Studies of Acetylperoxy Radicals Produced by Photolysis of Biacetyl in Aerated Benzene Solutions. Ion-Pair Formation with Tetramethyl-*p*-phenylenediamine

Mikio Hoshino,* Masahiko Kagata, Hiroshi Seki, and Hideharu Seto

Contribution from The Institute of Physical and Chemical Research,
Wako, Saitama 351-01, Japan

Received August 21, 1995⊗

Abstract: Spin-trapping studies of the radicals produced by photolysis of biacetyl in degassed benzene confirmed the formation of acetyl radicals as a major product and methyl radicals as a minor one. In aerated benzene, the trapped radicals are ascribed to the acetylperoxy radical yielded by the reaction of the acetyl radical and oxygen. The laser photolysis studies of biacetyl in aerated benzene containing tetramethyl-*p*-phenylenediamine, TMPD, demonstrate that the acetylperoxy radicals react with TMPD to give the weakly interacting complex which turns to the ion-pair complex with the rate constant 6.7×10^5 s^{-1}. The absorption spectrum of the ion-pair complex resembles that of the cation radical of TMPD. The quantum yield for the formation of the acetylperoxy radicals produced by photolysis of biacetyl in benzene is estimated as 0.41. The addition of cyclohexene and norbornadiene is found to increase the rate for the formation of the ion-pair complex, indicating that the acetylperoxy radicals react with these olefins: the rate constants are 2.1×10^6 M^{-1} s^{-1} for cyclohexene and 1.8×10^7 M^{-1} s^{-1} for norbornadiene.

Introduction

Since an earlier finding by Shimizu and Bartlett,[1] photochemical epoxidation of olefins sensitized by α-diketones in aerated solutions has been the subject of extensive studies because of the wide utility of this reaction in organic synthesis.[2−7] Epoxides are produced by oxygen atom transfer from peroxy type intermediates to olefins. The intermediates have been suggested to be either (1) the exciplex or σ-biradical formed between the triplet α-diketone and dioxygen[1] or (2) the acylperoxy radicals.[6] The product analysis and the kinetic studies on the photo-epoxidation reaction support the view that the intermediate responsible for oxygen atom transfer to olefins is the acylperoxy radicals.[7−9]

Acylperoxy radicals are key intermediates in epoxidation of olefins[10−12] as well as in atmospheric chemistry.[13,14] Thus, the detection of acylperoxy radicals is an important subject for full understanding of their chemical properties. Acylperoxy radicals are produced by the photochemical reaction of α-diketones in aerated solutions: photolysis of α-diketones gives acyl radicals which react with dioxygen, leading to the formation of acylperoxy radicals.[7]

Acetylperoxy radicals in the gas phase have been produced by hydrogen abstraction of chlorine atom from acetaldehyde in the presence of oxygen.[15,16] In the present study, acetylperoxy radicals are produced by photolysis of biacetyl in aerated benzene solutions. Radicals produced from photolysis of biacetyl were studied by the spin-trapping method. Laser photolysis studies revealed that the acetylperoxy radicals in aerated benzene solutions react with tetramethyl-*p*-phenylenediamine, TMPD, to yield the ion-pair complex. The rates for the reactions between olefins and acetylperoxy radicals were determined by the measurements of the formation rates of the ion-pair complex as a function of the olefin concentration.

Experimental Section

Reagent grade biacetyl, norbornadiene, cyclohexene, acetonitrile, cyclohexane, and benzene were supplied from Wako Pure Chem. Ind. Ltd. 5,5-Dimethyl-1-pyrroline *N*-oxide (DMPO) from Tokyo Kasei Ind. Ltd. was used as a spin-trapping reagent. Tetramethyl-*p*-phenylenediamine from Aldrich Chem. Co. Inc. was purified by sublimation under reduced pressure.

Absorption and ESR spectra were recorded on a Hitachi 330 spectrophotometer and a jeol JES FE 3AX X-band spectrometer, respectively.

Laser photolysis was carried out with the use of a Nd-YAG laser (JK Lasers Ltd., Model HY 500) equipped with the second (532 nm), third (355 nm), and fourth (266 nm) harmonic generators. The detection system of the transient spectra was described elsewhere.[17]

Steady light photolysis of sample solutions was made with a 250 W mercury lamp (Ushio 250 D) equipped with cutoff filters.

Sample solutions, if necessary, were degassed on a vacuum line to ca. 10^{-5} Torr.

Results

Spin Trapping. Figure 1 shows the ESR spectra observed for degassed and aerated benzene solutions of 0.1 M biacetyl

---

⊗ Abstract published in *Advance ACS Abstracts,* February 15, 1996.

(1) Shimizu, N.; Bartlett, P. D. *J. Am. Chem. Soc.* **1976**, *98*, 4173−4200.

(2) Bartlett, P. D.; Roof, A. A. M.; Shimizu, N. *J. Am. Chem. Soc.* **1982**, *104*, 3130−3113.

(3) Clennan, E. L.; Speth, D. R.; Bartlett, P. D. *J. Org. Chem.* **1983**, *48*, 1246−1250.

(4) Shepherd, J. P. *J. Org. Chem.* **1983**, *48*, 337−342.

(5) Bartlett, P. D.; Becherer, J. *Tetrahedron Lett.* **1978**, *33*, 2983−2986.

(6) Sawaki, Y.; Foote, C. S. *J. Org. Chem.* **1983**, *48*, 4934−4940.

(7) Sawaki, Y.; Ogata, Y. *J. Org. Chem.* **1984**, *49*, 3345−3349.

(8) Sawaki, Y.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 2049−2053.

(9) Sawaki, Y. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 3464−3470.

