it has been shown that reaction 1 occurs at thermal collision energies. Currently available thermodynamic data are not of sufficient accuracy to indicate whether reaction 1 is endothermic or exothermic. However, it is clear from the results presented that this reaction must be exothermic to account for the observation of CeO_2^+ at thermal collision energies and the observation of chemielectrons with energies of ~1 eV. There is therefore clearly a need for more accurate thermodynamic data on the cerium–oxygen system. Nevertheless, the qualitative discussion presented in this paper demonstrates how chemielectron spectroscopy is capable of probing the potential energy surfaces of reacting systems and providing complementary information on molecular ions to that obtained from photoelectron spectroscopy. Related work is currently in progress on other lanthanide plus oxygen chemiionization reactions. In particular, the La + O_2, Pr + O_2, and Nd + O_2 reactions are being studied, and for these reactions available cross sections[12] suggest that the analogue of reaction 6 is faster than in the Ce + O_2 case.

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Hydrogen-Abstraction Reactivity of Excited-State Para-Substituted Benzyl Radicals in Solution at Room Temperature

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Abstract: In contrast to almost no H-abstraction reactivity of the ground-state para-substituted benzyl radicals (*p*-X-benzyls: X = CN, Cl, F, and OCH_3) toward 1,4-cyclohexadiene (CHD), a significant fluorescence quenching by CHD in hexane at room temperature was confirmed for their fluorescent excited states, which may be assigned to $2B_2$ for *p*-cyanobenzyl and $1A_2$ for the other three *p*-X-benzyls. The quenching reveals a marked substituent effect: the quenching rate constant of $3.2 \times 10^9\ M^{-1}\ s^{-1}$ for *p*-cyanobenzyl fluorescence is much larger than that of $9.4 \times 10^5\ M^{-1}\ s^{-1}$ for *p*-methoxybenzyl fluorescence. The excited-state H-abstraction of *p*-cyanobenzyl from a H-donating CHD was directly demonstrated by the transient absorption induced upon the 308-nm pulse excitation of the ground-state *p*-cyanobenzyl. The marked substituent effect upon the quenching by CHD implies that $1A_2$ and $2B_2$ states have considerably different unpaired electron densities at the benzyl position.

Various multiphoton processes are operative in the organic photochemical reactions induced by intense laser pulses. One of the most efficient biphotonic processes is the photolysis of the transient species such as excited states and/or various reactive intermediates. Many free radicals are known as the reactive intermediate in the organic photochemistry. The study of the reactivity of the excited-state aromatic free radical would be thus expected to elucidate the laser-induced organic photochemistry, which is usually performed in the liquid phase at room temperature. Such a study (one of the photochemistry of transient species) is an attractive and current subject in the physical organic chemistry. The unimolecular rearrangement in the lowest excited doublet state has been confirmed for the very long-lived triphenylmethyl[1] and the stable perchlorotriphenylmethyl[2] radicals in solution at room temperature. Upon photoexcitation of unstable aromatic radicals (benzophenone ketyl[3] and the several arylmethyl radicals such as diphenylmethyl[4] and 1-naphthylmethyl[5]), furthermore, the intermolecular reactions with various substrates have been demonstrated to take place in solution at room temperature.[3-7] Long-lived excited-state radicals are generally preferable for the intermolecular reactions in fluid solution.

It has been demonstrated that the fluorescent-state benzyl radical (the prototype of arylmethyl radicals) in solution at room temperature is very short-lived (≤1 ns) owing to an extensively temperature-dependent nonradiative relaxation.[8,9] However, the fluorescence lifetimes of *p*-chlorobenzyl and *p*-methoxybenzyl in hexane at room temperature have recently been determined to be 81 ± 5[9] and 120 ± 5 ns,[10] which are much longer than that of benzyl. Such relatively long fluorescence lifetimes stimulated us to study the intermolecular reactivity of some para-substituted benzyls in the fluorescent excited state.

Based upon the kinetics and spectra of the fluorescence and absorption induced upon the 308-nm pulse excitation of the ground-state *p*-X-benzyl radical (X = OCH_3, F, Cl, or CN) in hexane at room temperature, we wish to report the quenching reaction of the excited-state *p*-X-benzyl by 1,4-cyclohexadiene known as a potential H donor. A pronounced substituent effect upon the quenching is discussed in terms of the $1A_2 \leftrightarrow 2B_2$ alternation of the lowest excited doublet state.

Experimental Section

p-(Chloromethyl)anisole (4-methoxybenzyl chloride, Tokyo Kasei), 4-fluorobenzyl bromide (Aldrich), and 4-chlorobenzyl chloride (Nakarai) were used after distillation under reduced pressure. α-Bromo-*p*-tolunitrile (4-cyanobenzyl bromide, Aldrich) was purified by recrystallization from

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(1) Bromberg, A.; Schmidt, K. H.; Meisel, D. *J. Am. Chem. Soc.* **1985**, *107*, 83.

(2) Fox, M. A.; Gaillard, E.; Chen, C.-C. *J. Am. Chem. Soc.* **1987**, *109*, 7088.

(3) Nagarajan, V.; Fessenden, R. W. *Chem. Phys. Lett.* **1984**, *112*, 207.

(4) Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396.

(5) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6368.

(6) Scaiano, J. C.; Johnston, L. J.; McGimpsey, W. G.; Weir, D. *Acc. Chem. Res.* **1988**, *21*, 22 and references therein.

(7) Johnston, L. J.; Lougnot, D. J.; Wintgens, V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1988**, *110*, 518.

(8) Meisel, D.; Das, P. K.; Hug, G. L.; Bhattacharyya, K.; Fessenden, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 4706.

(9) Tokumura, K.; Udagawa, M.; Ozaki, T.; Itoh, M. *Chem. Phys. Lett.* **1987**, *141*, 558.

(10) Tokumura, K.; Ozaki, T.; Udagawa, M.; Itoh, M. *J. Phys. Chem.* **1989**, *93*, 161.

