Pressure Dependence of Vinylperoxyl Radical Formation in the Reaction of Vinyl Radical with Molecular Oxygen

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Pressure dependence of vinylperoxyl radical formation in the reaction of the vinyl radical with molecular oxygen has been studied using a laser photolysis/cavity ring-down spectroscopy technique. The absorption spectra of vinyl radical and the product in the reaction were measured in the same spectral range from 439 to 465 nm. Varying the third body carrier gas of Ar from 10 to 120 Torr had obvious effect on the production of the vinylperoxyl radical.

The overall rate constants of the reaction of vinyl radical (C_2H_3) with molecular oxygen was found to be pressure independent.[1,2] A previous study reported a slightly negative temperature dependence of the reaction rate constant $k_1 = (6.92 \pm 0.17) \times 10^{-12} \exp[(120 \pm 12\,\text{K})/T]\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$.[1] Because of exothermicity of the reaction of vinyl radical with molecular oxygen, many product channels can be accessible.[2] Fahr et al.[3] measured the UV–vis absorption spectrum of vinylperoxyl radical ($C_2H_3O_2$) from the reaction of $C_2H_3 + O_2$ at a total pressure of 10 and 50 Torr. Mebel et al.[2] calculated the rate constants for the formation of various products and examined the pressure dependence of the rate constant for each channel. In their results, the pressure-dependent rate constants for each channel indicated a recombination of O_2 with the vinyl radical to form a stabilized vinylperoxyl radical.

$$C_2H_3 + O_2 \rightleftarrows C_2H_3O_2^{\ddagger} \xrightarrow{M} C_2H_3O_2$$
$$\longrightarrow \text{other products} \qquad (1)$$

where $C_2H_3O_2^{\ddagger}$ is the vibrational excited vinylperoxyl radical and M is the third-body. The $HCO + H_2CO$ channel is a main product channel under low-pressure condition.[1,2] We report here the formation of $C_2H_3O_2$ product in the reaction of the vinyl radical with molecular oxygen as a function of total pressure, measured by employing cavity ring-down spectroscopy (CRDS) coupled with pulsed laser photolysis.

The apparatus is described in detail elsewhere.[4,5] A 193.3-nm output of an excimer laser was used to photolyze a suitable precursor to generate vinyl radicals. An excimer pumped dye laser was used to probe absorption of the C_2H_3 and $C_2H_3O_2$. The ring-down cavity was 0.625-m long and consisted of a pair of high reflectance mirrors ($R > 0.9998$ at 445 nm). The initial vinyl concentrations were typically in the range of $(1–10) \times 10^{13}$ molecule cm^{-3}. All experiments were performed at room temperature (298 ± 3 K).

The absorption spectrum of the vinyl radicals in the wavelength range from 439 to 465 nm was observed in order to compare with the absorption spectrum in the presence of O_2. The vinyl radicals were generated from 193.3-nm ArF excimer laser photolysis of mixtures of C_2H_3X/Ar (X = Br and Cl). Figure 1 shows the observed absorption spectrum of the vinyl radical produced from 193.3-nm photolysis of C_2H_3Br at a total pressure of 40 Torr in Ar. Delay time between the probe and the photolysis laser was adjusted to 5 µs. This spectrum exhibits absorption with a maximum at about 446.5 nm. This is in good agreement with the absorption spectrum of the vinyl radical which has been previously reported.[4] In the presence of excess O_2, the absorption spectrum was measured at the same wavelength region with delay time of 100 µs. The reaction rate of the vinyl radical with molecular oxygen is ca. $1 \times 10^{-11}\,\text{cm}^3\,\text{molecule}^{-1}\,\text{s}^{-1}$ at room temperature and the concentration of O_2 is 1.7×10^{16} molecule cm^{-3}, so all vinyl radicals are thought to disappear from the cavity by the $C_2H_3 + O_2$ reaction and the effect of the vinyl radicals on the absorption spectrum can be neglected at this delay time. Figure 1 also shows the observed absorption spectrum in the presence of O_2. This spectrum is clearly different from the absorption spectrum under the absence of O_2. Using C_2H_3Cl as a precursor of the vinyl radical instead of C_2H_3Br, the same absorption spectrum was measured.

