Near-infrared Cavity Ring-down Spectroscopic Study of the Reaction of Methylperoxy Radical with Nitrogen Monoxide

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Time-resolved near-infrared cavity ring-down spectroscopy was applied to the kinetics of the gas-phase reaction of CH_3O_2 with NO at 100 Torr total pressure and 298 K. After flash photolysis of the $CH_4/Cl_2/O_2/N_2$ mixture at 355 nm or the $CH_3I/O_2/N_2$ mixture at 266 nm, the CH_3O_2 absorption at 1.36 µm was monitored for the kinetic study. The reaction rate constants determined in two different radical sources are essentially the same and in agreement with the recently proposed values.

Peroxy radicals (RO_2) are critical intermediates in atmospheric and combustion chemistry, which are formed during the low-temperature oxidation of organic compounds.[1] Recently high concentrations of RO_2 up to 80 pptv in the marine boundary layer (MBL) have been reported.[2] RO_2 in the atmosphere converts NO into NO_2, results in the formation O_3, and then contributes HO_x (OH and HO_2 radicals) cycles:[1]

$$RO_2 + NO \rightarrow RO + NO_2 \quad (1)$$

$$NO_2 + h\nu \rightarrow NO + O(^3P) \quad (2)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \quad (3)$$

where M is a third body. Because of its significant roles, the reactions of RO_2 have been widely studied.[3] Typically a UV absorption centered at ≈240 nm that comes from the B^2A''–X^2A'' transition of RO_2 has been used for kinetic study.[3] However, this absorption region is wide (half-width ≈40 nm), broad, and unstructured. Hence, it is essentially difficult to monitor only RO_2 absorption without interferences of unwanted absorbed species. RO_2 uniquely has a structured A^2A'–X^2A'' transition at much longer wavelength, typically in the near-infrared (NIR) regions. Use of the NIR region absorption has great advantages for the kinetic study because 1) it avoids complications due to the spectral overlap in the presence of other species, and 2) there is no effect of UV flash photolysis scattering, which occurs undesirably during the generation of RO_2 radicals. However, it is usually difficult to generate tunable NIR light, and the absorption cross section σ at this region is small 10^{-20}–10^{-22} cm^2 moleucle^{-1}. Cavity ring-down spectroscopy (CRDS)[4,5] combined with an optical parametric oscillator laser is a powerful absorption spectroscopic method and has an extremely long effective optical path under atmospheric relevant conditions. Miller and co-workers are the first to monitor RO_2 absorptions in the NIR region using a combination of CRDS and a dye-laser-pumped Raman shifter.[6] Here we report a novel application to a kinetic study of the gas-phase reaction of CH_3O_2 with NO using time-resolved NIR-CRDS with two different CH_3O_2 generation systems under atmospheric relevant conditions.

The CRDS apparatus used in the present study is essentially the same as previous studies.[7,8] The system employed a photolysis laser (Spectra Physics, GCR-250, 266 or 355 nm) and a probe laser (Spectra Physics, MOPO-SL, 1.36 µm, spectral resolution 0.2 cm^{-1}). After the photolysis laser pulse beam traversed a glass tube reactor, the probe laser pulse beam was injected nearly collinear to the axis of the photolysis laser through one of two high-reflectivity mirrors. In the presence of an absorbing species, the light intensity within the cavity is given by eq 4.

$$I(t) = I_0 \exp(-t/\tau) = I_0 \exp(-t/\tau_0 - \sigma n c L_R t/L_C) \quad (4)$$

where I_0 and $I(t)$ are the light intensities at time 0 and t, τ is the cavity ring-down time with photolysis beam, τ_0 is the cavity ring-down time without photolysis laser light (typically 5 µs), L_R is the length of the reaction region (0.46 ± 0.02 m), L_C is the cavity length (1.04 m), c is the velocity of light, and n and σ are the concentration and the absorption cross section of absorbing species, respectively. By varying the delay between the photolysis and probe laser pulses, the concentration of CH_3O_2 was monitored as a function of delay time. Further experimental information is available in Supporting Information (SI).[11]

Figure 1 shows a typical cavity ring-down spectrum of CH_3O_2 in the 7365–7405 cm^{-1} region measured 5 ms after 355 nm flash photolysis of a $CH_4/Cl_2/O_2/N_2$ mixture at 100 Torr, 298 K with 0.02 nm step. The spectral baseline was taken in this wavenumber range without photolysis conditions. The peak at 7376 cm^{-1} is attributable to the 0–0 band head of the A^2A'–X^2A'' transition of CH_3O_2.[6] Cl atom was generated by 355 nm photolysis of Cl_2. Cl atom reacts with excess CH_4 ($[CH_4]_0 > 10^4[Cl]_0$) to form CH_3 radical, which rapidly reacts with O_2 to form CH_3O_2 within a few microseconds.

$$Cl_2 + h\nu(355\,\text{nm}) \rightarrow 2Cl \quad (5)$$

$$CH_4 + Cl \rightarrow CH_3 + HCl \quad (6)$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \quad (7)$$

The observed structured absorption spectrum of CH_3O_2 reasonably agrees with the previous reported one measured in the 193 nm photolysis of acetone in the presence of O_2 at 250 Torr of Ne/O_2 mixture.[6]

Figure 2 shows a typical decay time profile of CH_3O_2 in the presence of NO. The decays were analyzed by considering 1st-