(10) Simmons, K. E.; Sickle, D. E. W. *J. Am. Chem. Soc.* **1973**, *95*, 7759−7763.

(11) Tsuchiya, F.; Ikawa, T. *Can. J. Chem.* **1969**, *47*, 3191−3197.

(12) Sickle, D. E.; Mayo, F. R.; Gould, E. S.; Arluck, R. M. *J. Am. Chem. Soc.* **1967**, *89*, 977−984.

(13) Kirchner, F.; Zabel, F.; Becker, K. H. Ber. *Bunsenges. Phys. Chem.* **1990**, *94*, 1379−1382.

(14) Tuazon, E. C.; Carter, W. P. L.; Atkinson, R. *J. Phys. Chem.* **1991**, *95*, 2434−2437.

(15) Addison, M. C.; Burrows, J. P.; Cox, R. A.; Patrick, R. *Chem. Phys. Lett.* **1980**, *73*, 283−287.

(16) Moortgat, G.; Veyret, B.; Lesclawx, R. *J. Phys. Chem.* **1989**, *93*, 2362−2368.

(17) Hoshino, M.; Imamura, M.; Watanabe, S.; Hama, Y. *J. Phys. Chem.* **1984**, *88*, 45−49.

0002-7863/96/1518-2160$12.00/0

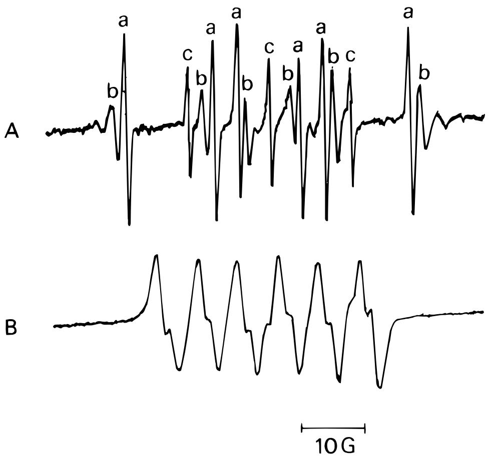

Figure 1. ESR spectra of the DMPO spin adducts observed after photolysis of (A) degassed and (B) aerated benzene solutions of 0.1 M biacetyl. Symbols, a, b, and c are the signals from the DMPO adducts of acetyl, methyl, and unidentified radicals, respectively.

containing 0.2 M DMPO after photolysis by the mercury lamp with a cutoff filter (λ < 330 nm). Three DMPO spin-adducts are detected after 5.0 min photolysis of biacetyl in degassed benzene: (a) acetyl radical adduct of DMPO ($A_N = 14.0$ G and $A_{H\beta} = 17.9$ G),[18,19] (b) methyl radical adduct of DMPO ($A_N = 14.2$ G and $A_{H\beta} = 20.7$ G),[18,19] and (c) unidentified radical adduct of DMPO ($A_N = 13.0$ G). The major signal is ascribed to the acetyl radical adduct of DMPO. The unidentified spin adduct c shows the hyperfine splitting due to a nitrogen atom and no hyperfine structure due to a β-hydrogen atom.

The ESR signal intensities of the spin adducts, a and b, showed a linear increase with an increase in the irradiation time. On the other hand, the increase in signal intensity of spin adduct c was found to exhibit an induction period. It, therefore, is suggested that the unidentified spin adduct c are the secondary photoproduct from the spin adducts, a or b.

The ESR spectrum of the spin adduct observed for an aerated benzene solution is markedly different from that for the degassed solution. The spin adduct in aerated benzene has $A_N = 13.1$ G, $A_{H\beta} = 6.7$ G, and $A_{H\gamma} = 1.25$ G. These ESR parameters indicate that the radical trapped by DMPO is an oxy radical[18,19] such as the acetylperoxy radical. This adduct is more stable than the acetoxy radical adduct of DMPO[20] and decays according to first order kinetics with a half-life of ca. 20 min. Because of the monophasic decay, the spin adduct is probably the single species. Laser photolysis of degassed and aerated benzene solutions of biacetyl in the presence of DMPO also gives the ESR spectra of the spin adducts mentioned above. It is noteworthy that the yield of the spin adducts in an aerated solution is much higher than those in degassed solution.

The spin trapping experiments are summarized as follows. Biacetyl in a degassed benzene solution undergoes photodissociation to yield acetyl radicals as a major product:

$$(\mathrm{CH_3{-}CO})_2 + h\nu \rightarrow 2\mathrm{CH_3CO}^\bullet \qquad (1)$$

The yield of the methyl radical is small in comparison with that of the acetyl radical. The major spin adduct detected in an aerated solution is considered to be the acetylperoxy radical which is produced by the reaction of the acetyl radical and oxygen.

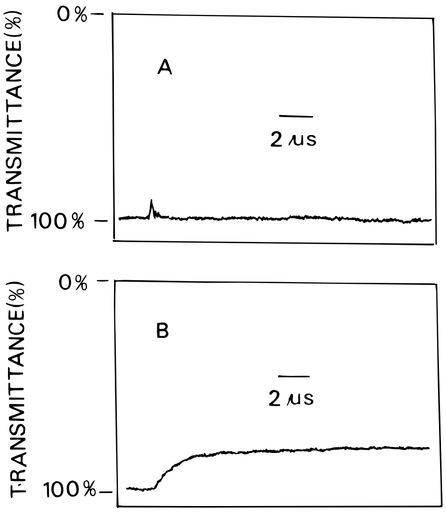

Figure 2. Oscilloscope traces monitored at 600 nm in 355-nm laser photolysis of (A) degassed and (B) oxygen saturated benzene solutions containing 0.1 M biacetyl and 1.1 × 10^{-4} M TMPD.

