Formation of Cyclohexadienyl-Type Radicals in the Photoreduction of Xanthone As Studied by a Laser Photolysis–ESR Technique

Yoshio Sakaguchi,[†] Hisaharu Hayashi,*,[†] Hisao Murai,[†,‡] and Yasumasa J. I'Haya[‡]

Contribution from The Institute of Physical and Chemical Research, Wako, Saitama 351-01, Japan, and Department of Materials Science and Laboratory of Magneto-Electron Physics, The University of Electro-Communications, Chofu, Tokyo 182, Japan. Received December 29, 1987

Abstract: The photochemical hydrogen abstraction reactions of xanthone with several hydrogen donors in organic solvents were investigated at room temperature with the aid of a time-resolved electron spin resonance technique. The cyclohexadienyl-type radical of xanthone, instead of its ketyl radical, was obtained when hydrogen donors having negatively charged hydrogens (such as sodium borohydride, triethylgermanium hydride, and tri-*n*-butyltin hydride) were applied. The use of a partially deuteriated xanthone revealed that hydrogen addition occurred at the 4-position. The reaction was found to occur from the lowest $\pi\pi^*$ triplet state instead of the lowest $n\pi^*$ triplet.

The relationship between the reactivity and nature of excited states is important in photochemistry. For aromatic or conjugated systems containing group 15 and 16 atoms, such as nitrogen and oxygen, the existence of $n\pi^*$ and $\pi\pi^*$ states makes their photochemical reactions kaleidoscopic. The lowest $n\pi^*$ state is generally believed to play a principal role in the photochemical hydrogen abstraction reactions by triplet carbonyls.[1] The resulting radicals in these reactions are established to be ketyl or semiquinone radicals owing to the high electrophilic reactivity of the carbonyl oxygen in the $n\pi^*$ triplet state.

On the other hand, the lowest $\pi\pi^*$ triplet state of carbonyl compounds has been considered to have low reactivity, though the charge-transfer (CT) interaction with amines has been considered to enhance the reactivity of the $\pi\pi^*$ triplet state significantly. In these reactions, the reaction at the carbonyl oxygen is confirmed.[2] Greater reactivity of the $\pi\pi^*$ triplet state is also achieved by lowering the bond dissociation energy of hydrogen donors. For this purpose, special hydrogen donors such as 1,4-cyclohexadiene and tri-*n*-butyltin hydride can be applied. For such hydrogen donors with weak C–H or M–H bonds, the resulting radicals, however, have also been believed to be ketyl or semiquinone radicals.[3,4]

Using a time-resolved laser flash photolysis–ESR technique, we have recently found the formation of cyclohexadienyl-type or benzyl-type radicals during the photochemical hydrogen abstraction reactions of aromatic ketones. These radicals were obtained for the reactions of xanthone,[5,6] acetophenone,[7] 2-acetonaphthone,[7] and flavone derivatives[8] using various inorganic or organometallic compounds as hydrogen donors. Interestingly, these unexpected radicals are produced via hydrogen abstraction by the ring carbons rather than by the carbonyl oxygen.

In this paper, we report the investigation of the reaction mechanism of this new class of hydrogen abstraction reactions of aromatic carbonyl compounds, using xanthone as a model compound. With the aid of a time-resolved laser flash photolysis–ESR technique, we directly observed the transient radicals produced in the photochemical hydrogen abstraction reactions of xanthone, varying widely solvents and hydrogen donors. The ketyl and cyclohexadienyl-type radicals of xanthone were found to be produced depending on the applied solvents and donors. We discuss this reactivity in terms of the characteristics of the hydrogen donors employed and excited states of xanthone.

Experimental Section

Materials. Xanthone was recrystallized repeatedly from a 2:1 (v/v) mixture of ethanol and water. 2,4,5,7-Tetradeuterioxanthone was synthesized from xanthone according to Laposa and Bramley.[9] NMR evidence indicated that over 90% of the product was deuteriated. Sodium

borohydride, sodium cyanoborohydride, tri-*n*-butyltin hydride (Kanto Chemical), sodium borodeuteride (Merck), and hydrazine monohydrate (Wako Pure Chemical) were used as received. Triethylgermanium hydride was a gift from Professor Kunio Mochida, Gakushuuin University, Japan. Its purity was checked by gas chromatography, IR, and NMR and confirmed to be more than 99%. 1,4-Cyclohexadiene (Tokyo Chemical), *N,N*-diethylaniline, and *N*-methylaniline (Wako Pure Chemical) were distilled prior to use. Solvents (2-propanol, acetonitrile, *n*-heptane, cyclohexane, benzene, ethyl acetate, and 1,4-dioxane) were of guaranteed grade and were used without further purification.

Laser Flash Photolysis–ESR System. The apparatus and the flow system of the sample solutions were similar to those described elsewhere.[10] A Varian E-109 X-band ESR spectrometer was used for time-resolved measurements without field modulation. The solutions employed were bubbled with pure nitrogen gas prior to the measurement. A Molectron UV24 nitrogen gas laser (λ = 337 nm) or a Lumonix EX510 excimer laser (XeCl, λ = 308 nm) was used as an exciting light source. All time-resolved ESR spectra were measured at room temperature with a time width of 0.2 μs.

To avoid thermal reactions with xanthone, samples containing sodium borohydride (deuteride) or hydrazine were used within 3 h or 30 min, respectively, following preparation.

Laser Flash Photolysis–Optical Absorption System. Transient absorption measurements were performed at room temperature by using the nitrogen gas laser or the third (λ = 355 nm) or fourth (λ = 266 nm) harmonics of a Quanta-Ray DCR-1 Nd:YAG laser as an exciting light source. The sample solutions were bubbled with pure nitrogen gas prior to the measurement. The measuring apparatus was similar to that described elsewhere.[11]

Results and Discussion

Time-Resolved ESR Studies of a New Radical. The time-resolved ESR spectrum was measured for the photochemical reaction of the 2-propanol solution of xanthone (X, 0.001 mol dm^{-3}). The ESR spectrum observed at a time delay of 1.2 μs after laser excitation is shown in Figure 1A. (All of the ESR spectra shown in this paper were measured at a time delay of 1.2 μs after excitation.) The spectrum exhibits signals that are emissive at lower fields and absorptive at middle and higher fields (E/A* pattern).

