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Flash Photolysis Study on the Addition Reaction of Alkylthiyl Radical to Olefins

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The transient absorption band appearing at 370 nm by flash photolysis of di-*t*-butyl dusilfide was assigned to the *t*-butylthiyl radical. Photolyses of the disulfide solutions containing olefins such as 1,1-diphenylethylene and styrene gave new transient bands in a wavelength region similar to that of the diphenylmethyl radical and benzyl radical, respectively. These new bands can be attributed to the radicals produced by the addition of the thiyl radical to olefins; $(Ph)_2\dot{C}$–CH_2–SR and H(Ph)C–CH_2–SR. Kinetic studies including the addition of the thiyl radical to olefins were performed.

A number of studies have been carried out on the reactivity of free radicals in solution by means of flash photolysis, attention being focused mainly on the recombination and hydrogen abstraction reactions of the radicals.[1–3] Flash kinetic spectroscopy was applied to the triplet anthracene[4] and the diarylcarbenes[5] for the addition reaction to olefins. Addition of the thiyl radical to olefin was followed indirectly in the competition reaction between thiolate anion and olefin.[6] However, no study seems to have been carried out on the detection of the radical produced from the addition of the primary formed radical by flash exposure to olefin. The thiyl radicals are known to react very rapidly with olefins by means of the rotating sector in the mode of anti-Markownikoff addition.[7,8] If this is the case, the absorption spectrum of the radical formed from the addition reaction having the structure $R'(R'')\dot{C}$–CH_2–SR might be detected.

Experimental

Di-*t*-butyl disulfide, styrene, and 1,1-diphenylethylene were purified by distillation under reduced pressure. Ferrocene was purified by sublimation after recrystallization. All the solvents were of spectrophotometric grade. The solutions were degassed up to 10^{-5} Torr. The flash photolysis apparatus of standard design[9] delivered a flash with an energy of up to 100 J from xenon-filled flash lamps with a half-peak duration of 20 μs. A band pass filter (Toshiba UV-D25) transmitting light between 240 nm and 400 nm was used. The quartz irradiation vessel, length 10 cm and diameter 1 cm, had optically flat quartz window at both ends. The photolysis was carried out at 23 °C.

Results and Discussion

Thiyl radicals are formed by the photolysis of disulfides. The derivatives of diphenyl disulfide give only thiyl radicals which exhibit absorption at around 500 nm.[2,10] Although dialkyl disulfides give the dithio radicals (RSS·) besides a large amount of the thiyl radical under the irradiation of light of a short wavelength such as 195 nm,[11] photolysis with light of a longer wavelength (>240 nm) has not been studied by means of the flash photolysis. Before studying the addition reaction of the alkylthiyl radical to olefin, the absorption spectra of the alkylthiyl radical should be examined.

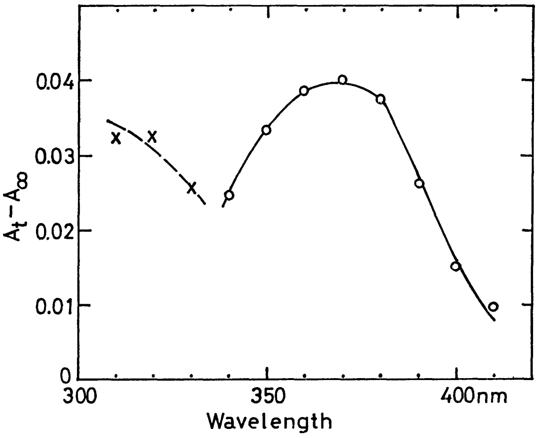

Fig. 1. Transient absorption spectra produced by the flash photolysis of the degassed hexane solution of di-*t*-butyl disulfide (5.0 mM). (a); Immediately after flash (-○-). (b); 500 μs after flash (-×-). A_t-A_∞ is difference of the absorbance at time *t* and time ∞ after flash.

