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

M. B. Blanco\textsuperscript{a,b}, I. Barnes\textsuperscript{a} and P. Wiesen\textsuperscript{a}

\textsuperscript{a}Physikalische Chemie/FBC, Bergische Universität Wuppertal, Wuppertal, Alemania. barnes@uni-wuppertal.de
\textsuperscript{b}Instituto de Investigaciones en Fisicoquímica, I.N.F.I.Q.C., Facultad de Ciencias Químicas, Universidad Nacional de Córdoba.

INTRODUCTION

Volatile Organic Compounds (VOCs), such as 4-hexen-3-one, 5-hexen-2-one, 5-hexen-2-one, and 3-penten-2-one, are emitted into the environment from different sources, including mechanical and biological treatment plants\textsuperscript{1}, as well as from biomass burning in Europe\textsuperscript{2}. Field and laboratory studies show that these compounds are also released into the atmosphere by the wounded leaves of plants\textsuperscript{3}. 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\textsubscript{2} radicals, O\textsubscript{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.

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\textsuperscript{-1}) recorded with a Thermo Nicolet Magna 520 FTIR equipped with a MCT detector.
- The photolysis of CH\textsubscript{3}ONO with 20 superactinic fluorescent lamps, Philips TLA 40W/05, with \(\lambda\text{max} = 360\) 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:

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

DISCUSSION AND CONCLUSIONS

The energies of the highest occupied molecular orbitals (\(E_{\text{HOMO}}\)) 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 \(\ln k_{\text{OH+ketone}}\) versus \(E_{\text{HOMO}}\) for the ketones. The following linear equation describes the slope in Figure 3:

\[
\ln k_{\text{OH+ketone}} (\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}) = -(2.06 \pm 0.04) - (25.2 \pm 0.27) E_{\text{HOMO}} (\text{eV})
\]

REFERENCES


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