(1) For reviews, see: Scaiano, J. C. *J. Photochem.* **1973/74**, *2*, 81.
(2) For reviews, see: Cohen, S. G.; Parola, A.; Parsons, G. H., Jr. *Chem. Rev.* **1973**, *73*, 141.
(3) Hammond, G. S.; Leermakers, P. A. *J. Am. Chem. Soc.* **1962**, *84*, 207.
(4) Brimage, D. R. G.; Davidson, R. S.; Lambeth, P. F. *J. Chem. Soc. C* **1971**, 1241.
(5) Sakaguchi, Y.; Hayashi, H.; Murai, H.; I'Haya, Y. J.; Mochida, K. *Chem. Phys. Lett.* **1985**, *120*, 401.
(6) Sakaguchi, Y.; Hayashi, H. *J. Phys. Chem.* **1986**, *90*, 550.
(7) Hayashi, H.; Sakaguchi, Y.; Murai, H.; I'Haya, Y. J. *J. Phys. Chem.* **1986**, *90*, 4403.
(8) Sakaguchi, Y.; Hayashi, H.; Murai, H.; I'Haya, Y. J. *J. Phys. Chem.* **1986**, *90*, 6416.
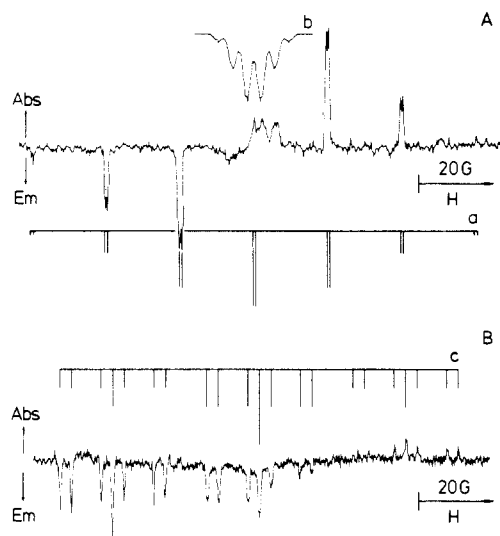(9) Laposa, J. D.; Bramley, R. *J. Phys. Chem.* **1984**, *88*, 4641.
(10) Murai, H.; Sakaguchi, Y.; Hayashi, H.; I'Haya, Y. J. *J. Phys. Chem.* **1986**, *90*, 113.
(11) Sakaguchi, Y.; Hayashi, H. *J. Phys. Chem.* **1984**, *88*, 1437.

†The Institute of Physical and Chemical Research.
‡The University of Electro-Communications.

Figure 1. Time-resolved ESR spectra, observed at a time delay of 1.2 μs after excitation of (A) the 2-propanol solution containing xanthone (0.001 mol dm⁻³) (microwave power, 2 mW) and (B) the solution containing xanthone (0.001 mol dm⁻³) and NaBH₄ (0.1 mol dm⁻³) (0.5 mW). Diagrams a, b, and c indicate the signal positions of the 2-hydroxy-2-propyl [(CH₃)₂ĊOH], xanthone ketyl (K•), and cyclohexadienyl-type (C•) radicals, respectively.

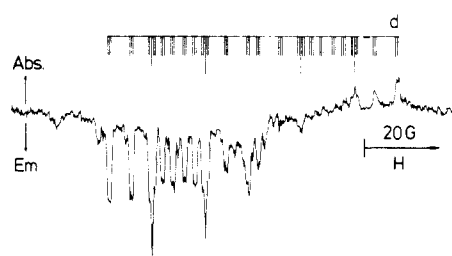Table I. Observed and Calculated Hyperfine Coupling Constants (in G)

radicals	position				
	1	2	3	4	OH
C• (diagram c)	14.1	3.1	10.9	39.1 × 2	
C•-d₁	14.0	2.9	11.0	39.4/5.9ᵃ	
C•-d₄ (diagram d)	14.1	0.45ᵃ	10.8	39.3/5.85ᵃ	
C•' (diagram e)	41.2 × 2	9.7	2.4	12.6	
cyclohexadienylᵇ (diagram g)	13.1	2.7 × 2	9.0 × 2	47.5 × 2	
xanthone ketylᶜ	4.05 × 2	0.96 × 2	3.78 × 2	0.61 × 2	3.39
radical 1ᵈ		8.9	4.3	11.7	
radical 2ᵈ	9.2		8.7	4.2	
radical 3ᵈ	3.8	7.7		8.2	
radical 4ᵈ	13.1	4.5	9.6		

ᵃHfc constants of deuterium. ᵇThe methylene protons are set at the 4-position for comparison. ᶜReference 13. ᵈCalculated value by an INDO method (ref 5).
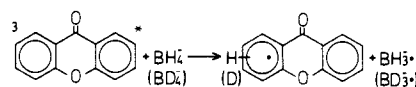
Scheme I
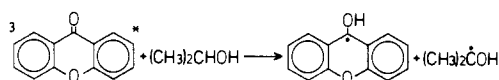
Longer time delays (not shown) indicated that the intensities of these signals decreased without changing their polarization patterns and without generating any new signals. Signals attributable to the 2-hydroxy-2-propyl radical [(CH₃)₂ĊOH] can be deduced from its hyperfine coupling (hfc) constants[12] as shown in diagram a. The signals observed in the middle of the spectrum can be assigned to the ketyl radical of xanthone (K•) because the observed positions agree with the positions of the simulated spectrum (diagram b). Here diagram b was obtained by the reported hfc constants of the ketyl radical as listed in Table I.[13]   In this diagram, the line width of each hyperfine line was taken to be 0.4 G. The polarization pattern of the spectrum is explained by the sum of the emission/absorption (E/A) pattern and totally absorptive (A) pattern. From this E/A pattern, this reaction can be considered to occur through a triplet precursor.[14]   Therefore, the present reaction can be explained as a typical hydrogen ab-

(12) Livingston, R.; Zeldes, H. *J. Chem. Phys.* 1966, 44, 1245.

(13) Wilson, R. *J. Chem. Soc. B* 1968, 1581.

(14) For example, see: Muus, L. T.; Atokins, P. W.; McLauchlan, K. A.; Pedersen, J. B. *Chemically Induced Magnetic Polarization*; Reidel: Dordrecht, The Netherlands, 1977.