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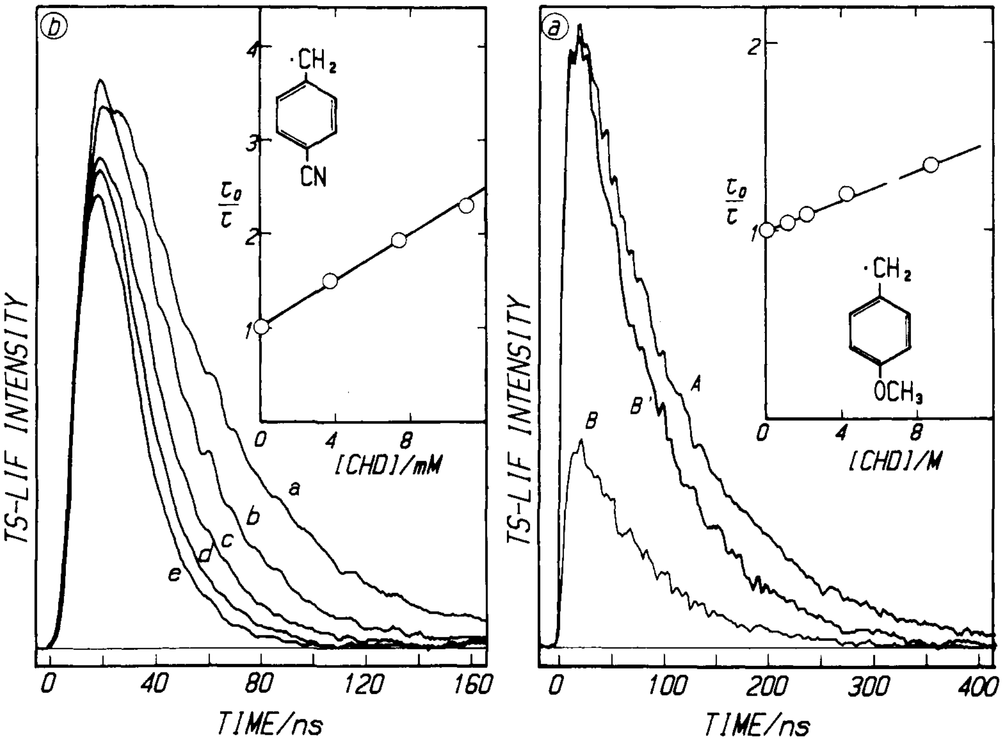

Figure 1. Oscillogram traces for the $D_1 \rightarrow D_0$ fluorescence of *p*-methoxybenzyl (a) and *p*-cyanobenzyl (b) in the presence of CHD. The concentrations of CHD are 0 (a and A), 3.63 (b), 7.27 (c), 10.9 (d), 14.5 (e), and 4360 mM (B and B′). The intensities of fluorescence signals (A and B′) are nearly normalized at maximum. The Stern–Volmer plots (τ_0/τ vs CHD concentration) are shown in the respective insets.

ethanol. Spectral grade hexane (Nakarai) without further purification was used as solvent to dissolve benzyl halides. 1,4-Cyclohexadiene (CHD) was purified by a silica column chromatography. Sample solutions were degassed by repeated freeze–pump–thaw cycles.

The 248-nm KrF laser pulse (14-ns fwhm, 75 mJ) was employed as the photolysis pulse to induce the homolytic scission of the CH_2–X bond in benzyl halide to yield a benzyl radical and a halogen atom, and the 308-nm XeCl laser pulse (13-ns fwhm, 80 mJ) was selected as the probe pulse to excite the radical in the ground state. Transient absorption and fluorescence spectra were measured by the laser-flash apparatus consisting of excimer lasers (Lambda Physik EMG 50E and 53MSC) with and without the monitoring pulsed xenon flash, respectively. The monitoring beam was cut off by an electromechanical shutter operating synchronously with the lasers. The delay time between the 248-nm and 308-nm pulses was controlled by a digital delay generator (BNC 7010) with the minimum resolution time of 100 ns. The electric signals from the photomultiplier (Hamamatsu Photonics R666 or R928) were digitized by a storagescope (Iwatsu TS 8123), and the kinetic and spectral analyses of the digitized data were carried out by a microcomputer (Fujitsu Micro 11BS or 16β).

Results and Discussion

High concentrations of free radical are often obtainable by the laser photolysis of its precursor in solution. As is distinct from the effective H-abstraction of alkyl radicals from H-containing solvents, most aromatic free radicals with unpaired electron delocalized over aromatic ring undergo various coupling reactions,[11-15] the rates of which are sufficiently slow to undertake the second pulse excitation. The $D_1 \rightarrow D_0$ fluorescence and the $D_n \leftarrow D_1$ absorption spectra were induced by the 308-nm XeCl laser pulse excitation of the transient para-substituted benzyls (*p*-X-benzyl) formed in the 248-nm KrF laser photolysis of *p*-X-benzyl halides in hexane at room temperature.[9,10] The fluorescence lifetimes (τ_0) were determined to be 120 ± 8 ns (*p*-methoxybenzyl), 200 ± 8 ns (*p*-fluorobenzyl), 81 ± 5 ns (*p*-chlorobenzyl), and 58 ± 4 ns (*p*-cyanobenzyl), respectively.

Fluorescence Quenching of Para-Substituted Benzyl Radicals by 1,4-Cyclohexadiene. The kinetic electron paramagnetic resonance experiment has demonstrated[16] that the ground-state benzyl radical does not abstract hydrogen from 1,4-cyclohexadiene (CHD), implying that the rate constant is less than 10^2 M^{-1} s^{-1} at 300 K, in contrast to the appreciable H-abstraction of alkyl radicals from CHD with rate constants of 10^4–10^5 M^{-1} s^{-1}. The delocalization of unpaired electrons over the benzene ring may be responsible for the inertness upon H-abstraction. However, CHD has been known as a potential H donor for the excited-state species: 94% of the quenching of benzophenone triplet (T_1) by CHD results in the H-abstraction with the rate constant of 2.73 × 10^8 M^{-1} s^{-1} in benzene at 300 K.[17] Furthermore, recent double-pulse experiments[4,5] have reported the fluorescence quenching processes of diphenylmethyl and 1-naphthylmethyl radicals by CHD, suggesting an excited-state H-abstraction. Hence, the quenching of a relatively long-lived fluorescence of *p*-X-benzyl (X = OCH_3, F, Cl, or CN) by CHD was examined to estimate the excited-state H-abstraction reactivity. Unfortunately, the fluorescent-state benzyl radical in solution at room temperature is too short-lived (≤1 ns) to undergo appreciable quenching by CHD.

