CHEMISTRY LETTERS, pp. 2121-2124, 1987. © 1987 The Chemical Society of Japan

Kinetic Study on Electron Transfer Photooxygenation of Aromatic Olefins. Quenching Rates of Olefin Radical Cations by Oxygen and Superoxide Anion

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Quenching rate constants of olefin radical cations by O_2 and $O_2^{-\bullet}$ were measured using laser flash photolysis. The interaction of stilbene radical cations with $O_2^{-\bullet}$ is almost diffusion-controlled; however, the reaction of O_2 with the radical cations of 1,2-diarylethylenes is more than three orders less efficient.

The photooxygenation of olefins induced by electron-transfer sensitizers has attracted current interest.[1-5] Cyanoaromatic compounds have been used in most work, and the oxygenating species has been supposed to be the superoxide anion ($O_2^{-\bullet}$) generated by electron transfer from the sensitizer radical anions to oxygen.[2] Recent studies, however, revealed not only involvement of singlet oxygen instead of $O_2^{-\bullet}$ [3] but also major roles of ground state oxygen[4] as the oxygenating species in some cyanoaromatics-sensitized photooxygenations. We also pointed out that electrochemically generated olefin radical cations react directly with O_2.[6] In connection with this work we attempted to compare the quenching rates of radical cations by $O_2^{-\bullet}$ and O_2, since under cyanoaromatics-sensitized oxygenation conditions the concentration of O_2 introduced is assumed to be, in general, much higher than that of $O_2^{-\bullet}$ generated. We now wish to present results on determination of these rate constants for the radical cations of stilbenes and styrylnaphthalene by means of laser flash spectroscopy.

9-Cyanoanthracene(CNA)-sensitized electron transfer[5] and photoionization were used to generate olefin radical cations at ambient temperature. The rates for quenching of radical cations with $O_2^{-\bullet}$ were measured in dimethyl sulfoxide (DMSO) since $O_2^{-\bullet}$ is not so stable in acetonitrile as to give reliable kinetic data. Thus, the transient absorption spectra of trans-stilbene (TS) were measured by irradiating CNA (1.0×10^{-4} M) with 351 nm laser pulses (XeF, up to 11 mJ/pulse, 14-ns fwhm) in DMSO in the presence of TS (0.01 M, M = mol/dm^3). The spectrum, exhibiting a strong band at 474 nm with a shoulder at 420 nm and a broad band around 740 nm, is in good agreement with the spectrum reported,[5,7] and clearly ascribed to $TS^{+\bullet}$. The use of higher intensity of laser pulses (40 mJ/pulse) exhibited, in addition to the strong $TS^{+\bullet}$ bands, broad bands in the 500-650 nm region, which can be attributed to $CNA^{-\bullet}$.[8]

The decay profile around 474 nm was nearly in the second-order for varying laser intensity, and analyzed according to Eq. 1, where k_2 and k_q are rate constants for recombination of $TS^{+\bullet}$ and $CNA^{-\bullet}$ and for $TS^{+\bullet}$ quenching by a quencher Q,

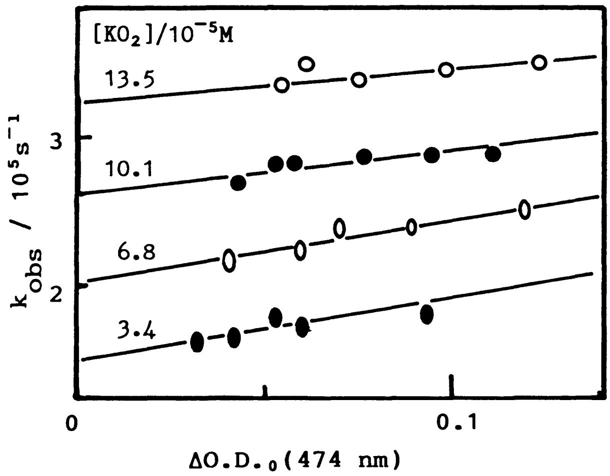

Fig. 1. Plots of k_{obs} vs. ΔOD_o at 474 nm.