Flash photolysis of the degassed solution of di-*t*-butyl disulfide gave the transient absorption spectra as shown in Fig. 1. The main band at 370 nm reaches maximum immediately after flash (*ca.* 40 μs) and decays rapidly with a half-life (τ) of 150 μs, a large decrease in the initial intensity being observed in the aerated solution. Another band can be seen in a shorter wavelength region than 330 nm. The band reaches maximum at *ca.* 500 μs after flash, decaying slowly with τ=*ca.* 3 ms, and is insensitive to oxygen. It thus can not be attributed to the free radical formed directly by the flash photolysis of disulfide. The band at 370 nm can not be assigned to the triplet←triplet absorption of disulfide, since its initial intensity and decay rate were not affected by addition of ferrocene which is known to be efficient triplet quencher,[12] and thus, it could be attributed to the *t*-butylthiyl radical. With another disulfide such as dibutyl disulfide, a weak absorption band, observed at 370 nm, is slightly longer as compared with that of HS· in gas phase reported by Norrish and Zeelenberg[13] and that of the thiyl radicals having amino acid group reported by Hoffman and Hayon.[14] $2k_r/\varepsilon$, in which ε is molar extinction coefficient and k_r the second order rate constant, was obtained from the slope of the second order plot at 370 nm. Assuming that ε of the thiyl radical at absorption maximum is similar to that of the thiyl radical having amino acid group (ε=300—600 $M^{-1}\,cm^{-1}$),[14] $2\,k_r$ was given as 2—4$\times 10^9$ $M^{-1}\,s^{-1}$ in hexane at 23 °C, suggesting that the thiyl radical decays predominantly with the recombination. Since these values are 4 times greater than those in liquid paraffin (5—10$\times 10^8\,M^{-1}\,s^{-1}$), the rate of recombination is thought to be a diffusion-controlled reaction.

When a mixed solution of 1,1-diphenylethylene and di-*t*-butyl disulfide was subjected to irradiation of flash light a new intense band was observed at 332 nm having a shoulder at 315 nm (Fig. 2). The absorbance at 332 nm was 30 times stronger than that of transient band observed without olefin. The transient spectrum shown in Fig. 2 is very similar to that of the diphenylmethyl radical.[15] Thus, the band could be assigned to the radical having diphenylmethyl radical moiety, which might be formed by the anti-Markownikoff addition of the thiyl radical to 1,1-diphenylethylene, $(Ph)_2\dot{C}\text{–}CH_2\text{–}SR$, to form a more stable intermediate radical. The mixed solution of disulfide and styrene gave a new sharp band at 322.5 nm (Fig. 3), the absorbance at this region being twice as strong as that of the transient band observed without styrene. A band at 370 nm, assigned to the thiyl radical, was also observed decaying more rapidly than the new band at 322.5 nm. Since the new band at 322.5 nm is very similar to that of the benzyl radical,[15] it can be attributed to the radical having benzyl radical moiety, which might be formed by the anti-Markownikoff addition of the thiyl radical to styrene, $H(Ph)\dot{C}\text{–}CH_2\text{–}SR$.

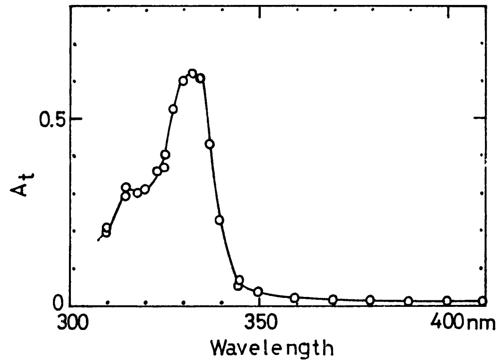

Fig. 2. Transient absorption spectrum produced by the flash photolysis (200 μs after flash) of the degassed hexane solution containing 1,1-diphenylethylene (2.3 mM) and di-*t*-butyl disulfide (2.0 mM).