The green $D_1 \rightarrow D_0$ fluorescence was induced by the 308-nm XeCl laser pulse excitation of the transient *p*-methoxybenzyl formed in the 248-nm KrF laser photolysis of *p*-(chloromethyl)anisole (CMA) in hexane at room temperature. Such two-step laser-induced fluorescence (TS LIF) signals were also measured at 500 nm in the presence of high concentrations of CHD. Figure 1a shows the oscillogram traces (A and B) for the 500-nm TS LIF with and without CHD (4360 mM). Since CHD is not transparent at the photolysis wavelength (248 nm) but transparent at the probe laser one (308 nm), the reduced TS LIF ($D_1 \rightarrow D_0$ fluorescence) intensity may be ascribed to the filter effect of CHD for the 248-nm laser photolysis of CMA to generate *p*-methoxybenzyl. Also shown in Figure 1a is the quenched TS

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(11) Langhals, H.; Fischer, H. *Chem. Ber.* **1978**, *111*, 543.

(12) Claridge, R. F. C.; Fischer, H. *J. Phys. Chem.* **1983**, *87*, 1960.

(13) Läufer, M.; Dreeskamp, H. *J. Magn. Reson.* **1984**, *60*, 357.

(14) Tokumura, K.; Udagawa, M.; Itoh, M. *J. Phys. Chem.* **1985**, *89*, 5147.

(15) Tokumura, K.; Mizukami, N.; Udagawa, M.; Itoh, M. *J. Phys. Chem.* **1986**, *90*, 3873.

(16) Hawari, J. A.; Engel, P. S.; Griller, D. *Int. J. Chem. Kinet.* **1979**, *11*, 621.

(17) Encinas, M. V.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 6393.

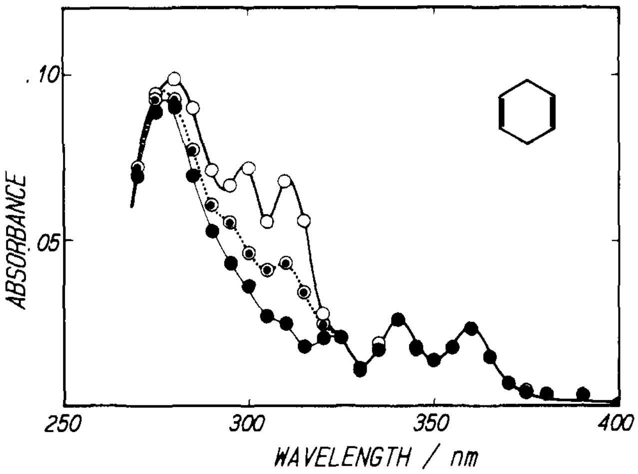

Figure 2. Time-resolved absorption spectra observed at 8 μs (○), 28 μs (⊙), and 200 μs (●) after the 248-nm laser pulse excitation of CHD (800 mM) in degassed hexane at room temperature.

LIF signal (B′), the intensity of which is normalized at maximum with the signal (A) in the absence of CHD in contrast to the decay feature. All the TS LIF signals exhibited a single exponential decay. The fluorescence lifetimes (τ) were determined in the various concentrations of CHD, and the Stern–Volmer plot of τ_0/τ is shown in the inset of Figure 1a. The quenching rate constant (k_q^*) was evaluated to be 9.4×10^5 M^{-1} s^{-1} from the slope of the Stern–Volmer plot. It is comparable to the rate constants (1.1×10^6 and $\sim 5 \times 10^5$ M^{-1} s^{-1} in cyclohexane at 300 K) reported for the fluorescence quenching of diphenylmethyl[4] and 1-naphthylmethyl[5] radicals, the unpaired electron of which can be considerably delocalized over π-conjugation system.

Whereas, the fluorescence of *p*-cyanobenzyl was efficiently quenched by small concentrations (3.63–14.5 mM) of CHD, as shown in Figure 1b, the k_q^* for the quenching of *p*-cyanobenzyl fluorescence was determined to be 3.2×10^9 M^{-1} s^{-1}, which is three orders of magnitude greater than that for the quenching of *p*-methoxybenzyl fluorescence. A relatively large k_q^* of 2.0×10^8 M^{-1} s^{-1} and a relatively small k_q^* of 6.3×10^6 M^{-1} s^{-1} were obtained for the fluorescence quenching of *p*-chlorobenzyl and *p*-fluorobenzyl, respectively. A marked para-substituent effect was thus confirmed for the fluorescence quenching of benzyl radical. The $D_n \leftarrow D_1$ absorption spectra as well as the bleaching of the $D_n \leftarrow D_0$ absorption spectra of these para-substituted benzyls would help in an interpretation of the marked substituent effect upon the reactions involved in the fluorescence quenching by CHD. Such spectra are obtainable by the two-step laser-induced-absorption measurements described in the next section.

