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Atmospheric chemical mechanims of the photooxidation of vinyl and allyl acetate initiated by Cl reactions

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Acetates have been widely released for decades into the atmosphere during their use in industrial activities. Moreover, they are also emitted from natural sources (vegetation and biomass combustion).(1) An additional potential source of these compounds is emission from automobiles; a number of acetates, including vinyl acetate (VA) and allyl acetate (AA), have been detected as products in the combustion of rape methyl esters used as fuel alternatives or additives. (2)

The gas-phase removal processes of unsaturated esters include OH, NO_3, Cl reactions. In recent years the oxidations of volatile organic compounds (VOCs) by the highly reactive chlorine atom has gained much attention mainly in the marine troposphere where significant chlorine atom concentration may be present. (3)

In this work we report a product study for the reactions of Cl atoms with vinyl acetate ($CH_3C(O)OCH{=}CH_2$) and allyl acetate ($CH_3C(O)OCH_2CH{=}CH_2$).

The experiments were conducted using a 1080 liters quartz-glass environmental chamber at (298$\pm$2) K in one atmosphere of synthetic air using *in situ* FTIR spectroscopy to monitor the organics.

Product identification and quantification under atmospheric conditions were performed for the first time for the reactions cited above.

The major products observed in the vinyl acetate with Cl reaction are formic acetic anhydride and acetic acid together with formyl chloride as co-product and for the reaction of allyl acetate with Cl atoms we observed acetoxyacetaldehyde, formic acetic anhydride and acetic acid.

The results are used to postulate atmospheric chemical mechanisms which can be incorporated into chemistry transport models to obtain estimations of the contributions of emissions of such compounds to ozone and other photooxidant formation in the troposphere.

This work is a part of an ongoing plan in our laboratory to study the kinetics and product distribution of the unsaturated esters degradations and their impact on air quality. (4-6)

References

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