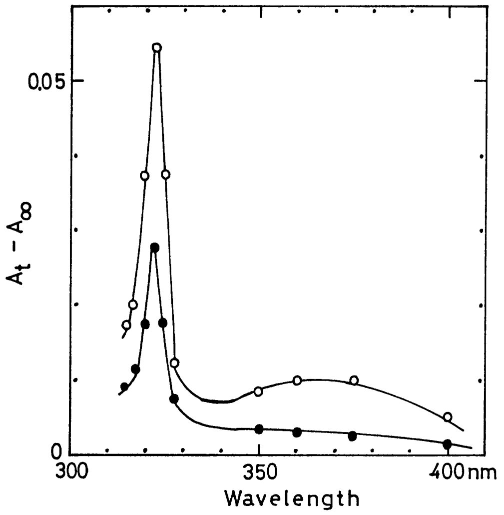

Fig. 3. Transient absorption spectra produced by the flash photolysis of the degassed solution containing styrene (140 mM) and di-*t*-butyl disulfide (4.9 mM). (a); 200 μs after flash (-○-). (b); 500 μs after flash (-●-).

It is most unlikely that these new bands are attributed to the radical ion formation, since no absorption bands due to the radical anions and cations of disulfide[16] and olefins[17] were observed for a mixed solution of disulfide and olefin even in the polar solvent such as dichloromethane. Possibility of the triplet←triplet absorption of olefins also should be examined. Even when 0.9 mM of ferrocene, an efficient triplet quencher, was added to the solution of disulfide and 1,1-diphenylethylene, no difference was observed either in the initial intensity or decay rate. Thus, any process involving the triplet states can not be included.

The new bands reached maximum intensity at 150 μs after flash, indicating that the absorption band related to the addition is attributed to the band at 370 nm rather than the shorter wavelength band than 330 nm band which is observed with flash light irradiation on the di-*t*-butyl disulfide solution without olefin. This is also supported by the effect of oxygen added. The band at 370 nm observed in the absence of olefin was very reactive to oxygen and scarcely observed in aerated solution, while the band at shorter wavelength was insensitive to oxygen. In the system containing olefins, no transient band due to the radicals formed from the addition reaction was observed in the presence of oxygen. The benzyl and diphenylmethyl radicals were reactive to oxygen as indicated by Porter and Windsor,[15] but this might mainly result from the reactivity of the primarily formed thiyl radical assigned to the band at 370 nm. It has been reported that small portion of dithio radical was formed [11,18] by photolysis of disulfide with the short wavelength light. Although no evidence for the formation of the dithio radical was obtained in our flash experiment, the dithio radical is known to be not reactive to olefin.[19] Furthermore, the alkyl radical, which may be formed as a pair of the dithio radical, is also known to add to olefin considerably more slowly (10^2—$10^3\,M^{-1}\,s^{-1}$) as compared with the thiyl radical.[7,20]

The observed reactions above can be accounted for by the following scheme:

$$\text{RSSR} \xrightarrow{h\nu} \text{RSSR*} \qquad (1)$$

$$\text{RSSR*} \longrightarrow 2\text{RS}\cdot \qquad (2)$$

$$2\text{RS}\cdot \xrightarrow{k_r} \text{RSSR} \qquad (3)$$

$$\text{RS}\cdot + \text{R}'(\text{R}'')\text{C=CH}_2 \xrightarrow{k_a} \underset{\textbf{I}}{\text{R}'(\text{R}'')\dot{\text{C}}\text{–CH}_2\text{–SR}} \qquad (4)$$