Two-Step Laser-Induced-Absorption Measurements for the Quenching of Fluorescent Excited-State *p*-Cyanobenzyl by 1,4-Cyclohexadiene. Since no green emission was observed upon the 248-nm pulse excitation of CHD followed by the 308-nm pulse excitation, the quenching of the *p*-X-benzyl fluorescence by CHD could be observed as described above. However, the 248-nm pulse excitation of CHD generates the transient species subjected to the subsequent 308-nm pulse excitation. Figure 2 shows the time-resolved absorption spectra observed upon the KrF laser photolysis of CHD (800 mM) in hexane at room temperature. The residual spectrum after the decay of the absorption bands around 300 nm is almost identical with the absorption spectrum of the photolyzed solution. The unknown photoproduct is therefore responsible for the residual spectrum at 270–400 nm. There are characteristic twin peaks at 308 and 314 nm in the published UV spectrum of cyclohexadienyl radical in adamantane matrix at 298 K.[18] The triplet-sensitized $T_n \leftarrow T_1$ absorption spectrum (λ_{max} = 302.5 nm)[19] has been reported for 1,3-cyclohexadiene in benzene. The observed UV transient absorption band may be ascribed to cyclohexadienyl radical and slightly longer lived T_1 state of CHD. However, the initial transient absorbance at 308 nm is less than 0.06. In order to reduce the direct photolysis of CHD as little as possible, an efficient quenching system requiring low concentration of CHD should be selected. The quenching of the excited-state *p*-cyanobenzyl by CHD was thus studied by the two-step laser-induced-absorption measurements.

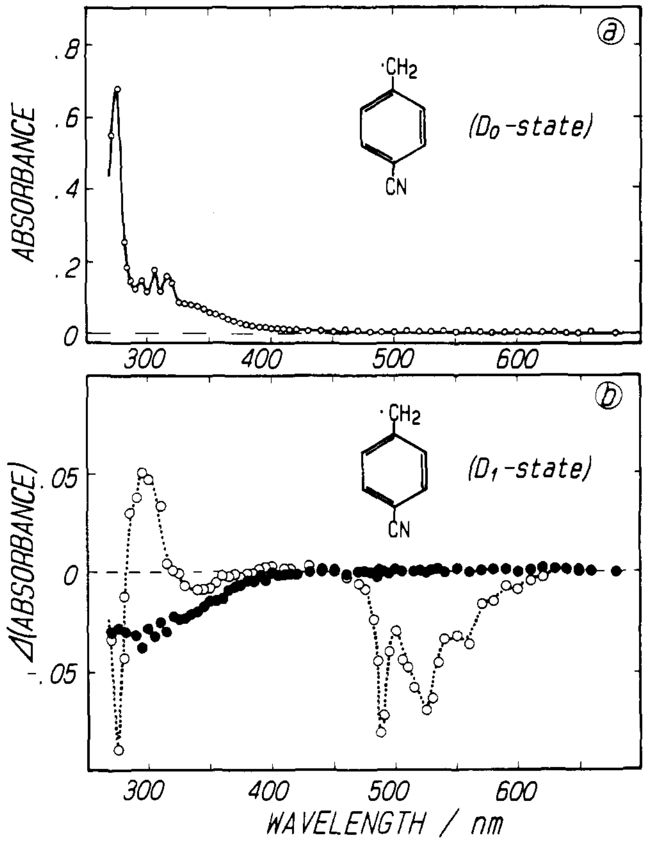

Figure 3. (a) Ordinary transient absorption spectrum observed at 330 ns after the 248-nm photolysis of the degassed hexane solution of α-bromo-*p*-tolunitrile (0.09 mM) at room temperature. (b) Time-resolved two-step laser-induced-absorption spectra observed at 20-ns (○) and 280-ns (●) after the 308-nm laser pulse excitation delayed by 600 ns from the 248-nm laser photolysis of the solution.

Figure 3a shows the transient absorption spectrum observed upon the 248-nm laser photolysis of α-bromo-*p*-tolunitrile in degassed hexane at room temperature. The spectrum consisting of the intense band (λ_{max} = 270 nm) with weaker bands (λ_{max} = 305 and 315 nm) is similar to the published spectrum (λ_{max} = 280, 310, 322 nm)[20] of *p*-cyanobenzyl formed by the reaction of e_{aq}^- with *p*-cyanobenzyl bromide followed by dehalogenation. It has been confirmed[10] that the $D_1 \rightarrow D_0$ fluorescence is induced upon both the 248-nm and the 308-nm pulse excitaton of *p*-methoxybenzyl formed in the 248-nm laser photolysis of *p*-(chloromethyl)anisole. Figure 4 shows the 500-nm fluorescence signals induced by the 248-nm pulse excitation of α-bromo-*p*-tolunitrile followed by the 308-nm pulse excitation. Both LIF signals exhibiting the same exponential decay of 58 ns are attributable to the $D_1 \rightarrow D_0$ fluorescence of *p*-cyanobenzyl. It is thus reasonable to assume that the $D_n \leftarrow D_1$ absorption signals revealed via the biphotonic processes are superimposed upon the $D_n \leftarrow D_0$ absorption signal exhibiting a second-order decay. Such a transient absorption signal was actually observed at 295 nm in the 248-nm pulse excitation of α-bromo-*p*-tolunitrile followed by the subsequent 308-nm pulse excitation.

The decaying TS LIA signal does not join in the transient absorption signal induced by the 248-nm pulse alone, and a bleaching persists. The TS LIA spectra can be depicted by plotting

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[18] Jordan, J. E.; Pratt, D. W.; Wood, D. E. *J. Am. Chem. Soc.* **1974**, *96*, 5588.

[19] Tóth, M. *Chem. Phys.* **1980**, *46*, 437.

[20] Neta, P.; Behar, D. *J. Am. Chem. Soc.* **1981**, *103*, 103.