Figure 2. Time-resolved ESR spectrum, observed at a time delay of 1.2 μs after excitation of the 2-propanol solution containing xanthone-2,4,5,7-d₄, (0.002 mol dm⁻³) and NaBH₄ (0.05 mol dm⁻³) (microwave power, 2 mW). Diagram d indicates the signal positions of the tetra-deuteriated cyclohexadienyl-type radical (C•-d₄).

Scheme II

straction reaction of the excited triplet state of xanthone (³X*) as depicted in Scheme I.

When sodium borohydride (NaBH₄) was added to the xanthone/2-propanol solution, the observed spectrum was drastically altered. The time-resolved ESR spectrum observed in the presence of NaBH₄ (0.1 mol dm⁻³), shown in Figure 1B, completely lacks contributions from the K• and (CH₃)₂ĊOH radicals. The observed signals are emissive at lower and middle fields and absorptive at higher fields (E*/A pattern), and they decayed monotonously without generating any other signals. The observed signal positions can be explained by a single radical (C•) indicated by diagram c in Figure 1B. This radical has a hyperfine structure consisting of two 39.1-, one 14.1-, one 10.9-, and one 3.1-G protons. These hfc constants are listed in Table I. The existence of two protons having such a large hfc constant as 39.1 G is characteristic of this radical. The E*/A polarization[14] of this radical indicates that this radical is also produced in the reaction of ³X*.

Upon addition of water to the NaBH₄-containing solution,[5] new signals appeared in the time-resolved ESR spectrum besides those of C•. These new signals can be assigned to the borane radical anions (¹¹BH₃•⁻ and ¹⁰BH₃•⁻) from their hfc constants.[15] The appearance of BH₃•⁻ means that C• is probably the hydrogen adduct of xanthone. When sodium borodeuteride (NaBD₄) was used as a hydrogen donor instead of NaBH₄, ESR signals due to BD₃•⁻ appeared in place of BH₃•, and one of the 39.1-G protons in C• was converted to a 5.9-G deuterium.[5] The hfc constants of this deuteriated radical (C•-d₁) are listed in Table I. Clearly, C• is an intermediate of the hydrogen abstraction reaction of ³X* with NaBH₄. Furthermore, on the basis of the hfc constants listed in Table I, we conclude that C• is completely different from the ordinary intermediate, K•.

Owing to the two protons having such a large hfc constant as 39.1 G and possible structures of hydrogen adduct of xanthone, C• can be assigned to a cyclohexadienyl-type radical of xanthone having two methylene protons. The hfc constant of methylene protons of the cyclohexadienyl radical was observed to be 47.5 G in 2-propanol as listed in Table I. The reaction that gives the time-resolved ESR spectrum in Figure 1B can be represented by Scheme II.   Here, four radicals (radicals 1-4) are possible
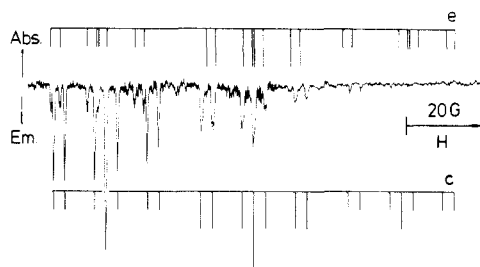

Radical 1   Radical 2   Radical 3   Radical 4
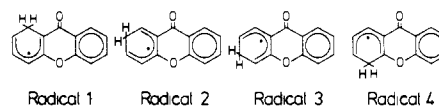
candidates for C•. The results obtained from an INDO calculation for the ring-proton hfc constants are listed in Table I.[5] Accordingly, radicals 2 and 3 can be eliminated as candidates, because the two ortho hydrogens of radicals 2 and 3 should have

(15) Giles, J. R. M.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* 1983, 743.

Figure 3. Time-resolved ESR spectrum, observed at a time delay of 1.2 μs after excitation of the 2-propanol solution containing xanthone (0.001 mol dm^{-3}) and tri-n-butyltin hydride (0.1 mol dm^{-3}) (microwave power, 2 mW). Diagrams c and e indicate the signal positions of C$^{\bullet}$ and another cyclohexadienyl-type (C$'^{\bullet}$) radical, respectively.

similar hfc constants. This fact cannot explain the observed hfc constants for C$^{\bullet}$.

This INDO calculation also indicated that C$^{\bullet}$ would be radical 4 rather than radical 1.[5] To test the validity of this assignment, we synthesized 2,4,5,7-tetradeuterioxanthone (X-d_4). If hydrogen addition occurs at the 1-position (4-position) of X-d_4, the generated cyclohexadienyl-type radical should have two hydrogen (one hydrogen and one deuterium) at the methylene group. We measured the time-resolved ESR spectrum of the 2-propanol solution containing X-d_4 (0.002 mol dm^{-3}) and NaBH$_4$ (0.05 mol dm^{-3}). The observed spectrum is shown in Figure 2 and the hfc constants of the generated cyclohexadienyl-type radical (C$^{\bullet}$-d_4, diagram d) are listed in Table I. The observed hfc constants of C$^{\bullet}$-d_4 indicate that this radical has one proton and one deuterium in its methylene group. Therefore, C$^{\bullet}$ was assigned to radical 4. Thus, C$^{\bullet}$, C$^{\bullet}$-d_1, and C$^{\bullet}$-d_4 were found to have the structures
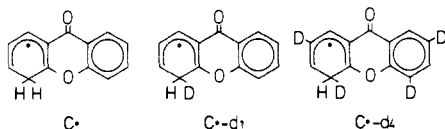

shown. The formation of a cyclohexadienyl-type radical instead of a ketyl radical as an intermediate in hydrogen abstractions by triplet carbonyls is unprecedented.[5-7]

