worth noting is the early suppression in acid solutions of the faint shoulder near 3620 cm^{-1}, generally ascribed to "free" OH. As for the stretching bands of H_3O^+ ions, they are expected at still lower frequencies than those of water because of the much stronger hydrogen bonds (2.52 Å vs. 2.84 Å).[18] What one observes, instead, is the much studied broadening, or continuum, on the low-frequency side of the main band, in both Raman and infrared spectra.[5,17] The only indication of a band is a vague hump around 2900 cm^{-1} on the continuum in the IR spectra of very concentrated acids. It has been assigned to the ν_3 vibration of H_3O^+ ions,[7,13] but this is certainly an oversimplification considering the complexity of these strong electrolytes. For example, with increasing acid concentration the separated, fully hydrated ions, $H_3O^+\cdot 3H_2O$, give place, first to ion pairs, then to triple ions, and finally to a quasi-lattice structure as in molten salts. Gradually, the hydrogen bonds, with marked directional character, are replaced by purely electrostatic interactions. (The undissociated HBr molecules present in the supersaturated solutions[14] can only act as hydrogen-bond donor with water, *not* as acceptor, even from H_3O^+). Each of the above species will have its own set of vibrational frequencies, slightly different from the others. In addition, these frequencies are spread out due to coupling with intermolecular and interionic vibrations. Finally, at very short O···O distances, the O–H vibrations eventually lead to proton transfer. This continuous distribution of O–H distances implies a continuous distribution of vibrational frequencies, as observed. Therefore, one should apply Occam's razor to such abstract concepts as "$H_5O_2^+$ groupings" or "O···H···O charged fragments", as recommended before.[6,24]

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Photoionization of Unsaturated Hydrocarbons at 249 nm in Acetonitrile. Visible Absorption Spectra of Radical Cations

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Irradiation at 249 nm of CH_3CN solutions of several unsaturated hydrocarbons leads to photoionization resulting in radical cations. Their identity was established by comparison with the products of the ionic photodissociation at 350 nm of exciplexes using chloranil as the electron acceptor. A monophotonic excitation mechanism is suggested, and visible absorption spectra (400–840 nm) of the radical cations and their dimers and their kinetics of disappearance are reported.

Introduction

The one-electron oxidation of molecules brings about drastic changes in the physical and chemical properties. The modified electronic structure in the radical cation causes, for example, a dramatic change in the absorption characteristics from the IR to the UV region[1] as well as a pronounced decrease (in most cases) of the bond strengths in unsaturated hydrocarbons[2] to name only two of the most important changing properties. A lot of interest has been given to the study of radical cations in condensed phase in relation to charge-separation processes in chemistry and biology,[3] and in industrial processes dealing with the liquefaction of coal.[4]

In the past, three techniques have been used extensively to study the reactivity and the absorption spectra of radical cations in the condensed phase: pulse radiolysis in the liquid phase,[5] γ radiolysis of frozen solutions at low temperatures,[6] and ionic photodissociation of exciplexes.[7]

We report the photoionization of unsaturated (aromatic and hydroaromatic) hydrocarbons in CH_3CN solution by excitation at 249 nm. Our method relies on the fact that, when the solute is excited to a singlet excited state, the system undergoes ionization in the polar environment because of the extensive stabilization of the radical cation and the negative species. In principle, there are two mechanistic alternatives in that the radical cation may be formed either by direct photoionization following the absorption of a sufficiently energetic photon or by fast dissociation from a well-defined excited state of the solute formed by the absorption of one (or more) photon(s). Considerable attention has been given to the mechanism of photoionization of organic molecules in fluid solutions, and both monophotonic[8] and biphotonic[9] processes have been found and discussed. The present work deals primarily with the quantitative assessment of the absorption spectra of radical cations and their kinetics of disappearance. One method of radical ion generation used was ionic photodissociation of exciplexes by exciting the system at 350 nm. This method is known to produce free radical cations and radical anions in concentrations high enough

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to allow spectroscopic detection, provided the negative free energy difference between the free ions and the exciplex is large enough. The new method of radical cation generation explored in this work consists of the photolysis of the hydrocarbon solution at 249 nm. The yield and the identity of the 249-nm photoionization product were determined by comparison with the results of the ionic photodissociation carried out at 350 nm. The new photoionization method proved useful in cases where the energetic requirement for the generation of radical ions by ionic photodissociation at 350 nm was not met. A fringe benefit of combining two different ways of generating ions is the quantitative measurement of the decay kinetics of the radical cations with the oppositely charged species.

