

Atmospheric Degradation of Allyl Trifluoroacetate: Gas-phase Reactivity Study Towards OH and Cl Radicals

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Unsaturated fluorinated esters (FESs) are produced during the atmospheric oxidation of some hydrofluoroethers (HFEs).¹ FESs can also be released into the atmosphere by their use as precursors for reactive polymers in various kinds of functional materials,^{2,3} and as potential solvents or co-solvents for Li-ion batteries.^{4,5} FESs are mainly removed from the troposphere by chemical reactions with OH radical and Cl atoms in coastal environments and polluted urban areas, where high Cl levels may originate from industrial and urban emissions.^{6,7} Another possible sink for FESs is dissolution in clouds and seawater.⁸

The aim of this study is to help in the knowledge of FESs' atmospheric chemistry and their environmental effects. Thus, smog chamber/GC techniques were used to investigate, for the first time, the atmospheric degradation of the unsaturated fluorinated ester, allyl trifluoroacetate (ATFA, $\text{CF}_3\text{C}(\text{O})\text{OCH}_2\text{CH}=\text{CH}_2$) by oxidation with OH radicals and Cl atoms at 298 K and atmospheric pressure of N_2 or air. The measured rate coefficients were (in units of $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$): $(9.3 \pm 3.8) \times 10^{-12}$ for the reaction with OH radical and $(1.7 \pm 0.2) \times 10^{-10}$ for the reaction with Cl atoms (errors are $\pm 2\sigma$).

In the OH-initiated oxidation of ATFA, the identified product can arise from OH addition to both carbons in the double bond and the later decomposition of the alkoxy radical formed. However, in the reaction with Cl atoms, the main detected product may come from the Cl addition to the terminal carbon atom and the subsequent reaction of the chloroalkoxy radical formed with O_2 .

Infrared spectrum of the ATFA was collected and its contribution to global warming was assessed by calculating its radiative efficiency. Combining these results with the kinetic data we found that its global warming potentials is negligible. Finally, the photochemical ozone creation potential was calculated, obtaining values lower than those of non-fluorinated unsaturated hydrocarbons.

References

- (1) Calvert, J.G.; Mellouli, A.; Orlando, J.J.; Pilling, M.J.; Wallington, T.J. *Oxford University Press: New York*, **2011**
- (2) Takagi, K.; Tomita, I.; Endo, T. *Macromolecules*, **1997**, 30, 7386–7390.
- (3) Girard, E.; Liu, X.; Marty, J.D.; Destarac, M. *Polym. Chem.*, **2014**, 5, 1013–1022.
- (4) Lu, W.; Xie, K.; Pan, Y.; Chen, Z.; Zheng, C. *J. Fluor. Chem.*, **2013**, 156, 136–143.
- (5) Zhao, L.; Okada, S.; Yamaki, J. *J. Power Sources*, **2013**, 244, 369–374.
- (6) Blanco, M.B.; Bejan, I.; Barnes, I.; Wiesen, P.; Teruel, M.A. *Chem. Phys. Lett.*, **2008**, 453, 18–23.
- (7) Tovar C.M. and Teruel, M.A. *Atmos. Environ.*, **2014**, 94, 489–495.
- (8) Kutsuna, S.; Chen, L.; Abe, T.; Mizukado, J.; Uchimaru, T.; Tokuhashi, K.; Sekiya, A. *Atmos. Environ.*, **2005**, 39, 5884–5892.