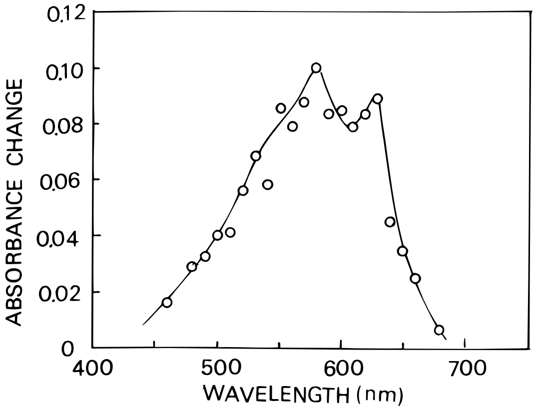

Figure 3. Transient absorption spectrum observed for an aerated benzene solution of 0.1 M biacetyl and 1.1 × 10^{-4} M TMPD, at 10 μs after 355-nm laser pulsing.

Laser Photolysis. The 355-nm laser photolysis for both aerated and degassed benzene solutions of 0.1 M biacetyl gives no transient absorption in the wavelength region λ > 450 nm. This fact indicates that acetyl and acetylperoxy radicals are hardly detected by the absorption spectroscopic method because their absorption spectra are located at the wavelengths shorter than those of biacetyl.[15,16] In the present study, TMPD, a strong electron donor, was used as a mediator for the detection of acetylperoxy radicals.

Both TMPD and biacetyl absorb light at 355 nm. Figure 2 shows the changes in transmittance at 600 nm observed with 355-nm laser photolysis for degassed and oxygen-saturated benzene solutions of 0.1 M biacetyl and 1.1 × 10^{-4} M TMPD. For the degassed benzene solution, no transient species were detected. The triplet TMPD produced was completely quenched by 0.1 M biacetyl. The 355-nm laser photolysis of a degassed benzene solution of 1.1 × 10^{-4} M TMPD confirmed that the triplet TMPD with the decay rate constant 1.1 × 10^6 s^{-1} is efficiently quenched by biacetyl with the rate constant 6.9 × 10^9 M^{-1} s^{-1}. As shown by B in Figure 2, the oxygen saturated solution affords the transient absorption: the absorbance at 600 nm gradually increases with time after laser pulsing and finally levels off. This transient species decays over a few microseconds.

Figure 3 shows the transient spectrum observed at 10 μs after laser pulsing for an oxygen saturated benzene solution of 0.1 M biacetyl and 1.1 × 10^{-4} M TMPD. The transient spectrum

---

(18) Buettner, G. R. *Free Radical Biol.* **1987**, *3*, 259−303.

(19) Janzen, E. G.; Liu, I.-P. *J. Magn. Reson.* **1973**, *9*, 510−512.

(20) Pryor, W. A.; Govindan, C. K.; Church, D. E. *J. Am. Chem. Soc.* **1982**, *104*, 7563−7566.

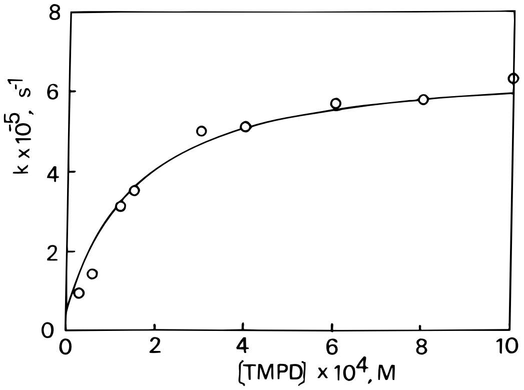

Figure 4. The rates for the formation of the ion-pair in aerated benzene detected at 600 nm, represented as a function of [TMPD].

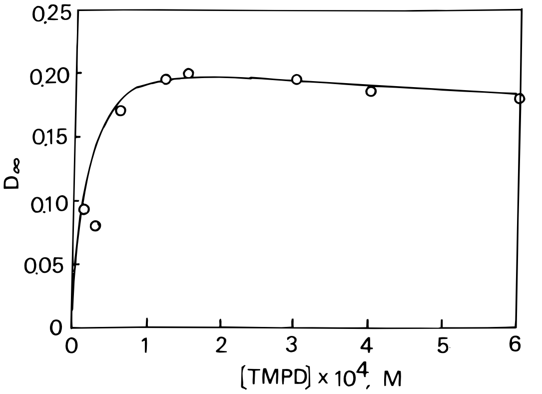

Figure 5. Absorbance, D_∞, represented as a function of [TMPD] (see text). The D_∞ values were calculated with the use of the equation, $D_\infty = D_\infty(\text{obsd})\cdot(\text{OD}_{\text{BA}} + \text{OD}_{\text{TMPD}})/\text{OD}_{\text{BA}}\cdot(1 - 10^{-(\text{ODBA}+\text{ODTMPD})})^{-1}$, where $D_\infty(\text{obsd})$ is the value experimentally obtained, and OD_{BA} and OD_{TMPD} are the absorbances of biacetyl and TMPD, respectively.

is very similar to the absorption spectrum of the TMPD cation radical, which has a strong absorption band centered around 600 nm.[21] The formation of the transient is interpreted in terms of the removal of an electron from TMPD by an oxidant generated with the photolysis of biacetyl in the aerated benzene solution. The spin-trapping study mentioned above indicates that the oxidant is the acetylperoxy radical. As will be mentioned later, the transient having an absorption band around 600 nm is ascribed to an ion-pair complex, $[\text{CH}_3\text{CO-O}_2{}^{-}\cdots\text{TMPD}^{\bullet+}]$, formed between acetylperoxy radical and TMPD.