RSSR* may not be the triplet state since the initial yield and decay rate of the thiyl radical was not affected by mixing with ferrocene. Decrease in thiyl radical formation by oxygen should be due to the reactivity of the thiyl radical to oxygen. In Reaction 4, k_a can be estimated from the decay of the thiyl radical. In the case of 1,1-diphenylethylene, however, the tail of the larger absorption band at 332 nm of radical **I** masked the band of the thiyl radical. For styrene, although the initial yield of the thiyl radical decreased with increase in the concentration of styrene, the increase in the decay rate of the band at 370 nm was observed. The decay kinetics fit the first order plottings up to 70% consumption in the styrene concentration range 1—11 mM. Further addition of styrene interfered in the analysis of the decay kinetics because of decrease in the initial yield. Pseudo-first order rate constants were proportional to the concentration of styrene as shown in Fig. 4. From the slope, a value 3.8×10^5 $M^{-1}\,s^{-1}$ ($\pm15\%$) was obtained, which might correspond to the addition rate, if the observed decrease in the initial yield was simply due to the decrease in the light intensity of a flash by the absorption of styrene. The rate constant is 10^2—10^3 times smaller than the value obtained by the rotating sector method.[7,8] We have no criterion more reliable. As regards our flash experiment, there is one disadvantage; we can not completely neglect the possibility that the decrease in the initial yield of the band at 370 nm in the presence of styrene is related to the faster reaction of thiyl radical with styrene. Even if the value estimated by the flash technique may be a lower limit for the addition reaction, this is larger than that of the alkyl radical,[19] and comparable to that of the diarylcarbenes (10^5 $M^{-1}\,s^{-1}$).[5]

The ralative rate of addition reaction can be given, since the initial yield of the band at 332 nm decreased by the addition of styrene to the solution of diphenylethylene and disulfide. The reduction of the absorbance with the system containing an equimolar amount (1.5 mM) of styrene and diphenylethylene was 40% as compared with the absorbance of 3.0 mM of diphenylethylene. Assuming that this decrease was caused by the competitive addition reaction of the thiyl radical to both olefins, the rate of addition to diphenylethylene is 1.3 times greater than that of styrene. The ratio might be comparable to that of methyl radical (ratio=2.0)[21] and diphenylcarbene (ratio=1.0).[5]

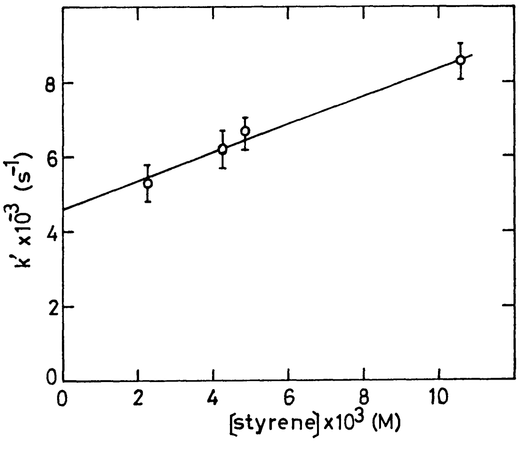

Fig. 4. Pseudo-first order rate constant (k') for the disappearance of the band at 370 nm as a function of styrene concentration.

Concerning the cause of the large absorbance observed for diphenylethylene compared with the case of styrene, the following factors might be mentioned: Large ε value, high addition rate, high efficient selectivity of anti-Markownikoff addition, and /or stability of radical **I** formed. In the absence of oxygen, decay of radical **I** formed can be caused by the recombination of the radicals, hydrogen abstraction from solvent, and addition to the remaining excess olefins. Half-lives of these radicals were 1 ms for diphenylethylene and 500 μs for styrene. In the case of diphenylethylene, a mixed order decay was observed. The decay kinetics of the styrene system at 322.5 nm band obeys the second order plot, giving $k/\varepsilon=5\times10^5$. In this case, ε of radical **I** may be similar to that of the benzyl radical. Choosing $\varepsilon=5500$ of the benzyl radical at absorption maximum as obtained by the pulse radiolysis technique,[22] the rate of the recombination of radical **I** was given to be 2.8×10^9 $M^{-1}\,s^{-1}$. The value is slightly smaller than that of the benzyl radical (3.1×10^9 $M^{-1}\,s^{-1}$).[22] The decay rate of radical **I** was not affected by the addition of styrene, since the rate constant of the propagating step is known to be very small for the polystyryl radical (100 $M^{-1}\,s^{-1}$ at room temperature).[23]

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