Rate of degradation of $CH_3CH=CHC(O)OCH=CH_2$ and $CH_3C(O)OCH=CHCH=CH_2$ in the troposphere

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Primary volatile organic compounds (VOCs) are emitted into the atmosphere from anthropogenic and biogenic (natural) sources. The fate and persistence of VOCs in the atmosphere is largely determined by their reactivity with different oxidant species present in the troposphere (generally OH radicals, NO_3 radicals and O_3 molecules). These reactions play an important role in determining the oxidation capacity and chemistry of the lower troposphere.[1]

The unsaturated esters vinyl crotonate ($CH_3CH=CHC(O)OCH=CH_2$) and 1-acetoxy-1,3-butadiene ($CH_3C(O)OCH=CHCH=CH_2$) are widely used in the production of polymers. Their copolymers are brittle resins, but they are used as cross-linking agents for other resins to raise the softening point and to increase abrasion resistance.[2,3] The widespread industrial use of these esters on a large scale unavoidably results in fugitive emissions of the compounds to the atmosphere.

As part of ongoing work to ascertain the atmospheric chemistry of esters, rate coefficients for the gas-phase reactions of vinyl crotonate and 1-acetoxy-1,3-butadiene with OH and NO_3 radicals and O_3 have been measured using a relative kinetic method. All the experiments were performed at room temperature (298±2 K) and atmospheric pressure in a 480 l cylindrical borosilicate glass photoreactor and in situ FTIR analysis was used to monitor the concentration-time behavior of the esters and the hydrocarbon reference compounds.[3] The *trans* isomer of vinyl crotonate was investigated whereas the sample of 1-acetoxy-1,3-butadiene was a mixture of *trans* and *cis* isomers.

The following rate coefficients (in units of cm^3 $molecule^{-1}s^{-1}$) have been obtained for the reactions of vinyl crotonate with the oxidants: $k_{OH} = (4.49 \pm 1.05) \times 10^{-11}$, $k_{NO3} = (2.12 \pm 0.53) \times 10^{-14}$ and $k_{O3} = (0.98 \pm 0.34) \times 10^{-17}$. For the corresponding reactions of 1-acetoxy-1,3-butadiene the following values were obtained: $k_{OH} = (9.07 \pm 0.30) \times 10^{-11}$, $k_{NO3} = (3.17 \pm 0.57) \times 10^{-14}$ and $k_{O3} = (2.71 \pm 0.64) \times 10^{-17}$.

To the best of our knowledge, this work represents the first experimental kinetic study of the reactions of OH and NO_3 radicals and O_3 molecules with vinyl crotonate and 1-acetoxy-1,3-butadiene. The kinetic data will be presented and discussed in terms of reactivity trends for reactions of atmospheric oxidants with unsaturated compounds. The implications of the results for the fate of the esters in the troposphere will also be addressed.

References

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