Biacetyl yields the excited triplet state upon laser excitation. In an aerated benzene, the triplet is quenched by oxygen to give singlet oxygen. It is interesting whether or not the singlet oxygen is able to oxidize TMPD. In order to confirm this point, an aerated benzene solution of 10^{-4} M anthracene and 10^{-4} M TMPD was subjected to a laser pulse: the triplet anthracene efficiently undergoes energy-transfer to oxygen giving rise to the formation of the singlet oxygen.[22] However, no formation of the TMPD cation radical was detected. The result implies that the singlet oxygen hardly oxidizes TMPD.

The rate for the formation of the ion-pair complex observed for an aerated benzene solution of 0.1 M biacetyl and 10^{-4} M TMPD strictly follows first order kinetics: the absorbance D measured at 600 nm is expressed as

$$D = D_\infty[1 - \exp(-kt)] \tag{2}$$

where D_∞ is the absorbance at infinite time. Figure 4 shows the rate constants k for the formation of the ion-pair complex monitored at 600 nm, represented as a function of the concentration of TMPD, [TMPD]. The rate constants increase with an increase in [TMPD] and tend to level off at higher concentrations of TMPD. The reaction mechanism for the formation of the ion-pair complex is described as

$$\text{CH}_3\text{CO}{-}\text{O}_2{}^{\bullet} \xrightarrow{k_\text{d}} \text{products} \tag{3}$$

$$\text{CH}_3\text{CO}{-}\text{O}_2{}^{\bullet} + \text{TMPD} \xrightleftharpoons[k_\text{b}]{k_\text{f}} [\text{CH}_3\text{CO}{-}\text{O}_2{}^{\bullet}\cdots\text{TMPD}] \tag{4}$$

$$[\text{CH}_3\text{CO}{-}\text{O}_2\cdots\text{TMPD}] \xrightarrow{k_1} [\text{CH}_3\text{CO}{-}\text{O}_2{}^{-}\cdots\text{TMPD}^{\bullet+}] \tag{5}$$

Acetylperoxy radicals are assumed to react with (1) both solvent molecules and biacetyl to give their products with the rate constant k_d and (2) with TMPD to yield the weakly interacting complex, $[\text{CH}_3\text{CO-O}_2\cdots\text{TMPD}]$, which subsequently turns to the ion-pair complex, $[\text{CH}_3\text{CO-O}_2{}^{-}\cdots\text{TMPD}^{\bullet+}]$.[23] The ion-pair complex exhibits the absorption spectrum similar to that of the TMPD cation radical.

From eqs 3−5, the rate constant k in eq 2 for the formation of the ion-pair complex, $[\text{CH}_3\text{CO-O}_2{}^{-}\cdots\text{TMPD}^{\bullet+}]$, is expressed by

$$k = (k_\text{d} + k_1K[\text{TMPD}])(1 + K[\text{TMPD}])^{-1} \tag{6}$$

where $K = k_\text{f}/k_\text{b}$. Equation 6 is transformed to

$$Y = (k - k_\text{d})[\text{TMPD}]^{-1} = k_1K - kK \tag{7}$$

The relationship between Y and k was examined by changing the value of k_d. When $k_\text{d} = 5.0 \times 10^4\ \text{s}^{-1}$, the plot of Y vs k gave a straight line. From the slope and the intercept of the line, k_1 and K were, respectively, obtained as $k_1 = (6.7 \pm 0.5) \times 10^5\ \text{s}^{-1}$ and $K = (7.0 \pm 0.5) \times 10^3\ \text{M}^{-1}$.

Equation 6 was derived on the assumption that the rate constant, k_eq, for establishment of the equilibrium in reaction 4 is larger than k_1: $k_\text{eq}/k_1 = (k_\text{f}[\text{TMPD}] + k_\text{b})/k_1 >> 1.0$. From the K value and the assumption $k_\text{f} = 1.1 \times 10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$,[24] k_b is estimated as $k_\text{b} = 1.6 \times 10^6\ \text{s}^{-1}$. With the use of k_f, k_b, and k_1 obtained above, the ratio k_eq/k_1 in the region $[\text{TMPD}] > 1.0 \times 10^{-4}$ is calculated as $k_\text{eq}/k_1 > 4.0$. Since the increase in the absorbance at 600 nm follows first order kinetics, the reaction 4 is considered to approximately attain the equilibrium during the formation of the ion-pair complex in the present system.

The absorbance D_∞ in eq 2 is formulated as

$$D_\infty = D_0k_1K[\text{TMPD}](k_\text{d} + k_1K[\text{TMPD}])^{-1} \tag{8}$$

Here D_0 is the absorbance at an infinite concentration of TMPD.

Figure 5 shows the absorbance, D_∞, at 600 nm observed for aerated benzene solutions of 0.1 M biacetyl and TMPD at 10 μs after 355 nm laser pulsing, represented as a function of the TMPD concentration. The absorbance increases with an

---

[21] Richard, J. T.; Thomas, J. K. *Trans. Faraday Soc.* **1970**, *66*, 621−632.

[22] Redmond, R. W.; Braslavsky, S. E. *Chem. Phys. Lett.* **1988**, *148*, 523−529.