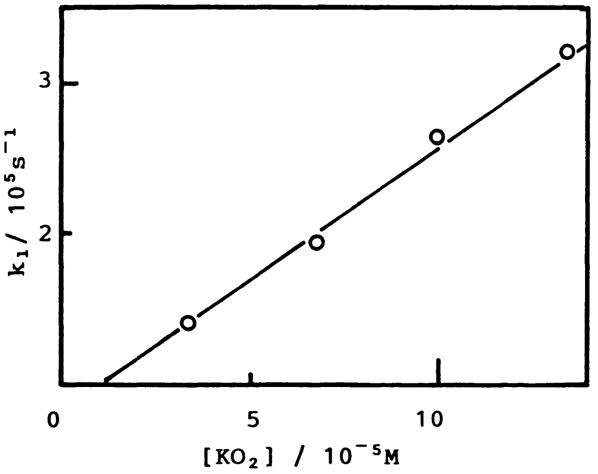

Fig. 2. Plot of intercept vs. $[KO_2]$.

respectively. In a short time range after laser excitation, $[CNA^{-\bullet}]$ can be regarded as being nearly equal to the initial concentration of $TS^{+\bullet}$ ($[TS^{+\bullet}]_o$), and then, the initial observed rate (k_{obs}) for the $TS^{+\bullet}$ decay is given by Eq. 2.

$$-d[TS^{+\bullet}]/dt = k_2[TS^{+\bullet}][CNA^{-\bullet}] + k_q[TS^{+\bullet}][Q] \qquad (1)$$

$$k_{obs} = -d(\ln[TS^{+\bullet}])/dt = k_2[TS^{+\bullet}]_o + k_q[Q] \qquad (2)$$

Plot of k_{obs} against $[TS^{+\bullet}]_o$ gives k_2 and $k_q[Q]$ (= k_1) as the slope and intercept of the straight line, respectively.9)

Figure 1 shows the plots of k_{obs} against the initial optical density (ΔOD_o) at 474 nm for varying laser intensity and four different concentrations of KO_2 [(3.4 - 13.5) x 10^{-4} M] in DMSO under argon atmosphere. The k_2/ε values obtained from these plots are in good agreement with each other and the use of 3.3 x 10^4 $M^{-1}cm^{-1}$ for ε7) gives 5.6 x 10^9 $M^{-1}s^{-1}$ for k_2.10) Plot of the intercepts k_1's obtained against $[KO_2]$ (Fig. 2) gives a straight line with a slope of (1.9 ± 0.1) x 10^9 $M^{-1}s^{-1}$ for a quenching rate constant of $TS^{+\bullet}$ by $O_2^{-\bullet}$.

The spectrum observed on direct irradiation with 308 nm laser pulses (XeCl, 100 mJ/pulse) of TS (8.0 x 10^{-5} M) in acetonitrile (Fig. 3) is in excellent agreement with that reported for $TS^{+\bullet}$.5,7,11) Since the initial optical density measured at 474 nm was linearly correlated with the square of laser intensity and was not affected by O_2, the formation of $TS^{+\bullet}$ must be through a biphotonic process.12) Similar irradiation of trans-2-styrylnaphthalene (SN, 2.5 x 10^{-5} M) with 308 nm pulses (20-50 mJ/pulse) gave a spectrum (Fig. 3) exhibiting a strong band at 500 nm and a broad one around 780 nm. This spectrum was ascribable to $SN^{+\bullet}$.12) For trans-4,4'-dimethoxystilbene (MS, 1.7 x 10^{-4} M), the spectrum (λ_{max} 530 and 770 nm, Fig. 3) was attributed to $MS^{+\bullet}$ 13) after Das' method.14)

The same method as used above was applied to determining the quenching rates of radical cations by O_2. Laser flash photolyses (308 nm) of TS, SN, and MS were performed with varying laser intensity under atmosphere of various partial pressures of O_2.15) Plots of k_{obs} (= $-d\ln[TS^{+\bullet}$, $SN^{+\bullet}$, or $MS^{+\bullet}]/dt$) against ΔOD_o at 474 (for $TS^{+\bullet}$), 500 (for $SN^{+\bullet}$), or 530 nm (for $MS^{+\bullet}$) for varying laser intensity afforded straight lines similar to those in Fig. 1. From the slopes the bimolecular decay constants of $TS^{+\bullet}$, $SN^{+\bullet}$, and $MS^{+\bullet}$ (recombination with solvated electron or $O_2^{-\bullet}$) were obtained as 4.1 x 10^{10}, 2.4 x 10^{10}, and 8.6 x 10^{9} $M^{-1}s^{-1}$, respectively.[10)] Plots of the intercepts against $[O_2]$ gave the rate constants for reaction of the radical cations with O_2 as (1.3 ± 0.2) x 10^{6} for $TS^{+\bullet}$, (1.8 ± 0.2) x 10^{6} for $SN^{+\bullet}$ (Fig. 4), and (7.2 ± 2.5) x 10^{5} $M^{-1}s^{-1}$ for $MS^{+\bullet}$.

