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Gas phase reactions of NO_3 radical with amides

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Amides constitute a large class of nitrogen containing volatile organic compounds (NVOCs) that may be found as atmospheric contaminants. They are widely used as solvents or starting materials or intermediates in different industries (synthetic polymers, manufacture of dyes, synthesis of pesticides, preparation of medicine, ...). The use of these volatile compounds may lead to their release into the atmosphere where they can be oxidised through different chemical processes. The atmospheric fate of amides in the gas phase is not well defined and require further study.

In this contribution, we present kinetic data for the reaction of nitrate radical with four amides : N,N-dimethyl formamide; N,N-dimethyl acetamide; N,N-dimethyl proprionamide and 1-methyl-2-pyrrolidinone.

Experiments were performed using a laser photolysis technique coupled with UV-Visible absorption detection. Nitrate radical was produced by photolysis of the gas mixture F_2 / N_2 / HNO_3 / amide at 351 nm and detected at 662 nm.

Typical initial mixtures fulfil these requirements :

$[F_2]$ = (1 - 3) 10^{+16} molecules cm^{-3} ; $[HNO_3]$ = (1 - 3)10^{+16} molecules cm^{-3}

[Amide] = (2 -15) 10^{+14} molecules cm^{-3}; $[NO_3]$ = (1 - 15)10^{+12} molecules cm^{-3}

Pressure (Torr) : 150 –200 ; Temperature (K) : 293 to 353

Under these conditions, the NO_3 optical density followed the pseudo-first order rate law.

The following k_{NO3} values (cm^3 $molecule^{-1}$ s^{-1}) were obtained at 298 K :

N,N-dimethylacetamide: (0.88$\pm$0.05)x10^{-13}

1-methyl-2-pyrrolidinone: $(1.45 \pm 0.20) \times 10^{-13}$.

Detailed kinetic results and the effect of the temperature on the kinetic data will be presented and discussed.