[23] An alternative mechanism was suggested by a reviewer:

$$\text{CH}_3\text{CO}{-}\text{O}_2{}^{\bullet} + \text{TMPD} \xrightleftharpoons[k_\text{b}]{k_\text{f}} [\text{CH}_3\text{CO}{-}\text{O}_2{}^{\bullet}\cdots\text{TMPD}] \tag{4}$$

$$\text{CH}_3\text{CO}{-}\text{O}_2{}^{\bullet} + \text{TMPD} \xrightarrow{k_1} [\text{CH}_3\text{CO}{-}\text{O}_2{}^{-}\cdots\text{TMPD}^{\bullet+}] \tag{5}$$

[24] Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry, Second Edition*; Marcel Dekker, New York, 1993.

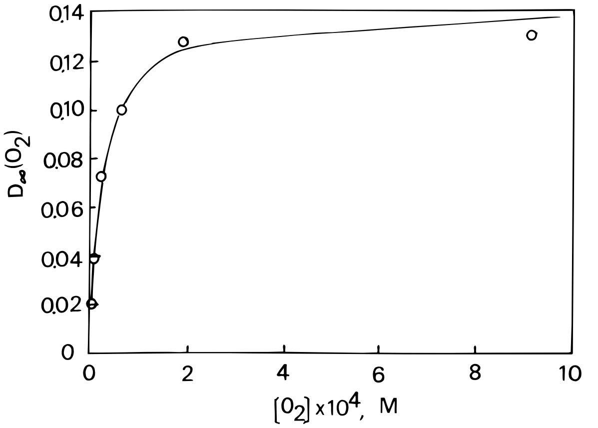

Figure 6. Absorbance, $D_\infty(O_2)$, represented as a function of $[O_2]$ (see text).

increase in [TMPD] in the range $0 < [\mathrm{TMPD}] < 1.8 \times 10^{-4}$ M and decreases in the range $[\mathrm{TMPD}] > 1.8 \times 10^{-4}$ M. This result cannot be explained by eq 8 and suggests that acetyl radicals produced by photolysis of biacetyl competitively react with oxygen and TMPD.

$$\mathrm{CH_3CO^\bullet + O_2 \xrightarrow{k_2} CH_3CO{-}O_2^\bullet} \tag{9}$$

$$\mathrm{CH_3CO^\bullet + TMPD \xrightarrow{k_p} products} \tag{10}$$

The increase in [TMPD] brings forth a decrease in the yield of acetylperoxy radicals, resulting in the decrease in the yield of the ion-pair complex. Thus, the absorbance, D_∞, in eq 8 is reformulated as

$$D_\infty = D_0 k_1 K[\mathrm{TMPD}]k_2[\mathrm{O_2}](k_d + k_1K[\mathrm{TMPD}])^{-1} \times (k_2[\mathrm{O_2}] + k_p[\mathrm{TMPD}])^{-1} \tag{11}$$

where D_0 is the absorbance at $k_p = 0$ and at an infinite concentration of TMPD. The plot of D_∞ vs [TMPD] is well reproduced by eq 11 with the use of $D_0 = 0.22$, $k_1 = 6.7 \times 10^5$ s^{-1}, $K = 7.0 \times 10^3$ M^{-1}, and $k_p(k_2[\mathrm{O_2}])^{-1} = 3.0 \times 10^2$ M^{-1}. Since the concentration of oxygen in a benzene solution at 1 atm air is 1.8×10^{-4} M, k_p/k_2 is obtained as 5.4×10^{-2}. On the basis of these results, it is concluded that (1) acetyl radicals trapped by oxygen are ca. 97% and (2) acetylperoxy radicals trapped by 1.0×10^{-4} M TMPD are 90% in aerated benzene solutions.

Figure 6 shows the absorbance, $D_\infty(O_2)$, at 600 nm observed for benzene solutions of 0.1 M biacetyl and 1.1×10^{-4} M TMPD after 355-nm laser pulsing, represented as a function of the oxygen concentration. At low concentrations of oxygen, acetyl radicals recombine to regenerate biacetyl.

$$\mathrm{2CH_3CO^\bullet \xrightarrow{k_{bi}} (CH_3CO)_2} \tag{12}$$

The value of $D_\infty(O_2)$ at 1 atm air is almost the same as that at 1 atm O_2, indicating that the recombination reaction in eq 12 is negligible at high concentrations of oxygen. From eqs 9, 10, and 12, the following equation is derived

$$-\mathrm{d}[(\mathrm{CH_3CO^\bullet})]/\mathrm{d}[(\mathrm{CH_3CO{-}O_2^\bullet})] = (k_{bi}[(\mathrm{CH_3CO^\bullet})] + k_p[\mathrm{TMPD}] + k_2[\mathrm{O_2}])(k_2[\mathrm{O_2}])^{-1} \tag{13}$$

At an infinite time, $[(\mathrm{CH_3CO^\bullet})] = 0$ and $[(\mathrm{CH_3CO\text{-}O_2^\bullet})] = R_\infty$. From eq 13, R_∞ is obtained as

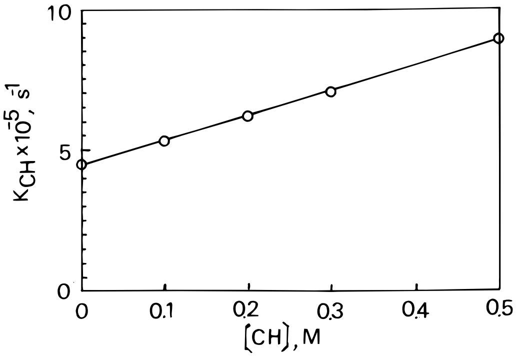

Figure 7. The rate constant, k_{CH}, for the formation of the ion-pair complex monitored at 600 nm, represented as a function of the cyclohexene concentration.