There are three possibilities for interaction of radical cations and $O_2^{-\bullet}$, a) hydrogen transfer, b) bond formation, and c) electron transfer. Hydrogen transfer is confined to the radical cations with acidic hydrogen atoms, and is not the case for $TS^{+\bullet}$. Although biradical intermediates can be generated through C-O bond formation to initiate autoxidation of olefins,[1b,4a)] no direct evidence has been obtained. Schaap[17)] reported low efficiency of the bond formation in oxidation of electron-rich olefins by Lewis acids in the presence of KO_2 and attributed this to high efficiency of electron transfer from $O_2^{-\bullet}$ to radical cations. Most of the reactions between cation radicals and $O_2^{-\bullet}$ reported so far[1,5,17)] are through electron transfer and the magnitude of the quenching rate constant determined above is a reasonable one for this mechanism.

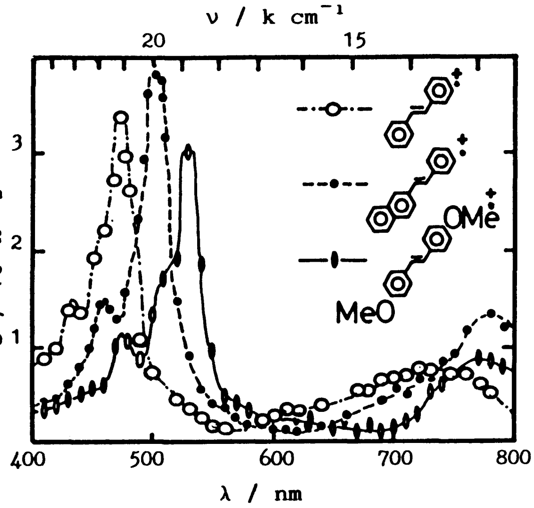

Fig. 3. Spectra of cation radicals.

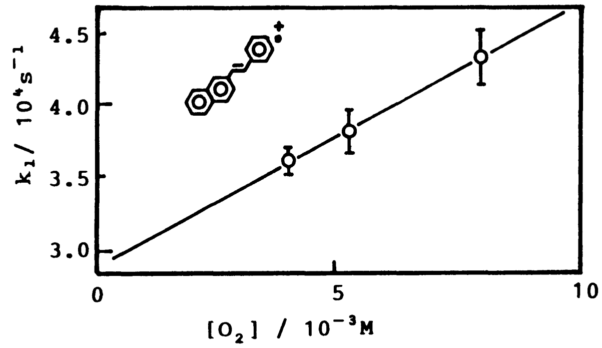

Fig. 4. Plot of intercept vs. $[O_2]$.

The quenching rate constants of radical cations by O_2 are in the order of 10^{6} $M^{-1}s^{-1}$. The reactions of radical cations with O_2 seem to be inefficient since both species are electron defficient. A direct reaction of olefin radical cations with O_2 has been reported for adamantylideneadamantane[18)] and intermediacy of its dioxetane radical cations was shown by ESR.[18d)] Thus, the quenching mechanism can be assumed to be C-O bond formation, and the rate constants determined are ascribed to this reaction. Their magnitude is two or three orders lower than that for neutral radicals.[15)] However, the quenching rates of radical cations by O_2 are nearly in the same order as those by $O_2^{-\bullet}$ under O_2 saturated condition ($[O_2]$ = 10^{-2} M), since the steady state concentration of $O_2^{-\bullet}$ in dye sensitized reactions is estimated to be less than 10^{-6} M, even when CNA is irradiated with 405 nm light from a 1200 W high pressure mercury lamp and the quantum yield for $O_2^{-\bullet}$ formation is unity. Taking into account the quenching mechanisms mentioned above, it is highly probable that the reactions of radical cations with O_2 play an important role in product formation in electron transfer induced oxygenations.

T.W.E. is grateful both to the Foreign Lectureship at University of Tsukuba and to the National Science Foundation (NSF INT 8407544, US-Japan Cooperation Program in Photosynthesis and Photoconversion).

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(Received July 3, 1987)