Next, we measured the time-resolved ESR spectra of the photoreduction of xanthone using different hydrogen donors and obtained the following results: (1) When sodium cyanoborohydride (NaBH$_3$CN), triethylgermanium hydride (Et$_3$GeH), and tri-n-butyltin hydride (Bu$_3$SnH) were used as hydrogen donors in wet and dry 2-propanol solutions, the spectra of C$^{\bullet}$ were observed. (2) When N,N-diethylaniline (Et$_2$NPh), N-methylaniline, hydrazine (H$_2$NNH$_2$), and 1,4-cyclohexadiene were used as hydrogen donors in 2-propanol, the spectra of K$^{\bullet}$ were observed. These time-resolved ESR spectra had the E*/A phase patterns, although the contribution of the E pattern varied widely. For example, the ESR spectra observed for the reactions with Bu$_3$SnH (0.1 mol dm^{-3}), H$_2$NNH$_2$ (0.1 mol dm^{-3}), and 1,4-cyclohexadiene (0.14 mol dm^{-3}) in 2-propanol are shown in Figures 3-5, respectively. In Figures 4 and 5, the radicals derived from donors such as the hydrazyl[16] and cyclohexadienyl[17] radicals were also observed besides K$^{\bullet}$. As shown in Figure 3, the signals from a tri-n-butylstannyl radical[18] were undetectable. The disappearance of this radical may be due to a fast hydrogen-exchange reaction with Bu$_3$SnH and/or a fast spin relaxation through the heavy atom effect of Sn.

A careful examination of the spectrum of Figure 3 reveals that weak signals due to another radical (diagram e) coexist in addition to those due to C$^{\bullet}$. The hfc constants of this radical (C$'^{\bullet}$) are listed in Table I. C$'^{\bullet}$ has two protons having a hfc constant of as large as 41.2 G. Thus, C$'^{\bullet}$ can also be considered as another cyclohexadienyl-type radical. Since the hfc constants of the ring
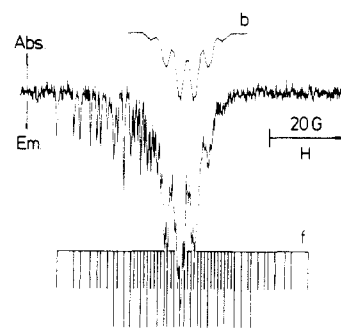
Figure 4. Time-resolved ESR spectrum, observed at a time delay of 1.2 μs after excitation of the 2-propanol solution containing xanthone (0.001 mol dm^{-3}) and hydrazine (0.1 mol dm^{-3}) (microwave power, 1 mW). Diagrams b and f indicate the signal positions of K$^{\bullet}$ and the hydrazyl (H$_2$NNH$^{\bullet}$) radical, respectively.
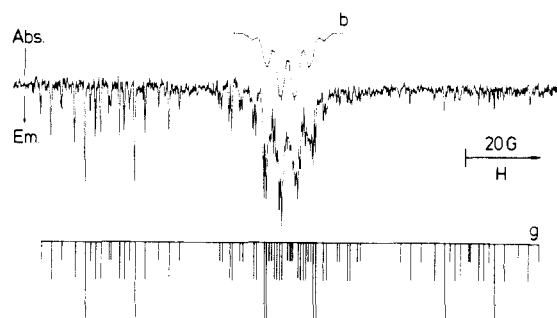
Figure 5. Time-resolved ESR spectrum, observed at a time delay of 1.2 μs after excitation of the 2-propanol solution containing xanthone (0.001 mol dm^{-3}) and 1,4-cyclohexadiene (0.14 mol dm^{-3}) (microwave power, 10 mW). Diagrams b and g indicate the signal positions of K$^{\bullet}$ and the cyclohexadienyl radical, respectively.

protons of C$'^{\bullet}$ are different from each other, C$'^{\bullet}$ is attributable to radical 1. The signals due to C$'^{\bullet}$ were also observed in the reaction with Et$_3$GeH, but not with NaBH$_4$ and NaBH$_3$CN. This implies that the selectivity of the reactions with borohydrides is better than the others.

We attempted to observe the nanosecond transient absorption spectrum of C$^{\bullet}$ at room temperature in the wavelength region of 350-700 nm using NaBH$_4$ and Bu$_3$SnH as hydrogen donors in 2-propanol, but only the quenching of ^{3}X* by NaBH$_4$ and Bu$_3$SnH was observed. At ~300 nm where the absorption due to C$^{\bullet}$ or C$'^{\bullet}$ is expected,[19] a very long-lived species, perhaps product, was observed. The quenching rate constants of ^{3}X* by NaBH$_4$ and Bu$_3$SnH in 2-propanol were 1.4 × 10^9 and 5.2 × 10^8 s^{-1} mol^{-1} dm^3, respectively. Since the diffusion-controlled rate in 2-propanol is ~3 × 10^9 s^{-1} mol^{-1} dm^3, these reactions appear to be relatively fast. Subsequent measurements using a system having picosecond resolution have confirmed our initial observations of the reaction with Bu$_3$SnH.

Solvent Dependence. To explain the mechanism of formation of the cyclohexadienyl-type radical, two factors should be considered: (1) the excited states of xanthone and (2) the nature of the hydrogen donors. In this section, the first factor will be discussed.

The locations of the lowest nπ^* and $\pi\pi^*$ triplet states of xanthone are believed to lie close to one another and depend largely on the nature of the solvent.[20,21] Therefore, we investigated the solvent dependence of the photoreduction reaction of xanthone with Bu$_3$SnH. Bu$_3$SnH was chosen because it dissolves in both polar and nonpolar solvents. The solvent dependence of the resulting radicals produced in the reactions of ^{3}X* with Bu$_3$SnH in several solvents is listed in Table II. The time-resolved ESR spectra in the absence of Bu$_3$SnH indicated either no signal (in acetonitrile, ethyl acetate, and benzene) or signals due to K$^{\bullet}$ and

(16) Malatesta, V.; Lindsay, D.; Horswill, E. C.; Ingold, K. U. *Can. J. Chem.* **1974**, *54*, 864.

(17) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.

(18) Lehnig, M. Dören, K. *J. Organomet. Chem.* **1981**, *210*, 331.

(19) Shida, T.; Hanazaki, I. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 646.

(20) Griesser, H. J.; Bramley, R. *Chem. Phys. Lett.* **1981**, *83*, 287.

(21) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747.

7482 *J. Am. Chem. Soc., Vol. 110, No. 22, 1988*

Sakaguchi et al.