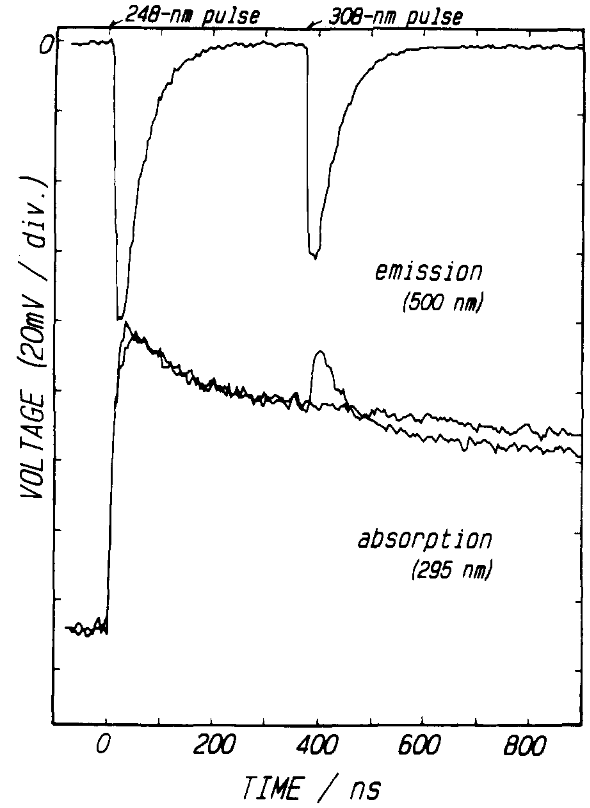

Figure 4. Oscillogram traces of the 295-nm transient absorption and the 500-nm fluorescence signals induced by the 248-nm laser pulse excitation of α-bromo-p-tolunitrile (0.09 mM) followed by the 308-nm laser pulse excitation. Also shown is an oscillogram trace of the 295-nm transient absorption induced by the 248-nm laser pulse excitation alone.

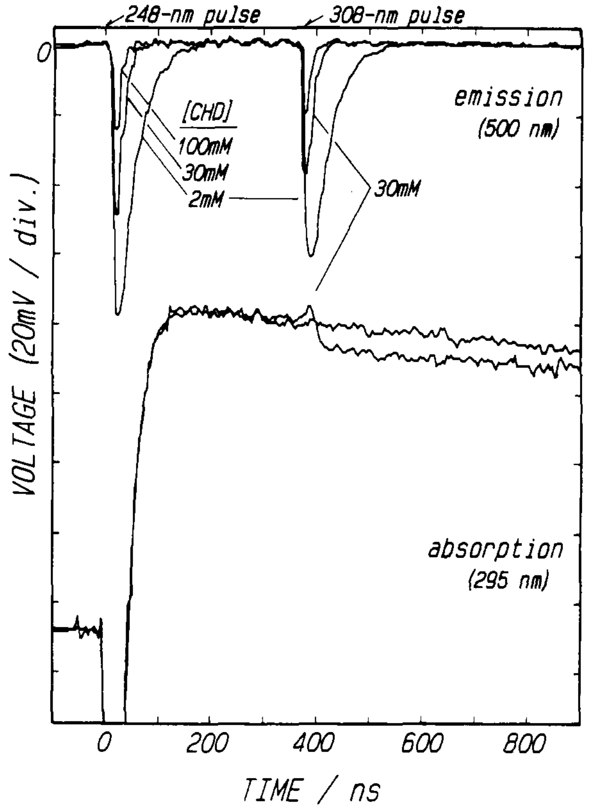

Figure 5. Oscillogram traces of the 295-nm transient absorption induced by the 248-nm laser pulse excitation of α-bromo-p-tolunitrile (0.09 mM) with and without the subsequent 308-nm laser pulse excitation. Also shown are the 500-nm LIF signals in the presence of CHD (2, 30, 100 mM): first laser pulse, 248 nm; second laser pulse, 308 nm.

log $[I_1(t)/I_2(t)]$ against wavelength. Here, $I_1(t)$ and $I_2(t)$ stand for the monitoring light intensity for the ordinary (one-step) LIA and TS LIA signals, respectively. Figure 3b shows the TS LIA spectra at 20 and 280 ns after the 308-nm pulse excitation delayed by ca. 600 ns from the 248-nm pulse excitation of α-bromo-p-tolunitrile, The spectrum at 20-ns delay was actually depicted by plotting log $(I_1/I_2(t))$ against wavelength. Here, the monitoring light intensity immediately before the 308-nm pulse excitation is designated as I_1. The $D_1 \rightarrow D_0$ fluorescence is responsible for the apparent negative absorption band (450–650 nm), and the UV TS LIA spectrum may be primarily recognized as the difference spectrum between the $D_n \leftarrow D_1$ and the $D_n \leftarrow D_0$ absorption spectra. The positive absorption band (λ_{max} = 295 nm) is thus regarded as the $D_n \leftarrow D_1$ absorption spectrum of p-cyanobenzyl, and the sharp negative band at 270 nm is due to the depletion of the intense $D_n \leftarrow D_0$ absorption peak.

The TS LIA spectrum was also taken at 280 ns after the 308-nm pulse excitation. At that time, the $D_1 \rightarrow D_0$ fluorescence has completely faded out. The negative absorption spectrum is similar to the inversion of the 330–400-nm broad absorption band (Figure 3a) due to unknown species formed in the 248-nm laser photolysis of α-bromo-p-tolunitrile. No significant bleaching of the $D_n \leftarrow D_0$ absorption is seen in this spectrum. Figure 5 shows the 500-nm $D_1 \rightarrow D_0$ fluorescence signals of p-cyanobenzyl induced by the 248-nm pulse excitation of α-bromo-p-tolunitrile followed by the 308-nm pulse excitation in the presence of CHD (2, 30, and 100 mM). The 295-nm transient absorption in the presence of 30 mM of CHD is also shown in Figure 5. Furthermore, Figure 6 shows the 295-nm TS LIA as well as the ordinary (one-step) LIA in the absence of CHD (a) and in the presence of CHD (b–d: 2, 5, 100 mM). The quenching of the excited-state p-cyanobenzyl is evident from the fact that the TS LIA ($D_n \leftarrow D_1$ absorption) decays faster with increasing concentration of CHD. In the considerable concentrations of CHD, the $D_n \leftarrow D_1$ absorption signal is hidden by the emission of CHD, as shown in Figure 6c,d.

