

Reactions of Ethylamines with Ozone: Rate Constants and OH Formation Yields

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Organic amines are emitted into the atmosphere from a variety of sources, e.g., industrial waste treatment, use as chemical absorber for CO₂ post-combustion capture, and animal husbandry operation and are removed from the atmosphere by the gas-phase reactions with oxidants as well as wet and dry deposition. The reactions of organic amines with ozone (O₃), one of the important oxidizing species, would contribute to the atmospheric lifetime of organic amines both in the daytime and nighttime. In this work, we have measured the rate constants for the reactions of O₃ with monoethylamine (MEA), diethylamine (DEA) and triethylamine (TEA) at ambient temperature and pressure. The yields of OH radical formation from the O₃ reactions were also been measured.

Experiments were conducted in a 6-m³ evacuable smog chamber. The rate constants of O₃ + ethylamines (EAs) reactions were measured by monitoring of O₃ decay under the condition of [EAs] >> [O₃]. Some of experiments were carried out under the second-order conditions, [EAs] ~ [O₃]. The rate constants measured under the second-order conditions are in agreement with those obtained from pseudo-first-order kinetic experiments. The rate constants for MEA, DEA, and TEA reactions are determined to be $(2.7 \pm 1.0) \times 10^{-19}$, $(1.4 \pm 0.7) \times 10^{-17}$, and $(1.1 \pm 0.3) \times 10^{-16}$ cm³ molecule⁻¹ s⁻¹, respectively. The rate constant obtained in this work for the reactions of DEA and TEA with O₃ are in agreement with literature values.¹

The OH yields for the reactions of O₃ with EAs were measured by using a relative rate method in the presence of OH tracer, 1,3,5-trimethylbenzene (TMB). The change of concentration of TMB relative to O₃ consumption was measured as a function of [TMB]/[EAs] ratio, and the OH yields for the O₃ + MEA and DEA were estimated be ~0.7. Contrary to the MEA and DEA reactions, no OH formation was observed in the O₃ + TEA reaction.

References

- (1) Gai, Y.-B.; Ge, M.-F., Wang, W.-G. *Acta Phys-Chim. Sin.* **2010**, 26, 1768-1772.