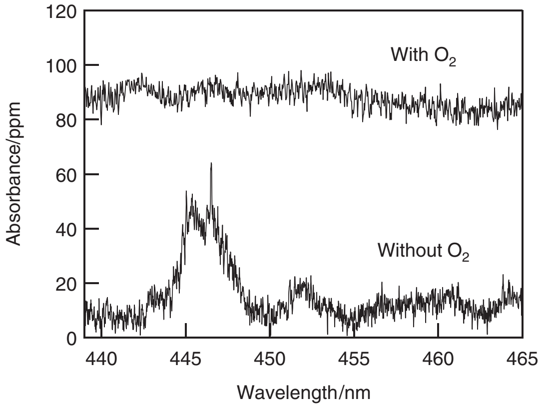

Figure 1. Absorption spectra of the C_2H_3 and $C_2H_3O_2$ detected by CRDS after photolysis of vinyl bromide at 193.3 nm, without and with added O_2. The stronger absorption in the presence of O_2 is attributable to $C_2H_3O_2$.

Absorption spectrum of the $C_2H_3O_2$ has been predicted by the quantum chemical calculations.[3,6] In order to assign the broad absorption spectra, we also performed theoretical analyses of the excitation energy and the oscillator strength of the vinylperoxyl radicals. The vinylperoxyl radical has two stable configurations; a trans and a cis form so labeled depending upon the O–O bond geometry with respect to the C–C bond. The formation of dioxyranylmethyl radical is also energetically accessible with an exothermic change of 101.7 kJ mol^{-1}.[2] The excitation energies and oscillator strengths were calculated at the time-dependent UB3LYP/aug-cc-pVTZ level of theory using Gaussian 03.[7,8] *cis*-$C_2H_3O_2$ shows absorption at around 430 nm and *trans*-$C_2H_3O_2$ shows at around 382 nm. Other reaction products (vinoxy, formaldehyde, etc.) in the reaction of the vinyl radical

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with O_2 are known to show no absorption in the wavelength range from 439 to 465 nm. Structured absorption spectra of formyl radical have been reported from 450 to 750 nm,[9] suggesting that the contribution of formyl radical can be ruled out in the observed wavelength region. Generally, alkylperoxyl radicals are known to have broad absorption assigned to the $\tilde{B} \leftarrow \tilde{X}$ electronic transition in the ultraviolet region.[10] According to the calculation results, the $\tilde{B} \leftarrow \tilde{X}$ electronic transition of the vinylperoxyl exhibits the visible absorption. The $\tilde{B} \leftarrow \tilde{X}$ transition of alkylperoxyl radical is essentially the promotion of a β electron from the second highest doubly occupied molecular orbital (2HOMO) to the singly occupied molecular orbital (SOMO).[6] The 2HOMO is predominantly π in character and the SOMO is π^* in character. For various peroxyl radicals, the SOMO is unchanged but the 2HOMO changes substantially with different substituents. In particular, 2HOMO of the vinylperoxyl radicals is influenced and the expected ultraviolet absorption shifts into the visible region because of the proximity of the open-shell orbital to an unsaturated alkyl group. The calculated absorption maximum of the dioxiranylmethyl radicals was at 420 nm. Mebel et al.[2] pointed out no stabilization of the dioxiranylmethyl radical was found, so the contribution of the dioxiranylmethyl radical in the visible absorption can be negligible.