Experimental Section

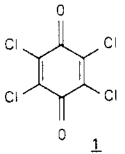
A standard laser-flash-photolysis system with a perpendicular probe-excitation arrangement was used. The photolysis light source was either a Lumonics TE 860// or a Lambda Physik EMG 500 excimer laser operated on a Kr/F_2 or Xe/F_2 gas mixture to obtain emission at 249 or 350 nm. The pulse duration was between 12 and 20 ns, and the pulse energy was measured with a Scientech 362 calorimeter-type power meter. The probe light was an Oriel 1000-W tungsten halogen incandenscent lamp operated in a CW mode. The last dynode of the photomultiplier (Hamamatsu R 928), which was specially modified to obtain fast response and high peak currents for short times, was gated by a 10–15-V gating pulse from a Hewlett-Packard 214A pulse generator (master trigger) for a duration of 100–140 μs; 60–80 μs after the gating pulse which turned on the photomultiplier, a second pulse generator (HP 214 A) triggered the laser. The output signal was amplified 5 times by means of a fast timing amplifier (ORTEC Model 574, bandwidth 300 MHz), whose output was displayed on a TEK 7844 (500 MHz) or TEK 485 (400 MHz) oscilloscope in 50-Ω termination and subsequently photographed by a fast camera (TEK C-51). The rise time of the whole transient processing electronics was estimated to be less than 10 ns. The monochromator was a Czerny-Turner, 0.45-m grating instrument (MPI) used in first order, and the 400-μm slit width used throughout this investigation corresponded to a spectral bandwidth of 0.7 nm. Appropriate fused-silica optical elements, filter solutions, and glass filters (Corning) were used. The fused-silica sample cell (1-cm square) was masked so as to allow the excitation of a slice of $10 \times 10 \times 1$ mm^3 of the solution, whereas the probing light irradiated a volume of $1 \times 10 \times 1$ mm^3.

Acetonitrile (MCB Omnisolv) was very slowly distilled twice in glass, and only the middle fraction was kept for further use. Experiments performed with a solvent specially dried on CaH_2 and distilled under vacuum directly into the sample cell (without any contact with air) gave identical spectroscopic and kinetic results. Chloranil (tetrachloro-*p*-benzoquinone, Pfaltz and Bauer) was recrystallized twice from benzene. The following chemicals were used without further purification: naphthalene (99%+, scintillation grade, Gold Label from Aldrich Chemical Co.), *trans*-stilbene (96%, Aldrich), bibenzyl (99.9%, MCB), diphenylmethane (99%, Aldrich), fluorene (Fluka, puriss), 9,10-dihydrophenanthrene (97%, Aldrich). Dibenzobicyclo[2.2.2]octadiene and triptycene were authentic samples provided by Dr. C. A. Grob, University of Basel, Switzerland.

Results and Discussion

As mentioned briefly in the Introduction, the "philosophy" of the present work is to demonstrate the identity of the species produced by excitation at 249 nm by comparison with the products of the ionic photodissociation of exciplexes, which are generated through excitation of the sensitizer chloranil (1) at 350 nm.

Ionic Photodissocation of Exciplexes upon Excitation at 350 nm Resulting in Radical Cations. It has been known for some time that excited electron acceptors, such as chloranil (1), are quenched efficiently by electron donors in polar solution.[7] The quenching pathway has been shown to involve the formation of an exciplex which decays in part into free, solvated radical cations of the electron donor D and radical anions of the electron acceptor A according to the following scheme:



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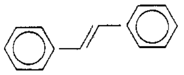

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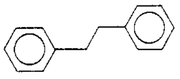

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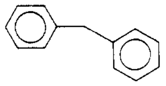

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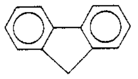

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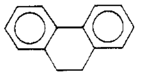

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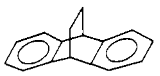

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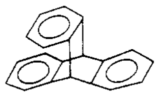

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$$A^* + D \xrightarrow{k_q} (D,A)^* \rightarrow ({}^2D^{+}\cdot,{}^2A^{-}\cdot) \underset{k_{rec}}{\overset{k_{sep}}{\rightleftharpoons}} {}^2D^{+}\cdot + {}^2A^{-}\cdot \quad (1)$$