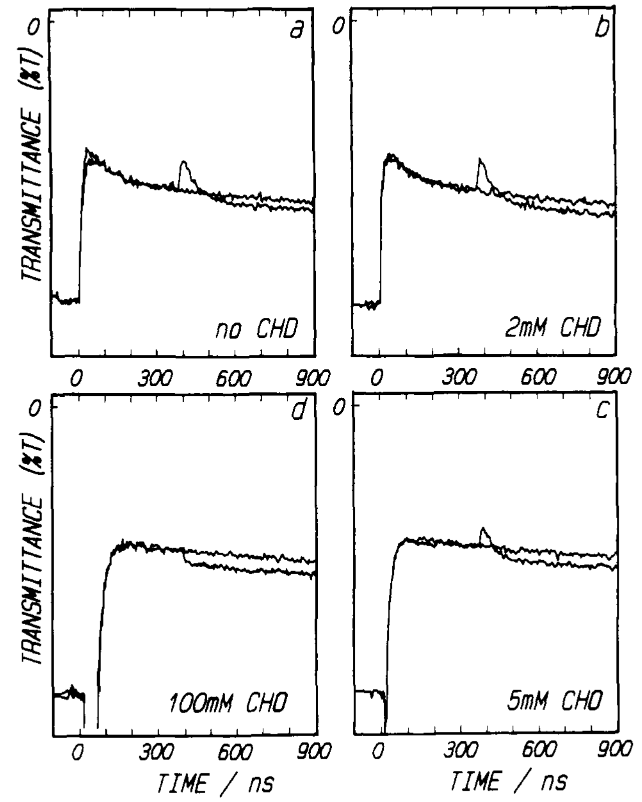

Figure 6. Oscillogram traces of the 295-nm transient absorption induced by the 248-nm laser pulse excitation of α-bromo-p-tolunitrile (0.09 mM) with and without the subsequent 308-nm laser pulse excitation in the absence of CHD (a) and in the presence of CHD: (b) 2 mM, (c) 5 mM, (d) 100 mM.

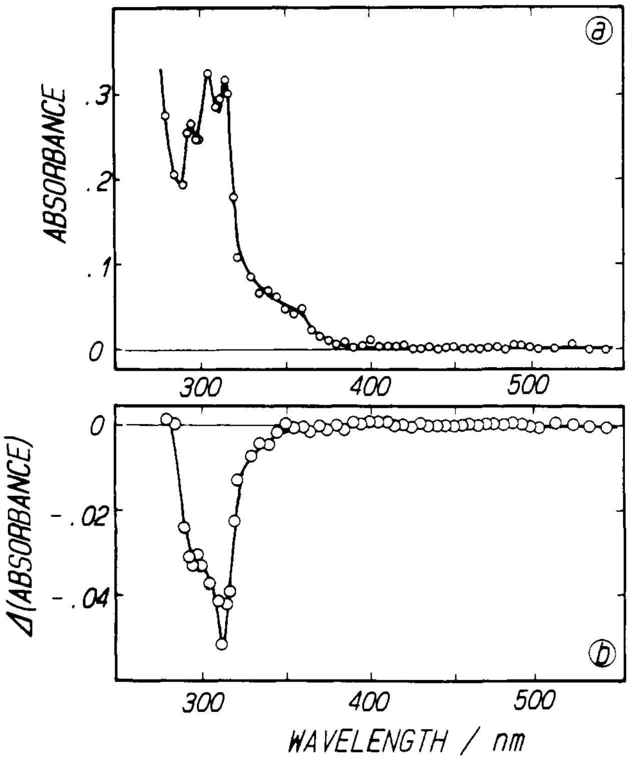

Figure 7. (a) Ordinary transient absorption spectrum observed at 300 ns after the 248-nm laser photolysis of α-bromo-*p*-tolunitrile (0.09 mM) in the presence of 100 mM of CHD in hexane at room temperature. (b) Two-step laser-induced-absorption spectrum observed at 140 ns after the 308-nm laser pulse excitation delayed by 370 ns from the 248-nm laser photolysis of the solution.

Figure 7a shows the transient absorption spectrum observed at 300 ns after the 248-nm pulse excitation of the solution of α-bromo-*p*-tolunitrile and CHD (100 mM).[21] The spectrum is similar to that (Figure 3a) in the absence of CHD. Three peaks around 300 nm are ascribed to the $D_n(2A_2) \leftarrow D_0(1B_2)$ absorption spectrum of *p*-cyanobenzyl, and the weak and broad absorption band around 350 nm may be due to unknown species,[22] as already described earlier. The H-abstraction of *p*-cyanobenzyl (D_1) from a CHD is assumed to generate a *p*-tolunitrile and a cyclohexadienyl radical. Almost the same absorption spectra of *p*-tolunitrile and α-bromo-*p*-tolunitrile prevent us from detecting the formation of *p*-tolunitrile in the TS–LIA measurements. The transient visible absorption spectrum (λ_{max} = 560 nm)[23] of cyclohexadienyl radical is not detectable owing to its poor molar extinction coefficient (<100 M^{-1} cm^{-1}).[4] However, the aforementioned UV spectrum of cyclohexadienyl is much more intense than the visible band.

The molar extinction coefficient of cyclohexadienyl has been reported to be 1.21×10^4 M^{-1} cm^{-1} at 318 nm,[24] while that of *p*-cyanobenzyl is ca. 5.0×10^3 M^{-1} cm^{-1} at 322 nm.[20] If the H-abstraction of the excited-state (D_1) *p*-cyanobenzyl from CHD to yield cyclohexadienyl is predominant, the TS–LIA spectrum around 320 nm should be fairly positive regardless to the negative absorption reflecting the bleaching of the weak spectrum due to unknown species. The persistent bleaching spectrum (Figure 7b) was actually obtained at 140 ns after the 308-nm pulse excitation delayed by 370 ns from the 248-nm pulse excitation of α-bromo-*p*-tolunitrile. It is considerably different from the bleaching spectrum (Figure 3b), reflecting the depletion of the unknown photoproduct in the absence of CHD, and it rather resembles the inversion of the $D_n(2A_2) \leftarrow D_0(1B_2)$ absorption spectrum. The lack of the bleaching peak corresponding to the 305-nm peak of the $D_n(2A_2) \leftarrow D_0(1B_2)$ absorption spectrum of *p*-cyanobenzyl implies the formation of cyclohexadienyl exhibiting a considerable absorption around 300 nm. From these facts, it is demonstrated that some fractions of the quenching actions of the excited-state *p*-cyanobenzyl by CHD result in the H-abstraction reaction to yield cyclohexadienyl.