$$R_\infty = (k_2[\mathrm{O_2}])(k_{bi})^{-1} \ln\, [k_{bi}R_0(k_2[\mathrm{O_2}] + k_p[\mathrm{TMPD}])^{-1} + 1] \tag{14}$$

where R_0 is the initial concentration of acetyl radical produced immediately after laser pulsing. The acetylperoxy radical reacts with TMPD according to eqs 3−5. Therefore, the absorbance, D_∞, at 600 nm is expressed as

$$D_\infty(\mathrm{O_2}) = D_\infty{}^{h} R_\infty \tag{16}$$

where $D_\infty{}^{h}$ is the absorbance at an infinite concentration of oxygen. The plot of $D_\infty(O_2)$ vs $[O_2]$ shown in Figure 6 is well reproduced with the use of $D_\infty{}^{h} = 0.135$, $k_2/k_{bi}R_0 = 2.22 \times 10^4$ M^{-1}, and $k_p[\mathrm{TMPD}]/k_{bi}R_0 = 0.1$. From the latter two values and $[\mathrm{TMPD}] = 1.1 \times 10^{-4}$ M, k_p/k_2 is calculated as 5.0×10^{-2}, which is in agreement with that obtained from the analysis of Figure 5. The ratio, k_2/k_{bi} , is estimated as 0.2 with the use of $R_0 = 8.6 \times 10^{-6}$ M: the method for the determination of R_0 will be shown later.

Cyclohexene, C_6H_{10}, is known to give its epoxide upon irradiation of the aerated benzene solution in the presence of biacetyl.[1] The formation of the epoxide is shown by

$$\mathrm{CH_3CO{-}O_2^\bullet + C_6H_{10} \xrightarrow{k_e} C_6H_{10}O + CH_3COO^\bullet} \tag{17}$$

The laser photolysis was carried out for benzene solutions containing biacetyl, TMPD, and C_6H_{10}.

Figure 7 shows the rate constant, k_{CH}, for the formation of the ion-pair complex between TMPD and acetylperoxy radical in benzene solutions of 0.1 M biacetyl and 2.0×10^{-4} M TMPD, represented as a function of the cyclohexene concentration, $[C_6H_{10}]$. From eqs 3−5 and 17, the rate constant, k_{CH}, is formulated as

$$k_{\mathrm{CH}} = (k_d + k_e[\mathrm{C_6H_{10}}] + k_1K[\mathrm{TMPD}])(1 + K[\mathrm{TMPD}])^{-1} \tag{18}$$

Equation 18 is transformed to

$$k_{\mathrm{CH}} = k + k_e[\mathrm{C_6H_{10}}](1 + K[\mathrm{TMPD}])^{-1} \tag{19}$$

where k is the rate constant at $[C_6H_{10}] = 0$. The value of k_e is determined as $(2.1 \pm 0.2) \times 10^6$ M^{-1} s^{-1} from the slope of the line in Figure 7, $[\mathrm{TMPD}] = 2.0 \times 10^{-4}$ M, and $K = 7.0 \times 10^3$ M^{-1}.

Figure 8 shows the absorbance, $D_\infty(\mathrm{CH})$, of the ion-pair complex at 600 nm observed for benzene solutions of 0.1 M biacetyl and 2.0×10^{-4} M TMPD, represented as a function of $[C_6H_{10}]$. The value of $D_\infty(\mathrm{CH})$ decreases with an increase in

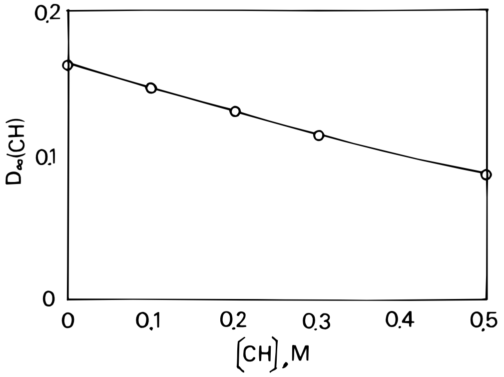

Figure 8. Absorbance, D_∞(CH), represented as a function of the cyclohexene concentration (see text).

[C_6H_{10}], suggesting that the acetoxy radical produced by eq 17 is the weaker oxidant of TMPD than the acetylperoxy radical. Presumably, the acetoxy radical reacts with cyclohexene and disappears before it oxidizes TMPD.

The absorbance D_∞(CH) is expressed as

$$D_\infty(\mathrm{CH}) = D_0(k_\mathrm{d} + k_1K[\mathrm{TMPD}]) \times (k_\mathrm{d} + k_\mathrm{e}[\mathrm{C_6H_{10}}] + k_1K[\mathrm{TMPD}])^{-1} \quad (20)$$

where D_0 is the absorbance at [C_6H_{10}] = 0. Since the rate constant k at [C_6H_{10}] = 0 is given by eq 6, eq 20 is rewritten as

$$D_0/D_\infty(\mathrm{CH}) = 1 + k_\mathrm{e}[\mathrm{C_6H_{10}}][k(1 + K[\mathrm{TMPD}])]^{-1} \quad (21)$$

the plot of D_0/D_∞(CH) vs [C_6H_{10}] gave a straight line. The rate constant k_e is determined as $(1.9 \pm 0.2) \times 10^6$ M^{-1} s^{-1} from the slope of the line, $K = 7.0 \times 10^3$ M^{-1}, and [TMPD] = 2.0×10^{-4} M. The value of k_e agrees well with that mentioned above.

The reaction of the acetylperoxy radical and norbornadiene in aerated benzene was also studied by measuring the rates for the formation of the ion-pair complex in the presence of the norbornadiene. The rate constant between the acetylperoxy radical and norbornadiene was determined as $(1.8 \pm 0.2) \times 10^7$ M^{-1} s^{-1}.