This reaction sequence has been applied successfully to observe the UV/vis absorption spectra of organic radical cations and anions in solution[10] in cases where the overall reaction is sufficiently exothermic according to the following equation:

$$\Delta G_{et} = E^{ox}(D/D^+) - E^{red}(A^-/A) - E_{00}(A^*) - C \quad (2)$$

where ΔG_{et} is the free energy of electron transfer, $E^{ox}(D/D^+)$ and E^{red} (A^-/A) are the oxidation and reduction potentials of the donor and acceptor in solution, $E_{00}(A^*)$ is the adiabatic excitation energy of the acceptor, and C is the Coulomb term for the ion pair ($C \sim 0.1$ eV). We have used chloranil (1) as electron acceptor, because it is converted with high quantum yield ($\phi \sim 1$) into its lowest triplet state, and its photochemistry and photophysics are well-known. The advantage of dealing with the triplet state is that the rate of deactivation of the exciplex ${}^3(D,A)^*$ and of the ion pair ${}^3({}^2D^{+}\cdot,{}^2A^{-}\cdot)$ back to the ground state is considerably slower than for the analogous singlet states.[11] Just after the end of the laser pulse a transient absorption peaking at 470 and 510 nm is observed. This absorption can be attributed to the triplet state of 1 for which a second-order decay constant of 7×10^9 M^{-1} s^{-1} has been measured in the system naphthalene–1.[13] After the

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(10) See, for example: Hino, T.; Akazawa, H.; Masuhara, H.; Mataga, N. *J. Phys. Chem.* **1976**, *80*, 33. Grellmann, K. H.; Watkins, A. R.; Weller, A. *Ibid.* **1972**, *76*, 469, 3132. Hentzschel, P.; Watkins, A. R. *Ibid.* **1976**, *80*, 494. Amouyal, E.; Bensasson, R. *J. Chem. Soc. Faraday Trans. 1* 1977, *73*, 1561.

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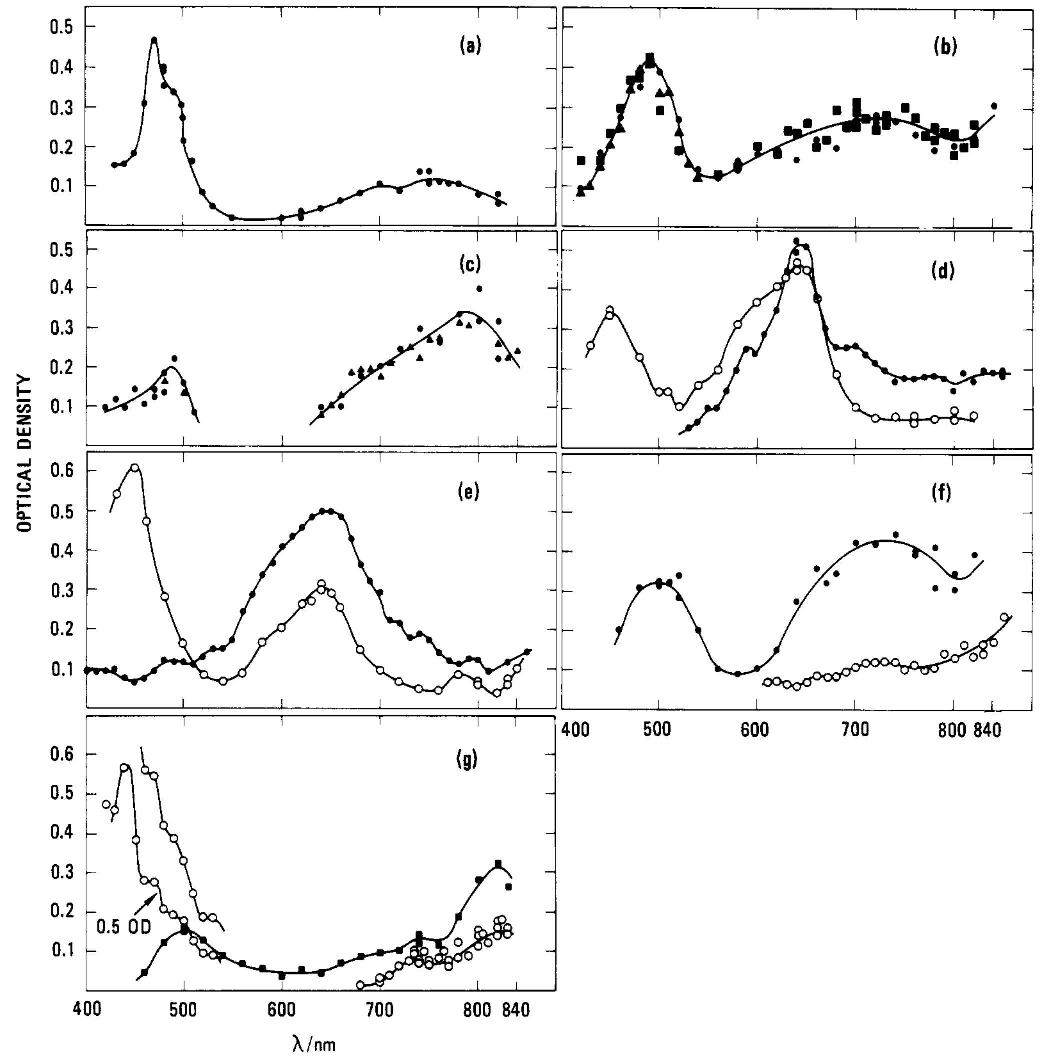