Table I. Rate Constants[a] for the Fluorescence Quenching of Para-Substituted Benzyl Radicals by CHD in Hexane at 300 K

X (*p*-X-benzyl)	$k_q{}^*/M^{-1}\ s^{-1}$	D_1 state
-CN	3.2×10^9	$2B_2$
-Cl	2.0×10^8	$1A_2$
-F	6.3×10^6	$1A_2$
$-OCH_3$	9.4×10^5	$1A_2$

[a] Standard deviation ca. 15%.

The photoselection method applied for benzyl and *p*-methylbenzyl in rigid glass at 77 K has indicated the assignment of $1A_2$ for their emitting state.[25] The energy levels of the close-lying lowest excited doublet states ($1A_2$ and $2B_2$) of benzyl may be perturbed by some substituents. Contrary to only a minor perturbation of the methyl group or chlorine atom at the para position of benzyl,[12] both *p*-methoxy[12] and *p*-cyano[20] groups make a strong perturbation to the electronic levels of benzyl system. The $D_1 \rightarrow D_0$ fluorescence spectra of *p*-methoxybenzyl and *p*-cyanobenzyl in rigid glass at 77 K exhibited the 0,0-band at 463 nm and 461 nm, respectively.[26] Nevertheless, we actually observed the considerably different $D_n \leftarrow D_1$ absorption spectra exhibiting the peak at 340 nm[10] for *p*-methoxybenzyl and at 295 nm for *p*-cyanobenzyl. Assuming that the allowed D_n state is severely dependent upon the nature of the lowest excited doublet state (D_1), the different D_1 states may be responsible for their quite different $D_n \leftarrow D_1$ absorption spectra. Very recently, Hiratsuka et al.[27-29] have determined the polarization degree of the fluorescence emission and excitation spectra of *p*-cyanobenzyl, *p*-carboxybenzyl, *p*-fluorobenzyl, and *p*-methoxybenzyl as well as benzyl itself stabilized in the polyvinyl alcohol film at 77 K. They assigned the emitting state of *p*-cyanobenzyl and *p*-carboxybenzyl to $2B_2$ contrary to the $1A_2$ assignment for other benzyl radicals, and they suggested that the strong π-electron-attracting group at the para position of benzyl causes an inversion of the close-lying $1A_2$ and $2B_2$ states. These facts are very consistent with the significantly different $D_n \leftarrow D_1$ absorption spectra of *p*-cyanobenzyl and *p*-methoxybenzyl described above.

A marked substituent effect was demonstrated for the quenching of the *p*-X-benzyl fluorescence and for the assignment of the lowest excited doublet state, as summarized in Table I. Although all the quenching actions of the excited-state *p*-X-benzyl by CHD do not lead to the H-abstraction from CHD, the excited-state H-abstraction reactivity is the primary factor for the fluorescence quenching by CHD. The marked substituent effect upon the quenching by CHD is therefore ascribed to the difference in the unpaired electron density, and it is assumed that the unpaired

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(21) The 248-nm laser photolysis of CHD (800 mM) gave rise to weak transient absorption spectra ascribable to the lowest triplet state and cyclohexadienyl radical, as described in the text. The 248-nm laser pulse excitation of CHD is much less for the solution containing both α-bromo-*p*-tolunitrile (0.09 mM) and CHD (100 mM) than for the solution of CHD (800 mM) alone.

(22) Methylated benzyl cations are known to be formed as a minority product in the UV steady-state illumination of methylated benzenes in rigid glass at 77 K. On the other hand, long-lived and broad spectra around 300 nm were confirmed in the transient absorption spectra of all *p*-X-benzyl halides examined. It is highly probable that the long-lived transient absorption is due to the *p*-X-benzyl cation formed by a consecutive and/or a simultaneous two 248-nm photon absorption of *p*-X-benzyl halide within the duration of KrF laser pulse.

(23) Effio, A.; Griller, D.; Ingold, K. U.; Scaiano, J. C.; Sheng, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 6063.

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

(25) Friedrich, D. M.; Albrecht, A. C. *J. Chem. Phys.* **1973**, *58*, 4766.

(26) In the $D_1 \rightarrow D_0$ fluorescence spectra of *p*-methoxybenzyl and *p*-cyanobenzyl in hexane at room temperature, the allowed component (0,0 band and its progressions) can be neglected compared to the vibronic bands.

(27) Hiratsuka, H.; Mori, K.; Shizuka, H.; Fukushima, M.; Obi, K. *Abstr. 1st Annu. Meeting Jpn. Chem. Soc.* **1988**, 37.

(28) Hiratsuka, H.; Yokoyama, T.; Murakata, S.; Mori, K.; Shizuka, H.; Fukushima, M.; Obi, K. *Abstr. Jpn. Symp. Mol. Struct. Spectra* **1988**, 532.

(29) Hiratsuka, H.; Mori, K.; Shizuka, H.; Fukushima, M.; Obi, K. *Chem. Phys. Lett.* **1989**, *157*, 35.

electron density at the benzyl position of $2B_2$ is considerably higher than that of $1A_2$ state. Significant mixing of the close-lying $2B_2$ (D_2) and $1A_2$ (D_1) might be responsible for a relatively high rate in the quenching of the *p*-chlorobenzyl fluorescence by CHD. From the analysis of the vibrational structure in the fluorescence excitation spectrum of *p*-fluorobenzyl in a supersonic jet, Fukushima and Obi[30] have demonstrated that the energy gap between $1A_2$ and $2B_2$ states is spread out by the introduction of fluorine atom at the para position of benzyl. Poor mixing of the two states might be therefore responsible for a low rate in the quenching of *p*-fluorobenzyl fluorescence by CHD. The predominant character of $1A_2$ is implied for the D_1 state of *p*-methoxybenzyl by a very low rate of 9.4×10^5 M^{-1} s^{-1} in the fluorescence quenching.