Table II. Solvent Dependence of the Formation of the Cyclohexadienyl-Type and Ketyl Radicals in the Reaction of ^{3}X* with Bu_3SnH

solvents	dielectric constants[a]	cyclohexadienyl-type	ketyl
n-heptane	1.924[b]	x	O
cyclohexane	2.015	x	O
1,4-dioxane	2.209	O	(O)[c]
benzene	2.275	O	O
ethyl acetate	6.02	O	O
2-propanol	19.92	O	x
acetonitrile	37.5[b]	O	x

[a] Values at 25 °C that are not specified otherwise. [b] Values at 20 °C. [c] It is not clear whether Bu_3SnH gives K* in 1,4-dioxane, since the 1,4-dioxanyl radical is also observed in the presence of Bu_3SnH.

Scheme III
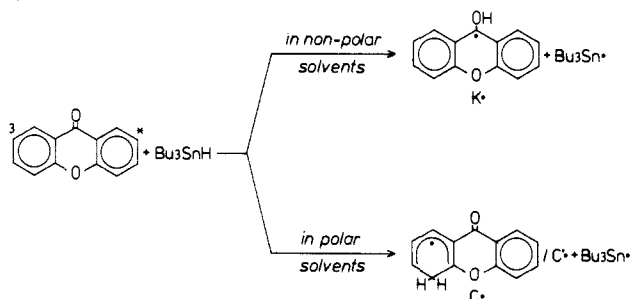
the radicals derived from solvents (in 2-propanol, 1,4-dioxane, cyclohexane, and n-heptane). Therefore, the hydrogen donor resulting in C* is attributed to be Bu_3SnH in the solvents where C* was found. Brimage et al. studied the products of the photoreduction reaction of xanthone with Bu_3SnH in benzene.[4] They isolated only pinacol and xanthydrol, which are attributable to the products from K*. The sum of their yields, however, accounts for only half of the xanthone consumed, raising the possibility that the remainder may be due to products from C* and C'*.

As shown in Table II, K* was observed for the reactions of ^{3}X* with Bu_3SnH in cyclohexane and n-heptane, but C* and C'* were not. On the basis of our ESR data alone, we cannot discount the possibility of a stepwise reaction; i.e., ^{3}X* abstracts a hydrogen from these solvents and the solvent-derived radicals abstract a hydrogen from Bu_3SnH. In an attempt to resolve this ambiguity, we measured the relative yield of K* in cyclohexane in the absence and presence of Bu_3SnH from the absorption around 600 nm using transient absorption spectroscopy. From this measurement, the relative yield of K* compared with the initial yield of ^{3}X* was found to increase by 30% in the presence of Bu_3SnH (0.05 mol dm^{-3}) compared to the yield in the absence of it. We can conclude that at least one-fourth of the K* is formed by direct hydrogen abstraction of ^{3}X* from Bu_3SnH in cyclohexane. This conclusion also holds well for n-heptane solution, since the rate of hydrogen abstraction by ^{3}X* from n-heptane is reported to be half of that from cyclohexane.[21] The solvents listed in Table II are placed in the order of the dielectric constant, ϵ. This table clearly shows that the generated radical changed from K* at low ϵ to C* at high ϵ as shown in Scheme III. At intermediate values of ϵ, both radicals are produced. This ϵ dependence agrees well with the solvent dependence of the location of the lowest nπ* and $\pi\pi$* triplet states of xanthone. Indeed, the location of the $\pi\pi$* triplet state is believed to be increasingly lowered with increasing solvent polarity. Scaiano estimated that the $\pi\pi$* triplet state of xanthone is 3.5 kcal mol^{-1} lower than the nπ* one in 2-propanol.[21] From this relationship, C* and C'* are considered to be formed from the lowest $\pi\pi$* triplet state of xanthone. On the other hand, K* is confirmed to be formed from the lowest nπ* state as previously indicated.[1,2]

In order to clarify the reactivity of the $\pi\pi$* triplet state, we investigated the photoreduction reactions of benzophenone, acetophenone, and 2-acetonaphthone with Bu_3SnH in various solvents.[7] Acetophenone showed similar solvent dependence as

Table III. Vertical Ionization Potentials (IPs) and Bond Dissociation Energies (BDEs) of Hydrogen Donors

compd	IP, eV	BDE, kcal mol^{-1}	compd	IP, eV	BDE, kcal mol^{-1}
BH_4^-	(5.10)[a]	(103)[b]	1,4-cyclo-hexadiene	8.80[j]	73.0[e]
Et_3GeH	9.6[c]	(81)[d]			
Bu_3SnH	8.8[c]	73.7[e]	2-propanol	10.36[k]	90.7[l]
Et_2NPh	7.20[f]	(84)[g]	1,4-dioxane	9.41[m]	(91.8)[n]
H_2NNH_2	8.1[h]	78.7[i]	cyclohexane	10.32[o]	93[p]
			n-heptane	10.20[q]	96[p]

[a] Calculated value: Daudel, R.; Kozmutza, C.; Goddard, J. D.; Csizmadia, I. G. *J. Mol. Struct.* **1978**, *50*, 363. [b] Estimated value: Reference 15. [c] Beltram, G.; Fehlner, T. P.; Mochida, K.; Kochi, J. K. *J. Electron Spectrosc. Relat. Phenom.* **1980**, *18*, 153. [d] The BDE of Et_3Ge-H has not been measured. For a substitute, that of Me_3Ge-H is presented: Doncaster, A. M.; Walsh, R. *J. Phys. Chem.* **1979**, *83*, 578. [e] Burkey, T. J.; Majewski, M.; Griller, D. *J. Am. Chem. Soc.* **1986**, *108*, 2218. [f] Maier, J. P.; Turner, D. W. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 521. [g] The BDE of $PhNEtCH(CH_3)-H$ has not been measured. For a substitute, that of $N(CH_3)_2CH_2-H$ is presented: Griller, D.; Lossing, F. P. *J. Am. Chem. Soc.* **1981**, *103*, 1586. The rates of hydrogen abstraction by *tert*-butoxy radical from Et_2NPh and $(CH_3)_3N$ are reported to be similar to each other, which indicates the resemblance between their BDEs: Griller, D.; Howard, J. A.; Marriot, P. R.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 619. [h] Adiabatic ionization potential: Meot-Ner, M.; Nelsen, S. F.; Willi, M. R.; Frigo, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 7384. [i] Gibson, S. T.; Greene, J. P.; Berkowitz, J. *J. Chem. Phys.* **1985**, *83*, 4319. [j] Kobayashi, T. *Phys. Lett. A* **1978**, *69A*, 31. [k] Katsumata, S.; Iwai, T.; Kimura, K. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3391. [l] Golden, D. M.; Benson, S. W. *Chem. Rev.* **1969**, *69*, 125. [m] Kobayashi, T.; Nagakura, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 1558. [n] The BDE of C–H of dioxane has not been measured. For a substitute, that of C–H of tetrahydrofuran at the corresponding position is presented (footnote *l*). [o] Bischof, P.; Hashmall, J. A.; Heilbronner, E.; Hornung, V. *Helv. Chim. Acta* **1969**, *52*, 1745. [p] Denisov, E. T.; Denisova, L. N. *Int. J. Chem. Kinet.* **1976**, *8*, 123. [q] Adiabatic ionization potential: Al-Joboury, M. I.; Turner, D. W. *J. Chem. Soc.* **1964**, 4434.