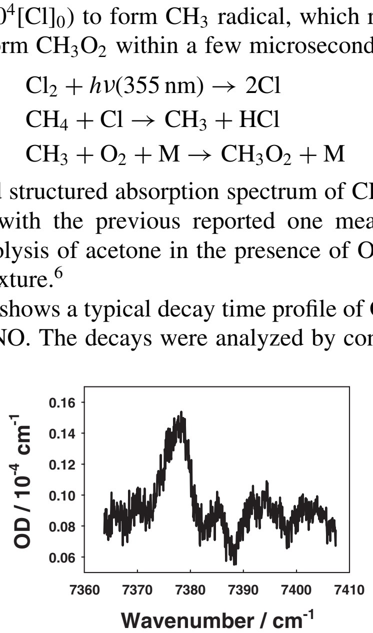

Figure 1. Absorption spectrum of CH_3O_2 appearing after 355 nm flash photolysis of $CH_4/Cl_2/O_2/N_2$ mixture at 298 K with 100 Torr total pressure. OD stands for optical density.

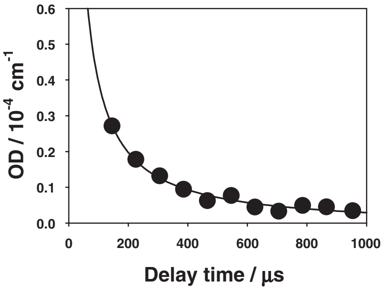

Figure 2. Typical decay time profile of CH_3O_2 absorption at 7375.7 cm^{-1} (1355.8 nm) in the presence of 3.2×10^{15} molecule cm^{-3} NO at 298 K, in 100 Torr of N_2 diluent, where $[CH_4]_0 = 1.6 \times 10^{17}$, $[Cl_2]_0 = 6.6 \times 10^{15}$, $[O_2] = 4.8 \times 10^{17}$, and $[NO]_0 = 3.2 \times 10^{15}$ molecule cm^{-3}. Fitting curve shows eq 9 fitting to the data. OD stands for optical density.

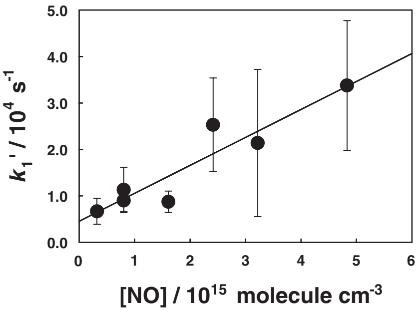

Figure 3. Second-order plot of CH_3O_2 + NO at 298 K in 100 Torr total pressure.

order (CH_3O_2 reaction with NO and the diffusion) and 2nd-order (CH_3O_2 self-reaction 8) losses.[7]

$$CH_3O_2 + CH_3O_2 \rightarrow 2CH_3O + O_2 \quad (8a)$$

$$\rightarrow \text{other products} \quad (8b)$$

$$[CH_3O_2]_t^{-1} = ([CH_3O_2]_0^{-1} + 2k_8/k_1')\exp(k_1't) - 2k_8/k_1' \quad (9)$$

where $[CH_3O_2]_0$ is the initial CH_3O_2 concentration, $[CH_3O_2]_t$ is the concentration of CH_3O_2 at time t, k_1' is the pseudo-first-order rate of loss of CH_3O_2 with respect to the reaction with NO, and k_8 is the reported self-reaction rate constant of CH_3O_2, 4.7×10^{-13} cm^3 molecule^{-1} s^{-1}.[8] The typical $[CH_3O_2]_0$ is estimated to be 10^{12}–10^{13} molecule cm^{-3}.[11] The concentration ratio was kept at $[NO]_0/[CH_3O_2]_0 > 50$. The secondary reactions are carefully checked.[11] The obtained k_1' values were plotted as a function of [NO] (Figure 3), yielding the CH_3O_2 + NO reaction rate constant of $(8.2 \pm 2.9) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} (the uncertainty is 2σ) at 298 K and 100 Torr total pressure, which is in excellent agreement with the previous JPL and IUPAC proposed values, $(7.7 \pm 1.2) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.[9,10]

We also performed the kinetic study by using a different reaction system. A $CH_3I/O_2/N_2$/NO mixture was photolyzed at 266 nm followed by CH_3 radical rapidly reacting with O_2 to form CH_3O_2 radical within a few microseconds.

$$CH_3I + h\nu(266\,\text{nm}) \rightarrow CH_3 + I \quad (10)$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \quad (7)$$

The 2nd-order plot analysis produces the CH_3O_2 + NO reaction rate constant of $(7.0 \pm 1.9) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 298 K, 100 Total pressure, where typical concentrations are $[CH_3I]_0 = (1–10) \times 10^{15}$, $[NO]_0 = (0.1–5.0) \times 10^{15}$, $[O_2] = 1.6 \times 10^{17}$ molecule cm^{-3}, respectively. This value is in fair agreement with the $CH_4/Cl_2/O_2/N_2$ system and, again, in good agreement with previously proposed values.[9,10] The average value of two different systems is $(7.6 \pm 2.4) \times 10^{-12}$ cm^3 moleucle^{-1} s^{-1}. Although the error at higher [NO] becomes inevitably large owing to the low CH_3O_2 absorption, the present NIR-CRDS method has a great advantage that it can preclude the complications of absorption overlap hindrances. NIR-CRDS could be applied to many significant scientific fields under ambient conditions.

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11 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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