

Kinetics of the Gas-phase Reactions of OH Radicals and O₃ with Aliphatic Amines

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Aliphatic amines emitted from a variety of sources into the atmosphere are removed by the gas-phase reactions as well as wet and dry deposition. Like other organic compounds, the reactions with OH radicals, ozone, and other reactive species would be possible removal processes of amines in the air. Therefore, their rate constants need to be obtained to estimate the atmospheric lifetimes of aliphatic amines. In this work, we have measured the rate constants for the gas-phase reactions of OH radicals (k_{OH}) and O₃ (k_{O_3}) with N-methyl-ethanamine (MEA) and diethylamine (DEA) at 298 K and 760 Torr total pressure of air.

Experiments were conducted in a 6-m³ evacuable photochemical reaction chamber. The concentration of reactants and products was measured by a long optical-path FTIR spectrometer. Prior to kinetic measurements, the decay in the concentration of the individual compounds (k_w^A) was measured in the chamber in the dark.

The kinetic measurements of the OH reactions were carried out in the amine–reference–NO–CH₃ONO–air photoirradiation system. The relative rate constant for the reactions of OH radicals with amines and the reference compounds was obtained from

$$\ln([\text{amine}]_0/[\text{amine}]_t) - k_w^A \times t = (k_{OH}/k_R) \times \ln([\text{Ref}]_0/[\text{Ref}]_t).$$

Here, k_R are the rate constant of OH reactions with reference compounds. Under our experimental conditions, the O-atom and O₃ reactions with amines and reference compounds were confirmed to have a negligible contribution to the OH kinetics. The obtained rate constants were summarized in Table 1.

The rate constants for the reactions of amines with O₃ were measured in the amine-O₃-CO-air system. Excess amount of CO was introduced to scavenge OH-radicals. The decay of amine was analyzed as

$$\ln([\text{amine}]_0/[\text{amine}]_t) = k_{O_3} \times \int [O_3] dt + k_w^A \times t.$$

The integration of the O₃ concentration over time was carried out numerically. The obtained rate constants were also summarized in Table 1.

Table 1. Summary of kinetic results and comparison with literature

amines	OH + amine reaction		O ₃ + amine reaction		
	reference compound ^{a)}	$k_{OH} / 10^{-10}$ ^{b)}		$k_{O_3} / 10^{-17}$ ^{b)}	
		this work	reference	this work	reference
(CH ₃) ₂ NH	–	–	0.67 ± 0.05 ^{1,2}	0.17 ± 0.02 ⁴	
MEA	Pr, Isp, TMB	1.0 ± 0.2		0.65 ± 0.08	
DEA	Pr, Isp, TMB	1.3 ± 0.2	1.2 ± 0.3 ³	1.6 ± 0.3	1.3 ± 0.2 ⁵

^{a)} Pr = propene, Isp = isoprene, TMB = 1,3,5-trimethylbenzene. ^{b)} Unit: cm³ molecule⁻¹ s⁻¹.

References

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