xanthone. With increasing solvent polarity, the yield of the cyclohexadienyl-type radical of acetophenone increased and that of its ketyl radical decreased. In the case of 2-acetonaphthone, its cyclohexadienyl-type radical was obtained in both polar and nonpolar solvents. On the other hand, benzophenone gave its ketyl radical even in polar solvents such as 2-propanol. This difference can also be explained by the nature of their low-lying triplet states. The lowest triplet states of benzophenone, acetophenone, and 2-acetonaphthone are believed to have the pure nπ*, mixed nπ* and $\pi\pi$*, and pure $\pi\pi$* characters, respectively. Thus, the $\pi\pi$* triplet state is generally confirmed to play an important role in the formation of the cyclohexadienyl-type radicals.

Effects of Hydrogen Donors. The second factor influencing photochemical hydrogen abstraction reactions is the nature of the hydrogen donor. In reactions of carbonyl compounds, two factors are emphasized: (1) the contribution of CT interaction and (2) the facility of the hydrogen abstraction. These two points can be interpreted by the ionization potentials (IPs) and the bond dissociation energies (BDEs). The IPs and BDEs of typical hydrogen donors investigated in the present study are listed in Table III.

One point that should be reconsidered is the CT interaction between ^{3}X* and Bu_3SnH in the formation of C*. The ϵ dependence of the formation of C* and K* shown in Table II might suggest some ionic precursors in the formation of C*, but this point can be discarded for the following reasons: (1) We detected no signal due to ionic species of xanthone in the reaction of ^{3}X* with $NaBH_4$, $NaBH_3CN$, Et_3GeH, or Bu_3SnH with the aid of the time-resolved ESR technique on the submicrosecond time scale and transient optical absorption ones on the nanosecond and picosecond time scales. (2) The formation of C* was observed in benzene and 1,4-dioxane, although their ϵ's are close to those of cyclohexane and n-heptane. The aromatic and ethereal solvents are shown to stabilize the $\pi\pi$* triplet state much more than the alkanes of similar ϵ's.[20] (3) The IPs of Et_3GeH and Bu_3SnH (which result in C* and C'*) are larger than those of Et_2NPh and

Formation of Cyclohexadienyl-Type Radicals

J. Am. Chem. Soc., Vol. 110, No. 22, 1988 7483

H_2NNH_2 (which result in K$^{\bullet}$). (4) The IP of 1,4-cyclohexadiene is fortunately almost the same as that of Bu_3SnH. The reaction of $^3X^*$ and 1,4-cyclohexadiene in 2-propanol was found, however, to result in K$^{\bullet}$ as shown in Figure 5.

The next point is the BDEs of the X–H bond of hydrogen donors. As listed in Table III, the BDEs of Bu_3SnH, 1,4-cyclohexadiene, and hydrazine are much smaller than others and are very similar to one another. Among these three hydrogen donors, the formation of C$^{\bullet}$ was only observed with Bu_3SnH. On the other hand, the BDE of BH_4^- is the largest among the donors listed in Table III,[22] but it results in C$^{\bullet}$. Therefore, we cannot find any dependence of the formation of C$^{\bullet}$ on the BDEs. The BDEs, however, can explain the selectivity between C$^{\bullet}$ and C''$^{\bullet}$. BH_4^- and BH_3CN^- are considered to react only at the most reactive point of the lowest $\pi\pi^*$ triplet state of xanthone since their BDEs are much larger than that of Bu_3SnH.

The above-mentioned facts point to the following conclusions: (1) The low ionization potential is not a critical factor to generate C$^{\bullet}$. (2) The low bond dissociation energy is not a critical factor, either. For example, the IP and BDE cannot explain the difference in the reactivities of Bu_3SnH and 1,4-cyclohexadiene. In order to explain the selectivity of hydrogen donors to form C$^{\bullet}$ or K$^{\bullet}$ from $^3X^*$, we must introduce another index.

The Charge on the Hydrogen Atom. In the hydrogen donors giving C$^{\bullet}$ ($NaBH_4$, $NaBH_3CN$, Et_3GeH, and Bu_3SnH), the hydrogens of the M–H bonds are considered to be negatively charged ($M^{\delta+}$–$H^{\delta-}$) from the electronegativity of atoms.[23] On the other hand, in the usual hydrogen donors such as hydrocarbons, alcohols, amines, and anilines, the hydrogens of the R–H bonds are positively charged ($R^{\delta-}$–$H^{\delta+}$). In fact, the IP and BDE of Bu_3SnH are very similar to those of 1,4-cyclohexadiene, but the hydrogens that are to be abstracted in these donors are considered to be oppositely charged. Such a difference in the charge of hydrogen can be considered to induce different reactivity in triplet carbonyls. We would like to call the hydrogen donors like Bu_3SnH "hydride-type" since their hydrogens to be abstracted are negatively charged. On the other hand, we would like to call the usual hydrogen donors "proton-type". Amines and anilines may be separately called "CT-type".[24]

Here we would like to compare the reactivities of these three types of hydrogen donors. The photoreduction reactions of triplet carbonyls with proton-type and CT-type hydrogen donors are well investigated, and their reaction mechanisms are established: Both type of donors react preferably with the lowest $n\pi^*$ triplet state and generate the ketyl or semiquinone radicals reflecting the large electrophilic reactivity at carbonyl oxygen in the $n\pi^*$ triplet state. CT-type donors enhance the reactions through the formation of CT complexes, which often increase the reactivity of the lowest $\pi\pi^*$ triplet state. In this case, the generated radicals are also the ketyl or semiquinone radicals. For hydride-type hydrogen donors we found the following characteristics: They react with both the lowest $n\pi^*$ and $\pi\pi^*$ triplet states of aromatic ketones. They give the ketyl radicals in the reactions through the $n\pi^*$ triplet state, but generate cyclohexadienyl-type or benzyl-type radicals through the $\pi\pi^*$ triplet state.[5-8] These facts indicate that the hydride-type hydrogen donors enable the reactions not only at the carbonyl oxygen but also at the ring carbons.

