

Rates of Tropospherically Significant $\text{CH}_3\text{O}_2\bullet + \text{NO}_2$ and $\text{CH}_3\text{CO}\bullet + \text{NO}$ Adduct Formations: Pulsed Laser Photolysis Transient Absorption (IR/VIS) Kinetics Studies

Aparajeo Chattopadhyay,* Monoj Samanta, and Tapas Chakraborty

Department of Physical Chemistry, Indian Association for the Cultivation of Science, 2A Raja S. C. Mullick Road, Jadavpur, Kolkata - 700032, India

* Corresponding author: pcac@iacs.res.in

A new pulsed laser photolysis transient absorption kinetics setup has been fabricated in order to measure the kinetics of important gas phase radical reactions. Organic radicals are generated by photolysis of a suitable precursor using 4th harmonic (266 nm) of a Nd:YAG laser and probed by a tunable mid-infrared Quantum cascade laser (QCL) in a linear stainless steel flow cell. This is a new method where radicals are probed in fingerprint region of their mid-IR spectrum and that IR signal is used to measure rate of the reaction for this radical with other atmospherically important species. To check for the reliability of the setup we have at first measured the rate constant of a well-studied atmospherically important reaction $\text{CH}_3\text{O}_2 + \text{NO}_2$ where CH_3O_2 radical was probed by CW output of QCL at 9.1 micron. Figure 1 shows typical signals of CH_3O_2 radical in presence and in absence of NO_2 . Rate constant of this reaction was studied in different pressure ranges and with different buffer gases under pseudo 1st order condition. The rate constant measured in the present study displays good agreement with the value reported by IUPAC.¹ A similar study was done to measure kinetics of $\text{CH}_3\text{CO} + \text{NO}$ reaction whose rate constant was never measured by absolute methods before. CH_3CO radical was probed and monitored by the 532 nm output of a diode laser and its reaction kinetics with NO was measured under pseudo first order reaction condition at low pressure and room temperature. Our estimated rate constant is somewhat smaller compared with the only available data, for which the reaction was studied by relative rate method.² In addition, product analysis and reaction kinetics was performed for a related association reaction $\text{CH}_3 + \text{NO}$ using FTIR spectroscopy.

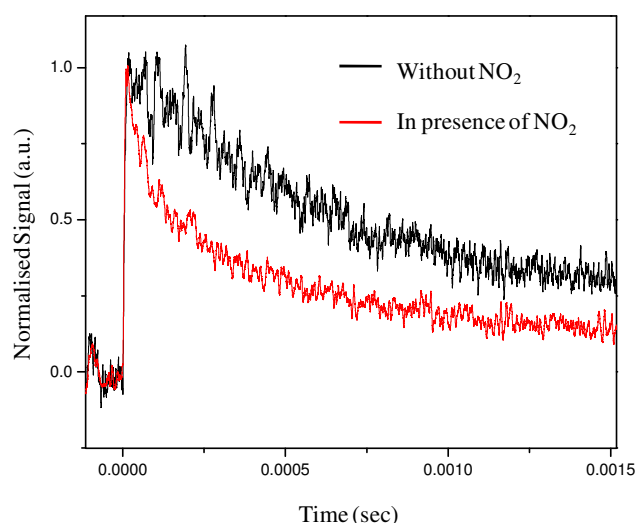


Figure 1 – CH_3O_2 signal with and without NO_2

References

- (1) IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation, (<http://iupac.pole-ether.fr>).
- (2) Sehested, J.; Christensen, L.K.; Nielsen, O.J.; Wallington, T.J. *Int. J. Chem. Kinet.* **1998**, *30*, 913-921.