kinetic data for the reactions of 5-hexen-2-one with OH radicals using 1-butene (○) and isobutene (□) as reference hydrocarbons.

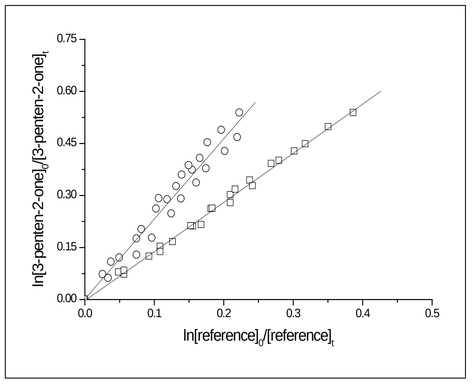


Fig. 2. Plots of the kinetic data for the reactions of 3-penetn-2-one with OH radicals using 1-butene (○) and isobutene (□) as reference hydrocarbons.

Reactant	Reference	Number of runs	$k_{Ketone}/k_{Reference}$	k_{Ketone} (cm^3 $molecule^{-1}s^{-1}$)
$CH_3CH=CHC(O)CH_2CH_3$ (4-hexen-3-one)	1-butene	3	2.91 ± 0.09	(9.14±2.10) × 10^{-11}
	Isobutene	4	1.74 ± 0.05	(8.94±2.05) × 10^{-11}
			Average	**(9.04±2.10) × 10^{-11}**
$CH_3C(O)CH_2CH_2CH=CH_2$ (5-hexen-2-one)	1-butene	3	1.66 ± 0.05	(5.21±1.20) × 10^{-11}
	Isobutene	3	1.00 ± 0.04	(5.14±1.23) × 10^{-11}
			Average	**(5.18±1.23) × 10^{-11}**
$CH_3CH=CHC(O)CH_3$ (3-penten-2-one)	1-butene	3	2.29 ± 0.09	(7.19±1.71) × 10^{-11}
	Isobutene	3	1.41 ± 0.02	(7.25±1.55) × 10^{-11}
			Average	**(7.22±1.71) × 10^{-11}**

DISCUSSION AND CONCLUSSIONS

The energies of the highest occupied molecular orbital (E_{HOMO}) for the unsaturated ketones (4-hexen-3-one, 5-hexen-2-one, 3-penten-2-one, methyl vinyl ketone and ethyl vinyl ketone) were calculated.

Figure 3 shows the correlation obtained for a plot of ln k versus E_{HOMO}, the following linear equation describes the slope in Figure 3 :

$$\ln k_{OH+ketone}\ (cm^3\ molecule^{-1}\ s^{-1}) = -(2.06 \pm 0.16)E_{HOMO} - (2.52 \pm 0.27)$$

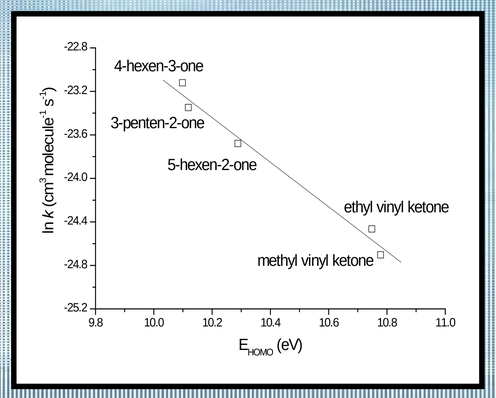


Fig. 3. Correlation plot of ln k *versus* calculated E_{HOMO} for the reactions of OH radicals with unsaturated ketones.

¤ The value obtained in this study for the reaction of OH radicals with 5-hexen-2-one of k_2 = (5.18 ± 1.23) × 10^{-11} cm^3 $molecule^{-1}s^{-1}$ is in very good agreement, within the experimental error, with that recently reported by Wang et al.[5] of k_2 = (4.49 ± 1.02) × 10^{-11} $cm^3molecule^{-1}s^{-1}$.

¤ To the best of our knowledge, no experimental kinetic data on the reactions of OH with 4-hexen-3-one and 3-penten-2-one have been reported.

¤ The good quality of the correlation of ln k versus E_{HOMO} can be used for estimations of rate coefficients for reactions of OH radicals with similar unsaturated ketones which have not yet been investigated.

¤ On the basis of the rate coefficients obtained in this work, tropospheric lifetimes for 4-hexen-3-one, 5-hexen-2-one and 3-penten-2-one, with respect to reaction with OH radicals, were estimated to be 2 and 3 hours, thus degradation initiated by OH radicals will be the main chemical removal process for these unsaturated ketones in the troposphere.

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