The formation of the vinylperoxyl radical is exothermic by about 194.1 kJ mol^{-1}.[2] In order to discern competition between the stabilization of the vinylperoxyl radical and subsequent reactions, the pressure dependence of the $C_2H_3O_2$ radical production was studied in the pressure range of 10–120 Torr by adding Ar to precursor mixture. Since the vinyl radicals have no absorption at around 440.0 nm, the pressure dependence of absorption of the vinylperoxyl radicals was observed at this wavelength. The vinylperoxyl radical production was largely increased with increasing the total pressure, but the vinyl radical production was not affected by the total pressure. Figure 2 shows the signal intensity ratio of the vinylperoxyl radicals and the vinyl radicals monitored at 440 and 446.5 nm, $I[C_2H_3O_2]/I[C_2H_3]$, as a function of total pressure. The experimental results suggested that the branching ratio of the vinylperoxyl radical production in the $C_2H_3 + O_2$ reaction was increased because the vinylperoxyl radicals were stabilized by the third-body M, as total pressure was increased. Mebel et al. calculated the stabilization of the vinylperoxyl radical. The branching ratio of the vinylperoxyl production is 0.5 at 760 Torr of N_2 and 3.4×10^{-3} at 2 Torr of He at room temperature.[2] Therefore, the concentration ratio of $[C_2H_3O_2]/[C_2H_3]$ would be located between 3.4×10^{-3} and 0.5 in the pressure range of 10 to 120 Torr. Although the branching fraction of the vinylperoxyl radical channel is less than unity, the absorbance of the vinylperoxyl radical is larger than that of the vinyl radical above 30 Torr. Therefore, the absorption cross-sections of the vinylperoxyl radical in the visible region are larger than that of the vinyl radical.

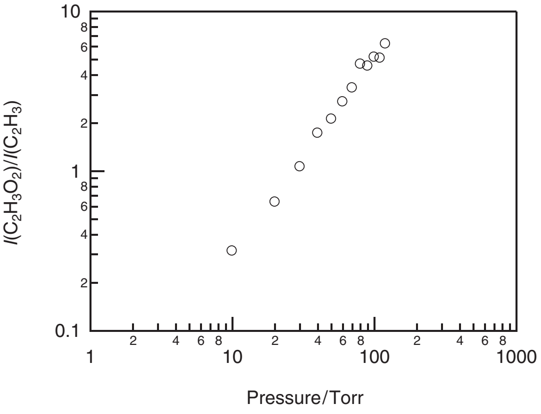

Figure 2. Pressure dependence of $I[C_2H_3O_2]/I[C_2H_3]$ as a function of total pressure.

Fahr et al. determined the absorption cross section of vinylperoxyl radical, $\sigma_{C_2H_3O_2} = 2.3 \times 10^{-19}$ cm^2 molecule^{-1} at 440 nm at 50 Torr.[3] In our experiments, the signal intensity ratio of $I[C_2H_3O_2]/I[C_2H_3]$ at 50 Torr is 2.1. Tonokura et al. estimated the absorption cross-section of the vinyl radical at 446.5 nm to be $\sigma_{C_2H_3} = 4 \times 10^{-19}$ cm^2 molecule^{-1} from the kinetic modeling of the vinyl radical self-reactions.[4] The method in the estimate of the cross-section strongly depends on the rate constants used in the simulation. Recently, Taatjes et al. reported the $\sigma_{C_2H_3}$ to be around 1×10^{-19} cm^2 molecule^{-1} at 446.5 nm.[11,12] They also determined the rate constant of the self-reaction of C_2H_3 of $(5 \pm 2) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}, which is far smaller than the literature value used in the simulation by Tonokura et al. Taking this value, the cross section at 446.5 nm from the kinetic modeling brings into be $(2 \pm 1) \times 10^{-19}$ cm^2 molecule^{-1}. The branching ratio of the stabilization of vinylperoxyl channel has a pressure dependent, so the $\sigma_{C_2H_3O_2}$ at 440 nm is predicted to be higher than 2×10^{-19} cm^2 molecule^{-1}. We can roughly estimate the lower limit of the $\sigma_{C_2H_3O_2}$ as follows. From Figure 2 the signal intensity ratio of $I[C_2H_3O_2]/I[C_2H_3]$ at 120 Torr is 6.3, and the branching fraction of $C_2H_3O_2$ channel at 760 Torr is 0.5.[2] From these two values and σ of C_2H_3, the lower limit of the $\sigma_{C_2H_3O_2}$ at 440 nm is estimated to be $>1 \times 10^{-18}$ cm^2 molecule^{-1}.

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