The quantum yield for the formation of the ion-pair was measured with the use of the laser photolysis technique.[25,26] The yield, ϕ, is represented by

$$\phi = \mathrm{OD}(600\ \mathrm{nm})/\epsilon_\mathrm{IP} I_\mathrm{abs}(N_\mathrm{A})^{-1} \quad (22)$$

where OD(600 nm) is the absorbance at 600 nm of the ion-pair complex produced after laser pulsing, ϵ_{IP}, the molar absorption coefficient of the ion-pair complex, I_{abs}, the number of quanta absorbed by biacetyl, and N_A is Avogadro's number. Since both biacetyl and TMPD in benzene absorb photons at 355 nm, I_{abs} is calculated by

$$I_\mathrm{abs} = I_\mathrm{abs}(T)\mathrm{OD_{BA}}(\mathrm{OD_{BA}} + \mathrm{OD_{TMPD}})^{-1} \quad (23)$$

Here $I_{abs}(T)$ is the total number of quanta absorbed by biacetyl and TMPD, and OD_{BA} and OD_T are, respectively, the absorbances of biacetyl and TMPD. A standard benzene solution of benzophenone with the same absorbance at 355 nm as that of the benzene solution of 0.1 M biacetyl and 1.0×10^{-4} M TMPD was prepared. The 355-nm laser photolysis of the standard solution gives triplet benzophenone. The initial absorbance, OD_{TB}, of triplet benzophenone, ^{3}Bp*, at 530 nm measured at 50 ns after pulsing is shown by

$$\mathrm{OD_{TB}} = \epsilon_\mathrm{TB} I_\mathrm{abs}(T)\phi_\mathrm{TB}(N_\mathrm{A})^{-1} \quad (24)$$

where ϵ_{TB} and ϕ_{TB} are the molar absorption coefficient of ^{3}Bp* at 530 nm ($\epsilon_{TB} = 7.6 \times 10^3$ $M^{-1}cm^{-1}$) and the yield of ^{3}Bp* ($\phi_{TB} = 1.0$).[27,28] From eqs 22−24, the quantum yield, ϕ, is obtained as

$$\phi = \phi_\mathrm{TB}\cdot\mathrm{OD}(600\ \mathrm{nm})/\mathrm{OD_{TB}}\cdot\epsilon_\mathrm{TB}/\epsilon_\mathrm{IP}\cdot(\mathrm{OD_{BA}} + \mathrm{OD_{TMPD}})/\mathrm{OD_{BA}} \quad (25)$$

On the assumption that the value of ϵ_{IP} is close to that of the molar absorption coefficient, ϵ_{TMPD^+}, of the TMPD cation radical at 600 nm in an aqueous solution ($\epsilon_{TMPD^+} = 1.01 \times 10^4$ M^{-1} cm^{-1}),[21] the yield ϕ is determined as 0.37. The ion-pair complex is produced by the reaction of acetylperoxy radicals and TMPD. Since acetylperoxy radicals trapped by 10^{-4} M TMPD are 90%, the quantum yield for the formation of the acetylperoxy radical is 0.41. The yield of acetyl radicals is calculated to be 0.42 because of the fact that acetyl radicals trapped by O_2 are 97% in an aerated benzene solution.

The initial concentration, R_0, of acetyl radicals produced from 0.1 M biacetyl in benzene by a laser shot is estimated as 8.6×10^{-6} M from the quantum yield 0.42 for the formation of the acetyl radical and the number of photons absorbed by biacetyl.

Laser Photolysis in Acetonitrile Solutions. A degassed acetonitrile solution containing 0.1 M biacetyl and 1.0×10^{-4} M TMPD was subjected to a 355 nm laser pulse. The transient spectrum having an absorption peak around 600 nm appeared within a duration of the laser pulse (20 ns). This result suggests that the excited triplet state of TMPD undergoes electron transfer to biacetyl to yield the TMPD cation radical in acetonitrile.

In contrast to the degassed solution, the absorbance at 600 nm in aerated acetonitrile gradually increases with time after laser pulsing. It is evident that the species responsible for the oxidation of TMPD in aerated acetonitrile is different from that in the degassed solution. The oxidant in the aerated acetonitrile solution is ascribed to the acetylperoxy radical which reacts with TMPD, yielding the ion-pair complex. The plot of the rate constants for the formation of the ion-pair complex vs [TMPD] gives a straight line. From the slope of the line, the bimolecular rate constant between the acetylperoxy radical and TMPD in acetonitrile is determined as 1.5×10^{10} M^{-1} s^{-1} which is close to that of the diffusion controlled process. The large bimolecular rate constant indicates that the weakly interacting complex formed between acetylperoxy radical and TMPD in acetonitrile readily interconverted into the ion-pair complex.

Laser Photolysis of Methyl Iodide. Methyl iodide photodissociates to give a methyl radical and an iodine atom.[29] The methyl radical produced in aerated solutions is considered to yield methylperoxy radical. The 266-nm laser photolysis studies of aerated acetonitrile and cyclohexane solutions containing (1−5) $\times 10^{-2}$ M methyl iodide and 10^{-4} M TMPD were carried out in order to discuss the differences in reactivity toward TMPD between acetylperoxy radical and methylperoxy radical. However, no transient absorptions were detected for both solutions in the wavelength region 360−800 nm. Probably, the rate for

---

(25) Hoshino, M.; Kogure, M.; Amano, K.; Hinohara, T. *J. Phys. Chem.* **1989**, *93*, 6655−6659.

(26) Yamaji, M.; Sekiguchi, T.; Hoshino, M.; Shizuka, H. *J. Phys. Chem.* **1992**, *96*, 9353−9359.