Figure 1. Visible absorption spectra of radical cations in CH_3CN. Open and filled symbols correspond to excitation at 350 nm in the presence of chloranil (**1**) and to excitation of only the hydrocarbon solution at 249 nm, respectively. The transient absorptions were all taken 20 ns after the start of the laser pulse, except for e, where the delay was 300 ns (see text). The concentrations were as follows. a: (**2**) = 4 mM. b: (**3**) = 4.5 mM. c: (**4**) = 4.5 mM. d: ●, (**5**) = .44 mM; ○, (**5**) = 4.3 mM and (**1**) = 3.2 mM. e: ●, (**6**) = 1.4 mM; ○, (**6**) = 4.8 mM and (**1**) = 3.1 mM. f: ●, (**7**) = 2.8 mM; ○, (**7**) = 7.3 mM and (**1**) = 4.9 mM. g: ■, (**8**) = 6.5 mM; ○, (**8**) = 6.3 mM and (**1**) = 4.8 mM.

short-lived triplet absorption, the absorptions of $1^{-}\cdot$ (around 450 nm[12]) and the corresponding radical cation emerge in the spectrum as shown in Figure 1 (open symbols). The radical cation of **2** has been previously observed in this way.[16] The results obtained with hydrocarbons **3** and **4** show a few differences with the others: The decay of the triplet state of **1** was remarkably slower even in the presence of sizable amounts of the quencher ($\sim 10^{-2}$ M); furthermore, no radical cation absorption was detected, whereas the absorption of the radical anion was readily observed, indicating an ionic photodissociation process. The absence of a detectable radical cation absorption can be explained on the basis of their gas-phase ionization (9.1 V for **3** and **4**) and solution oxidation potentials (2.25 V vs. SCE, estimated) leading to a significantly lower value for k_q ($\sim 10^8$ M^{-1} s^{-1}).[7] Presumably, the radical cation is formed at such a low rate that its decay was as fast as its rate of formation so that it escaped observation under our experimental conditions.

Because of the separation of absorption systems in $1^{-}\cdot$ and the radical cations, the optical spectra could be calibrated. With ϵ_{450} = 9700 M^{-1} cm^{-1} for $1^{-}\cdot$,[12] we obtain the molar decadic absorption coefficients displayed in Table I. All of these values were derived by assuming that the radical cation does not absorb at 450 nm (a reasonable assumption as we shall see in the next section) and that it has not decayed significantly during the first 20 ns, the duration of the laser pulse. Therefore, the ϵ values given in Table I are lower limits. Recently, ϵ_{685} = 2970 M^{-1} cm^{-1} has been found for naphthalene radical cation in C_3H_7CN.[13] Although we find the same ratio of optical densities at 450 and 685 nm after the laser flash as in ref 13, our ϵ value is almost twice as high (5300 M^{-1} cm^{-1}). Kira et al.[14] found ϵ = 6800 M^{-1} cm^{-1} for the corresponding maximum in a Freon matrix at 77 K. The agreement between our result and that in ref 14 is considered to be satisfactory in view of the difference in temperature and solvent and taking into account that our values represent lower limits.

