



Simulation chamber study of the oxidation of acetic acid by OH radicals - Detection of reaction products by CW-CRDS in the near-infrared range

S. Crunaire (1,2), A. Tomas (1), P. Coddeville (1), C. Fittschen (2) and B. Lemoine (3)

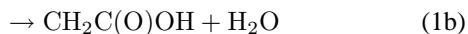
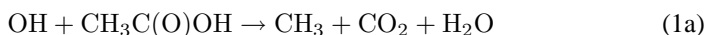
(1) Département Chimie-Environnement, École des Mines de Douai, Douai, France, (2) PC2A, "Physico-Chimie des Processus de Combustion et de l'Atmosphère", UMR CNRS 8522, Université des Sciences et Technologies de Lille, Villeneuve d'Ascq, France, (3) PhLAM, "Physique des Lasers, Atomes et Molécules", UMR CNRS 8523, Université des Sciences et Technologies de Lille, Villeneuve d'Ascq, France (crunaire@ensm-douai.fr / Fax: +333 27 71 26 12)

Although anthropogenic emissions of volatile organic compounds (VOCs) in France seem to decrease for several years, the part of oxygenated VOCs remains constant. Among these compounds, carboxylic acids have become an issue of growing interest in the past two decades.

Low molecular weight carboxylic acids like acetic acid have been recognized as potentially important especially in urban polluted atmospheres where concentrations can exceed $20 \mu\text{g}/\text{m}^3$ [1]. The contribution of direct emissions of this compound from anthropogenic and biogenic sources is evaluated to 48 Tg/year [1] and a total photochemical source strength of 120 Tg/year is reported [2].

The photooxidation chain of $\text{CH}_3\text{C}(\text{O})\text{OH}$ contributes to the production of photooxidants, so that the implications in the atmospheric HO_x budget are important [3]. However, models usually do not take these effects into account because too little is known about the fate of $\text{CH}_3\text{C}(\text{O})\text{OH}$ in the atmosphere. Therefore, to assess its tropospheric impact, the determination of the products distribution of the reaction is needed.

Two channels are expected to occur in the OH-initiated oxidation of acetic acid:



The channel of hydrogen atom abstraction from the carboxyl group (pathway (1a)) is the preferential pathway [4-5]. Recently, a branching fraction of $(64 \pm 17) \%$ was determined for this channel between 249 and 300 K by detecting CO_2 in a high-pressure turbulent flow reactor coupled to a chemical ionisation mass spectrometer [5].

Here we will present a new determination of the branching ratio of acetic acid oxidation in the presence of hydroxyl radicals at atmospheric conditions (298 K and 760 Torr) in a simulation smog chamber (300L photoreactor made of Teflon and equipped with an irradiation device to study the photochemical reactions in the UV and visible range) by measuring the CO_2 formation rate.

A setup based on the very recent spectroscopic technique, CW-CRDS (Continuous Wave – Cavity Ring Down Spectroscopy) [6] was developed for this purpose and coupled to the smog chamber. This coupling is the first reported to our knowledge and will be described in details here.

References:

- [1] Chebbi A. and P. Carlier, *Atmos. Environ.*, vol. 30, pp. 4233-4249, 1996.
- [2] Baboukas E. D., M. Kanakidou, and N. Mihalopoulos, *J. Geophys. Res.*, vol. 105, pp. 14459-14471, 2000.
- [3] Atkinson R. and J. Arey, *Chem. Rev.*, vol. 103, pp. 4605-4638, 2003.
- [4] Butkovskaya N. I., A. Kukui, N. Pouvesle, and G. Le Bras, *J. Phys. Chem. A*, vol. 108, pp. 7021-7026, 2004.
- [5] Romanini D., A. A. Kachanov, N. Sadeghi, and F. Stoeckel, *Chem. Phys. Lett.*, vol. 264, pp. 316-322, 1997.