Gas phase-reactions of acrylic acid and allyl alcohol with Cl radical in the troposphere

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Introduction

The atmospheric degradation of most organic compounds is initiated by reaction with OH radical and also by reactions with NO_3 and O_3 (Atkinson, 2000). However, there is increasing interest in the potential for chlorine atoms to contribute to tropospheric chemistry in the marine boundary layer and in coastal regions, where significant chlorine atom concentrations may be present (Spicer et al., 1998). However, it is important to obtain knowledge of these reaction rates in order to asses the role of these reactions in atmospheric chemistry at global or regional scales.

Acrylic acid ($CH_2CHCOOH$) is used in the production of floor polish formulations, emulsion polymers, paint formulations, and paper coatings. It is produced naturally by marine algae and in the rumen fluid of sheep (Howard, 1990). Saturated and unsaturated alcohols, as allyl alcohol (CH_2CHCH_2OH), are emitted into the atmosphere by vegetation (Köning et al., 1995). Finally, both acrylic acid and allyl alcohol are considered as hazardous air pollutants (EPA, accessed January 2005).

Experimental, results and discussion

The investigations were performed using the absolute discharge flow-mass spectrometry technique (DF-MS). The temperature dependence (260-333 K) of the reaction rate constants at 1 Torr have been determined under pseudo-first-order conditions with the organic compound in excess over Cl atom. The resulting Arrhenius expressions are $k_1 = (1.3\pm0.9)10^{-13}\exp(1600\pm200)/T$ cm^3molecule^{-1}s^{-1} for reaction of Cl + $CH_2CHCOOH$ (1) and, $k_2 = (1.1\pm0.5)10^{-11}\exp(470\pm135)/T$ cm^3molecule^{-1}s^{-1} for reaction of Cl + CH_2CHCH_2OH (2). Concerning the pressure range studied (from 0.5 to 3 Torr) at 298 K, we have found a pressure dependence for reactions (1) and (2)

with rate coefficients increasing when pressure was increased.

Both reactions can proceed through two different pathways, an abstraction channel giving HCl and/or the formation of the corresponding adduct. At room temperature and 1 Torr, products of abstraction and addition channels have been detected for both reactions. By mass spectrometric quantification, the branching ratio for channels giving HCl, was determined as 0.13 ± 0.05 for reaction (1) and 0.57 ± 0.06 for reaction (2).

For reaction of acrylic acid + Cl (1), a yield on HCl of only 13%, the negative activation energy, a low pre-exponential factor, the increase of the phenomenological rate constant with increasing pressure and the M.S. detection of signals possibly coming from the argued adduct, they clearly suggest that the dominant reaction pathways is the addition to form an association complex (ClCH$_2$CHCOOH*) which may decompose back to reactants or be collisionally stabilised. A minor route giving HCl with a branching ratio of 0.13 ± 0.05 has also been found. This product may be originated from a direct abstraction process and from an addition-elimination sequence.

The results obtained for the degradation of CH$_2$CHCH$_2$OH, a yield of 0.57 ± 0.06 and the values of the kinetic rate constants suggest that abstraction of the weakly bound allylic hydrogen is the main pathway for reaction (2).

Atmospheric implications: From the results obtained in this work, chlorine atoms reaction is expected to play a significant role, compared to OH and NO$_3$, in the degradation of the studied organic compounds at dawn in the marine boundary layer and in coastal areas. That may be also the case of some urban contaminated areas, where high levels of chlorine may be originated from industrial emissions (Galán et al., 2002).

Furthermore our low-pressure measurements (p≤3 Torr) clearly suggest a pressure dependence of the rate constants. Under low-pressure conditions thermalization of the association complex may be inefficient. In this sense, under atmospheric conditions, higher rate constants, up to one order of magnitude, could be obtained for reactions (1) and (2).

References

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