TABLE I: Molar Decadic Absorption Coefficients ($\epsilon/(M^{-1}\ cm^{-1})$) of Radical Cations

D	λ_{max}/nm	$\epsilon(M^{-1}\ cm^{-1})$
naphthalene radical cation	685 (650, 620)	$(5.3 \pm 0.1) \times 10^3$
$5^{+}\cdot$	640	$(1.3 \pm 0.1) \times 10^4$
$6^{+}\cdot$	640	$(1.1 \pm 0.1) \times 10^4$
$7^{+}\cdot$	>840 (720)	$(1.9 \pm 0.1) \times 10^3$ [a]
$8^{+}\cdot$	>840 (820)	$(2.7 \pm 0.2) \times 10^3$ [b]

[a] Measured at 720 nm. [b] Measured at 820 nm.

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[16] Gschwind, R. Ph.D. Thesis, University of Basel, Basel, Switzerland, 1979.

TABLE II: Absorption Coefficients (σ_{249}), Fraction of Excited Molecules (f_{30}), Concentrations of Donor Hydrocarbon ([D]) and Corresponding Radical Cation ([$D^{+}\cdot$]), and Relative Yield of Ionization (Φ_I) upon Irradiation with a 249-nm Light Pulse of 30-mJ Energy[a]

D	σ_{249}[b]/cm^2	f_{30}[c]	[D], M	[$D^{+}\cdot$], M	Φ_I[d]
2	2.4×10^{-17}	0.989	4×10^{-3}	7.6×10^{-6}	1.95×10^{-3}
3	5.2×10^{-19}	0.094	4.6×10^{-3}		
4	9.6×10^{-19}	0.167	4.6×10^{-3}		
5	6.1×10^{-17}	0.999	4.4×10^{-4}	4.0×10^{-5}	0.091
6	3.8×10^{-17}	0.999	1.4×10^{-3}	4.5×10^{-5}	0.032
7	1.9×10^{-18}	0.305	2.8×10^{-3}	2.3×10^{-4}	0.269
8	5.7×10^{-18}	0.661	6.5×10^{-3}	1.2×10^{-4}	0.028

[a] 30 mJ/pulse upon 0.2 cm^2 corresponds to a fluence (Φ_0) of 1.9×10^{17} photons/cm^2. [b] $\sigma = 2303\epsilon/N_L$ with ϵ/(M^{-1} cm^{-1}). [c] $f = 1 - e^{-I_0 t\sigma} = 1 - e^{-\Phi_0 t}$. [d] $\Phi_I = [D^{+}\cdot]/[D^*]$ with $[D^*] = f_{30}[D]$.

The only other value for ϵ in the literature, which may be compared to the ones for $5^{+}\cdot$ and $6^{+}\cdot$, is $\epsilon_{690} = 1.66 \times 10^4$ M^{-1} cm^{-1} for biphenyl radical cation in dichloromethane.[15] The spectral shift of 1130 cm^{-1} in maximum absorbance of $5^{+}\cdot$ and $6^{+}\cdot$ vs. biphenyl radical cation can only be explained by a solvent shift because the structure of biphenyl radical cation is thought to be planar as for $5^{+}\cdot$ and $6^{+}\cdot$. The spectra of naphthalene radical cation and *trans*-stilbene radical cation (2) in the presence of 1 are not shown because they were identical with published spectra.[13,16]

Photoionization at 249 nm. Transient Absorption Spectra in the Red (600–840 nm). The literature to date has primarily discussed the photoionization of phenols and amines.[8,17] One of the aims of the present study is the generation and characterization of radical cations of aromatic hydrocarbons in polar solution by photoionization according to eq 3. The visible absorption spectra are

$$D \xrightarrow{h\nu} {}^1D^* \rightarrow {}^2D^{+}\cdot + e^- \xrightarrow{k_{rec}} D \qquad (3)$$

displayed in Figure 1 (filled symbols), and, by comparison with the spectra obtained by ionic photodissociation of exciplexes, we conclude that in all cases where reference spectra could be obtained (2, 5–8), radical cations were generated, although the width and the shape of corresponding bands may differ to a certain extent. Similarly, we assign the red absorption (600–800 nm) of 3 and 4 to their corresponding radical cations. The spectrum of naphthalene (not shown in Figure 1) was identical with the published spectrum,[13] and the spectrum of $2^{+}\cdot$ is almost identical with the one previously published[16] except for the shoulder at 490 nm. To the best of our knowledge, the radical cation spectra of the aromatic hydrocarbons 3–8 in solution have not been published previously. The rise time of the transient red absorption was measured to be 10–20 ns and is thus shorter than or equal to the duration of the laser pulse. In particular, no increase in transient-absorption signal was monitored after the laser pulse. For 5 and 6, accurate measurements of signal rise times below 600 nm were increasingly difficult because of the interference of fluorescence and/or scattered light from the laser which made the rise time appear longer.