(27) Bensasson, R.; Land, E. J. *Trans. Faraday Soc.* **1971**, *67*, 1904−1915.

(28) Hoshino, M.; Shizuka, H. In *Photo-induced Electron Transfer*; Fox, M. A., Chanon, N., Eds.; Elsevier: Amsterdam, 1988; Part C, p 313.

(29) Markel, F.; Myer, A. B. *Chem. Phys. Lett.* **1990**, *167*, 175−182.

electron transfer from TMPD to the methylperoxy radical is very slow in comparison with that of acetylperoxy radicals.

Previous studies have shown that TMPD in aqueous solutions transfers an electron to methylperoxy radicals with the rate constant 8×10^6 M^{-1} s^{-1}.[30] This value is 2 orders of magnitude smaller than that (1.5×10^{10} M^{-1} s^{-1}) obtained with acetylperoxy radical in acetonitrile, indicating that methylperoxy radical is less electrophilic than acetylperoxy radical.

Discussion

Photochemistry of biacetyl has mainly been studied in the gas phase.[31,32] The product analysis indicates that the photolysis of biacetyl in the gas phase at an excitation wavelength of 366 nm gives acetyl radical and methyl radical as primary photoproducts.[31]

The spin trapping study with the use of DMPO confirmed that the photolysis of biacetyl in degassed benzene gives acetyl radicals as a major photoproduct and methyl radicals as a minor one. Thus, the primary photochemical products from biacetyl in benzene are concluded to be the same as those in gas phase. In the aerated benzene, the radicals trapped by DMPO are considered to be acetylperoxy radicals, which are yielded by the addition reaction of oxygen to acetyl radical. The ESR parameters observed for the acetylperoxy radical adduct of DMPO are different from those of the acetoxy radical.[20] The methylperoxy radical adduct of DMPO was not detected, suggesting that the adduct has a lifetime too short to be detected by the present spin-trapping technique.

The 355 nm laser photolysis of biacetyl in aerated benzene and acetonitrile solutions containing TMPD has shown that TMPD suffers oxidation to form the ion-pair complex. The oxidant is either the methylperoxy radical or the acetylperoxy radical. The laser photolysis studies of methyl iodide in aerated acetonitrile revealed that methylperoxy radical hardly oxidizes TMPD. Therefore, the methylperoxy radical is considered to make a minimum contribution to the oxidation of TMPD in benzene solutions.

The oxidant produced by photolysis of biacetyl in aerated benzene is ascribed to the acetylperoxy radical, which reacts with TMPD to yield the weakly interacting complex with an equilibrium constant $K = 7.0 \times 10^3$ M^{-1}. The weak complex interconverted into the ion-pair with the rate constant 6.7×10^5 s^{-1}. The absorption spectrum of the weak complex could not be detected in the wavelength range 450−800 nm. The ion-pair complex, on the other hand, has a $TMPD^{\bullet+}$-like absorption band around 600 nm.

The reactivities of acylperoxy radicals toward various olefins have been studied by measuring the relative rates for epoxidation. The electrophilic addition of acylperoxy radicals to olefins has been confirmed by the fact that the acylperoxy radical adds to olefins 10^5-faster than the alkylperoxy radical.[7] In agreement with these studies, the observations, that (1) the acetylperoxy radical forms the ion pair complex with TMPD and (2) the methylperoxy radical does not lead to the conclusion that the acetylperoxy radical is more electrophilic than the methylperoxy radical.

The acetyl radical, a precursor of the acetylperoxy radical, is found to react with TMPD. The rate constant is ca. 20 times slower than that between acetyl radical and oxygen. The reaction product of acetyl radical and TMPD could be an acetyl radical adduct of TMPD.

The acetyl radicals in aerated benzene decay according to (1) the reaction with oxygen with rate constant k_2 and (2) the recombination reaction with rate constant k_{bi} to regenerate biacetyl. The ratio, k_2/k_{bi}, is ca. 0.2, indicating that the rate for recombination is five times larger than that for reaction between the acetyl radical and oxygen. In an aerated benzene solution, acetyl radical is mostly trapped by oxygen and the recombination reaction between the acetyl radicals is suppressed, leading to the observation that the yield of the spin adducts in aerated benzene is larger than that in degassed benzene.

The quantum yields for the formation of acetyl radical and acetylperoxy radicals were estimated as 0.42 and 0.41, respectively. A biacetyl molecule produces two acetyl radicals by photodecomposition. The yield for the photodecomposition of biacetyl in benzene is calculated as 0.21.

The rate constant for the formation of the ion-pair complex between TMPD and the acetylperoxy radical increases with an increase in the concentrations of olefins, cyclohexene, and norbornadiene. This fact is satisfactorily explained by assuming that the acetylperoxy radicals are removed by these olefins. The acetylperoxy radical reacts with cyclohexene and norbornadiene with the rate constants 2.1×10^6 and 1.8×10^7 s^{-1}, respectively. These values are one or two order of magnitude larger than the rate constants (ca. 10^5 M^{-1} s^{-1}) for the addition of benzoylperoxy radicals to olefins.[7]

Acknowledgment. This work is partly supported by a Grant in Aid on Priority-Area-Research “Photoreaction Dynamics” from the Ministry of Education, Science, and Culture, Japan (06239267).

JA952886Q

---

(30) Jovanovic, S. V.; Jankovic, I.; Josimovic, L. *J. Am. Chem. Soc.* **1992**, *114*, 9018−9021.

(31) Bell, W. E.; Blacet, F. E. *J. Am. Chem. Soc.* **1954**, *76*, 5332−5337.

(32) Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; John Wiley, New York, 1966.