We attributed the specialty of the hydride-type hydrogen donors to the repulsion between the carbonyl oxygen and hydrogen atom. In the lowest $n\pi^*$ triplet state of carbonyl compounds, the elec-

trophilic carbonyl oxygen is very reactive. Therefore, the carbonyl oxygen can abstract a hydrogen from any hydrogen donor irrespective of the charge of hydrogen. On the other hand, the most reactive point may not be the carbonyl oxygen in the lowest $\pi\pi^*$ triplet states of carbonyl compounds, then the cyclohexadienyl-type or benzyl-type radicals can be formed depending on their reactivities.

Reactivity of the Lowest $\pi\pi^*$ Triplet State of Carbonyl Compounds. The formation of cyclohexadienyl-type or benzyl-type radicals shed a new light on the photochemistry of carbonyl compounds that has been overlooked. Our results are very simple: Not only the lowest $n\pi^*$ but also the lowest $\pi\pi^*$ triplet states have their particular reactivities in the hydrogen abstraction reactions.

The intrinsic reactivity of the lowest $\pi\pi^*$ triplet state for the hydrogen abstraction has scarcely been recognized. We can find only two predecessors who attributed the reactivity of carbonyl compounds to the $\pi\pi^*$ triplet state. Twenty years ago, Osugi et al. investigated the photoreduction reaction of 9-acetylanthracene with Bu_3SnH.[25] Fisch et al. recently studied the reaction of 2-acetonaphthone and its derivatives with Bu_3SnH.[26] These groups found the reduction at the aromatic rings instead of the carbonyl oxygen. Both groups imagined the cyclohexadienyl-type radicals as intermediates, but they could not prove the existence of these new radicals. Especially, the former group attempted to detect reaction intermediates with a transient optical absorption spectroscopy. Their proposals for the reactivities of the lowest $\pi\pi^*$ state are in agreement with our conclusion, but they gave no direct evidence to support their proposals. They applied Bu_3SnH simply as a hydrogen donor having a small BDE which might enhance the reaction from the $\pi\pi^*$ triplet state of carbonyl compounds. This is not correct, as we have shown above. The reaction of this type needs hydride-type hydrogen donors. Buckley and McLauchlan studied the photoreduction reactions of aza aromatics.[27] In these molecules, both $n\pi^*$ and $\pi\pi^*$ states are reactive, but the hydrogen abstraction occurs at the nitrogen atom in the both cases.

Regioselectivity. According to the observed time-resolved ESR spectra in the reactions of the lowest $\pi\pi^*$ triplet state of xanthone and hydride-type hydrogen donors, the 4-position of xanthone is found to be most reactive. However, we could not explain the regioselectivity of the present reaction, though we have attempted ab initio molecular orbital calculations with the aid of GAUSSIAN82 with STO-3G basis.[28,29] The detailed theoretical studies on the photoreduction reactions of carbonyl compounds[30] are based on the alkyl aldehydes and are not extendable to the reactions of the aromatic ketones having larger π systems. The advanced molecular orbital calculations including molecular deformations and better basis sets are far beyond the scope of the present study.

Conclusion

With a time-resolved ESR technique, we discovered that xanthone in the lowest $\pi\pi^*$ triplet state abstracts a hydrogen efficiently from sodium borohydride, sodium cyanoborohydride, triethylgermanium hydride, or tri-*n*-butyltin hydride and that it produces the cyclohexadienyl-type radicals instead of the ketyl radical. We determined the main reaction point to be the 4-position using 2,4,5,7-tetradeuterioxanthone. The photoreaction of xanthone with tri-*n*-butyltin hydride showed solvent dependence. With increasing solvent polarity, the hydrogen adduct of xanthone changed from the ordinary ketyl radical to the cyclo-

(22) The BDE of BH_4^- calculated in ref 15 may be overestimated. The BDE of BH_4^- was calculated to be 7 kJ mol^{-1} ($\sim$1.7 kcal mol^{-1}) smaller than that of methane (104.9 kcal mol^{-1}: Baghal-Vayjooee, M. H.; Colussi, A. J.; Benson, S. W. *J. Am. Chem. Soc.* **1978**, *100*, 3214). Therefore, the BDE of BH_4^- is considered qualitatively to be larger than or comparable to the BDEs of alkanes such as *n*-heptane and cyclohexane and not to be smaller than them.

(23) For example, see: Pritchard, H. O.; Skinner, H. A. *Chem. Rev.* **1955**, *55*, 745.

(24) Here we intend to characterize the hydrogen atom donors by the charge on the hydrogen atom and their reaction mechanism. Hydride-type, proton-type, and CT-type donors do not mean hydride, proton, and simple electron donors, respectively, but mean hydrogen atom donors having different characters.

(25) Osugi, J.; Kusuhara, S.; Hirayama, S. *Rev. Phys. Chem. Jpn.* **1967**, *37*, 94.

(26) Fisch, M. H.; Dannenberg, J. J.; Pereyre, M.; Anderson, W. G.; Rens, J.; Grossman, W. E. L. *Tetrahedron* **1984**, *40*, 293.

(27) Buckley, C. D.; McLauchlan, K. A. *Mol. Phys.* **1985**, *54*, 1.

(28) Binkley, J. S.; Frisch, M. J.; De Frees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Pople, J. A. *GAUSSIAN82*; Carnegie-Mellon Chem. Publ. Unit: Pittsburgh, PA, 1982.

(29) Molecular structure of xanthone: Biswas, S. C.; Sen, R. K. *Indian J. Pure Appl. Phys.* **1982**, *20*, 414.