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Registry No. CHD, 628-41-1; *p*-cyanobenzyl radical, 4939-73-5; *p*-chlorobenzyl radical, 3327-51-3; *p*-fluorobenzyl radical, 2194-09-4; *p*-methoxybenzyl radical, 3494-45-9.

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[30] Fukushima, M.; Obi, K. *Abstr. Jpn. Symp. Mol. Struct. Spectra* **1986**, 182; **1987**, 582.

Evaluation of the Arrhenius Parameters for the Thermal Isomerization of a Gaseous Ion. The Temperature Dependence of the Cyclohexylium Ion Unimolecular Rearrangement

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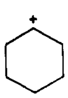
Abstract: Gas-phase isomerization of cyclohexylium ion (**1**), obtained via protonation of cyclohexene and of bicyclo[3.1.0]hexane and via hydride-ion abstraction from cyclohexane by $C_nH_5^+$ ($n = 1, 2$) and by s-$C_3H_7^+$ ions, has been investigated by a radiolytic technique in CH_4 and C_3H_8 in the pressure range from 106 to 1480 Torr. Temperature-dependence studies in the temperature interval from 310 to 353 K have provided the activation parameters of the *thermal* rearrangement of **1** into 1-methylcyclopentylium ion (**2**) in CH_4 at 750 Torr and in C_3H_8 at 1480 Torr. Least-squares analysis of the two mutually consistent sets of data leads to an activation energy of 7.4 ± 1 kcal mol^{-1} and to a preexponential factor of $10^{12\pm1.3}$ s^{-1}. These values represent the first estimates of the activation parameters of a unimolecular isomerization of a gaseous ion thermally equilibrated with the bath gas, i.e., under conditions which allow meaningful comparison with solution kinetics. The results support previous evidence for the existence of gaseous **1**, providing a quantitative evaluation of the energy barrier for its rearrangement into **2**. The more extensive formation of **2** from the protonation of bicyclo[3.1.0]hexane than that of cyclohexene is consistent with the long-postulated protonated-cyclopropane route in the branching rearrangement of cycloalkylium ions.

Cyclohexylium cation (**1**), well-characterized as an ionic intermediate in solution,[1] has long escaped detection in the gas phase, owing to its fast rearrangement into the 1-methylcyclopentyl isomer (**2**), occurring in a shorter time than required for analysis by structurally diagnostic mass spectrometric techniques, e.g., collisional activation (CA) spectrometry.[2] In previous papers[3,4] we have presented evidence for the existence of **1** in the gas phase, with a lifetime exceeding 10^{-8}–10^{-7} s, based on the results obtained with a radiolytic[5] and a nuclear-decay technique,[6] which allow structural and kinetic studies of gaseous ions in a wide pressure range. While demonstrating that **1** is indeed a legitimate ionic intermediate in the gas phase, characterized by a local minimum on the $C_6H_{11}^+$ energy surface,[7] our results confirmed its facile rearrangement into structure **2**, more stable by 11 kcal mol^{-1},[8] the activation energy of the process being roughly estimated as ≤10 kcal mol^{-1}.[4]



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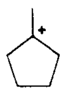

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We report now a more detailed investigation of the gas-phase isomerization of **1**, including an attempt at estimating its empirical activation parameters by temperature-dependence experiments in the pressure range from 106 to 1480 Torr.

It should be emphasized that meaningful evaluation of activation parameters comparable to those ordinarily measured in solution requires that the ions undergoing isomerization be thermally equilibrated with a bath gas of defined temperature, and that their rearrangement can be monitored by sufficiently fast techniques. These conditions can hardly be achieved by current mass spectrometric approaches, where the ionization process imparts excess internal energy to the charged species, whose collisional thermalization is generally inefficient at the low pressures attainable

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[1] (a) Olah, G. A.; Schleyer, P. v. R., Eds. *Carbonium Ions*; Wiley-Interscience: New York, 1970; Vol. 2, Chapters 14 and 15. (b) Brouwer, D. M.; Hogeveen, H. *Prog. Phys. Org. Chem.* **1971**, *9*, 179.

[2] Wesdemiotis, C.; Wolfschütz, R.; Schwarz, H. *Tetrahedron* **1980**, *36*, 275.

[3] Attinã, M.; Cacace, F.; Giacomello, P. *J. Am. Chem. Soc.* **1981**, *103*, 4711.

[4] Attinã, M.; Cacace, F.; Cipollini, R.; Speranza, M. *J. Am. Chem. Soc.* **1985**, *107*, 4824.

[5] (a) Cacace, F. In *Kinetics of Ion-Molecule Reactions*; Ausloos, P., Ed.; Plenum Press: New York, 1979; p 199. (b) Cacace, F. *Radiat. Phys. Chem.* **1982**, *20*, 99. (c) Speranza, M. *Gazz. Chim. Ital.* **1983**, *113*, 37. (d) Cacace, F. In *Structure/Reactivity and Thermochemistry of Ions*; Ausloos, P., Lias, S. G., Eds.; Reidel: Dordrecht, 1987; p 467. (e) Cacace, F. *Acc. Chem. Res.* **1988**, *21*, 215. For experimental details, see ref 20 and 21.

[6] Cacace, F.; Speranza, M. *Techniques for the Study of Ion Molecule Reactions*; Farrar, J. M., Saunders, W., Jr., Eds.; Wiley-Interscience: New York, 1988; Chapter VI.

[7] Our experimental findings are supported by later theoretical calculations. Cf.: Viruela-Martin, P. M.; Nebot, I.; Viruela-Martin, R.; Planelles, J. *J. Chem. Soc., Perkin Trans. 2* **1986**, 49.

[8] All thermochemical data are based (a) on the compilation of: Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695, except for the heat of formation of c-$C_6H_{11}^+$, 179 kcal mol^{-1}, taken from: (b) Lossing, F. P.; Holmes, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 6917.