(30) Bigot, B. *Isr. J. Chem.* **1983**, *23*, 116. Dewar, M. J. S.; Doubleday, C. *J. Am. Chem. Soc.* **1978**, *100*, 4935. Salem, L. *J. Am. Chem. Soc.* **1974**, *96*, 3486.

hexadienyl-type radicals. We explained this solvent effect on the reaction switching in terms of the location of the lowest $n\pi^*$ and $\pi\pi^*$ triplet states. To classify the hydrogen donors that give cyclohexadienyl-type radicals, we propose a new criterion, the charge of hydrogen atom to be abstracted. The donors that give cyclohexadienyl-type radicals have negatively charged, hydride-type, hydrogens. On the other hand, the usual donors have positively charged hydrogens. They are separated into proton-type and CT-type donors according to established concepts. The established ideas such as the charge-transfer interaction and bond dissociation energy cannot explain the difference in the reactivities between tri-n-butyltin hydride and 1,4-cyclohexadiene.

Through the present study we have extended the studies on the photoreduction reactions of triplet carbonyls to a much wider field by exploring the intrinsic reactivity of the $\pi\pi^*$ triplet state which has been overlooked. Besides these physicochemical interests, synthetic aspects may also become useful in the photoreduction reactions of aromatic carbonyl compounds from their $\pi\pi^*$ triplet states.

Protonation of 1,3,5-Triaminobenzenes in Aqueous Solutions. Thermodynamics and Kinetics of the Formation of Stable σ-Complexes

Wilhelm Knoche,* Wolfgang W. Schoeller, Reinhard Schomäcker, and Siegmund Vogel

Contribution from the Fakultät für Chemie, Universität Bielefeld, Postfach 8640, 4800 Bielefeld 1, West Germany. Received January 5, 1988

Abstract: 1,3,5-Tripyrrolidinobenzene (pK_a = 9.62), 2-methyl-1,3,5-tripyrrolidinobenzene (pK_a = 12.75), 2-ethyl-1,3,5-tripyrrolidinobenzene (pK_a = 13.7), and 1,3,5-trimorpholinobenzene (pK_a = 2.45) bind protons to the aromatic ring leading to the formation of σ-complexes in basic and weakly acidic aqueous solutions. Equilibrium and kinetics of the formation of the σ-complexes have been studied. The data obtained correlate well with data quoted in the literature for σ-complexes in superacidic media.

Electrophilic aromatic substitutions belong to the most fundamental reactions in organic chemistry. They proceed via a two-step mechanism: in the first step an electrophile X^+ is added to the benzene ring and a σ-complex is formed, in which the cyclic π-conjunction is interrupted; in the second step, a proton leaves the σ-complex and the aromatic structure is restored.

This two-step mechanism is now generally accepted. It was originally derived from chemical isotope studies,[1] which yield an indirect proof for the existence of a σ-complex as an intermediate, but do not allow us to identify separately the reaction steps involved. The existence of a σ-complex has been proved by protonation studies in superacidic media.[2] Effenberger et al.[3] synthesized triaminobenzenes, which form stable σ-complexes. Their structures are now well characterized.[4] These complexes were isolated as perchlorate salts, and their UV and NMR spectra show clearly that protonation occurs at the aromatic ring and not at the nitrogen atoms. Scheme I shows one of the possible mesomeric forms of the σ-complex for 1,3,5-tripyrrolidinobenzene. Thus, the protonation of these aminobenzenes may be used as a model reaction for electrophilic aromatic substitutions, where equilibrium

Scheme I
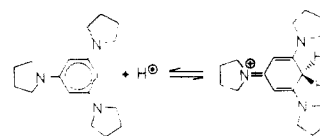
and kinetics of the formation of the σ-complex can be studied in detail.

In this contribution, results are reported for the triaminobenzenes 1,3,5-tripyrrolidinobenzene (TPB), 2-methyl-1,3,5-tripyrrolidinobenzene (MeTPB), 2-ethyl-1,3,5-tripyrrolidinobenzene (EtTPB), 1,3,5-trimorpholinobenzene (TMB), and 1,3,5-tripiperidinobenzene (TPiB). The structures of these components are given in Figure 1. For MeTPB and EtTPB only protonation of the alkyl-substituted carbon atom is observed.

Experimental Section

All reagents were of analytical grade except the substituted benzenes, which were prepared according to ref 3. For TPB, the progress of the protonation was observed spectrophotometrically at λ = 387 nm, for MeTPB, EtTPB, and TMB at λ = 400 nm, where the aromatic compounds do not absorb and the monoprotonated σ-complexes show absorption maxima. Stopped-flow and pressure-jump techniques were employed for the kinetic measurements. Slow reactions were followed with a standard UV/vis spectrophotometer. All kinetic experiments were performed under pseudo-first-order conditions; i.e., for the kinetic measurements, the optical absorbance is described by eq 1 with A_0 the am-

$$A = A_0 \exp(-t/\tau) + A_e \qquad (1)$$

plitude of the relaxation effect, $\tau = k_{obs}^{-1}$, and A_e the absorbance at equilibrium. All results refer to 25 °C and the solvent 90:10 (v/v)

(1) Melander, L. *Isotope Effects on Reaction Rates*; Ronald: New York, 1960.

(2) (a) Olah, G. A.; Schlosberg, R. H.; Porter, R. D.; Mo, Y. K.; Kelley, D. P.; Mateescu, G. D. *J. Am. Chem. Soc.* **1972**, *94*, 2034. (b) Köhler, H.; Scheibe, A. *Z. Anorg. Allg. Chem.* **1956**, *285*, 221. (c) Yamaoka, T.; Hosoya, H.; Nagakura, S. *Tetrahedron* **1970**, *26*, 4125. (d) Kresge, A. J.; Chiang, Y.; Hakka, L. E. *J. Am. Chem. Soc.* **1971**, *93*, 6167.

(3) Effenberger, F.; Mack, K. E.; Nagel, K.; Niess, R. *Chem. Ber.* **1977**, *110*, 165.

(4) Effenberger, F.; Reisinger, F.; Schönwälder, K. H.; Bäuerle, P.; Stezowski, J. J.; Jogun, K. H.; Schöllkopf, K.; Stohrer, W. D. *J. Am. Chem. Soc.* **1987**, *109*, 882.