Table II presents data on the relative photoionization efficiency Φ_I, expressed as the concentration ratio of the radical cation ([$D^{+}\cdot$]) and the excited precursor ([D*]). It is evident that Φ_I varies over a large range from 0.2% for 2 to 27% for 7, although the associated uncertainties in the concentration of the excited precursor ([D*]) may amount to a factor of 2–3 due to the optical thickness of the samples. This fact leads to an overestimation of [D*], so that the true Φ_I values may be larger. Furthermore, in the case of 5 and 6, the calculated concentrations for the radical cations [$D^{+}\cdot$] possibly represent upper limits because of the possible presence of radical anions (cf. below) which contribute to the optical density in the spectral region where the radical cation concentration was measured (640 nm). The given values for Φ_I from Table II therefore represent lower limits for the relative photoionization yields with a possible (partial) cancellation of errors for 5 and 6. Taken with a grain of salt, Table II shows that photoionization at 249 nm is, in most cases, an important reaction channel for the deactivation of an excited hydrocarbon in the polar solvent.

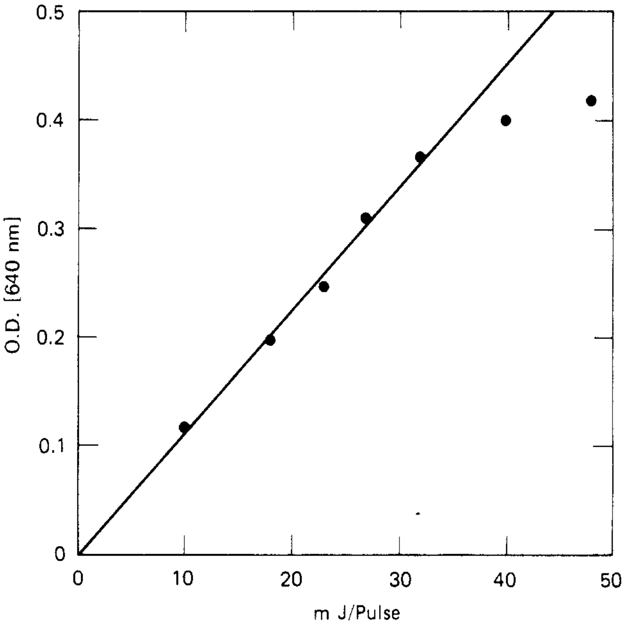

Figure 2. Dependence of ion yield as a function of laser power at 249 nm for photoionization of 1,2-dihydrophenanthrene (6).

Intensity Dependence. We observed a linear dependence of the ion yield (as measured by the optical density at the end of the laser flash) upon pulse energy or power, with an indication of saturation at high power. Experiments have been performed on 5, 6 (Figure 2), and 7 with similar results in all three cases. On the basis of this linear relationship between ion concentration and pulse energy, we suggest the photoionization process to be monophotonic. It has been reported[9] that a linear dependence, although a necessary condition, is by no means proof for the monophotonic nature of the ionization process. This same linear dependence could also result from a two-photon excitation scheme where the absorption cross section for the second excitation step is much larger than the one for absorption of the first photon (typically 10 times). The result is a nearly linear dependence except for a short quadratic regime at very low energies. This concept has been proposed in photoionization studies of large organic molecules with the third harmonic of the Nd:YAG laser emission at 353 nm.[9] We prefer the monophotonic excitation model for the following two reasons: (1) The present data do not require the somewhat artificial concept of sequential two-photon excitation. (2) No ions are observed in cyclohexane solvent (see below).

If the ionization were a two-photon excitation, irradiation in the nonpolar solvent should have resulted in some ionization, everything else being equal, because two 249-nm photons (9.96 eV) exceed the lowest gas-phase ionization

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TABLE III: Second-Order Rate Constants for Radical Cation ($D^{+\cdot}$) and ($D_2^{+\cdot}$) Disappearance

D	(k/ϵ)/ (cm s^{-1})	$10^{-10}k$/ (M^{-1} s^{-1})	λ/nm
naphthalene	1.5×10^7	8.0 ± 1.0	685
3	2.4×10^6		490
	8.1×10^6		720
4	1.4×10^7		480
	6.9×10^7		780
	6.6×10^7		800
5	6.1×10^6	7.9	640
	1.6×10^7	7.6	730
	2.1×10^7	9.5	820
6	8.4×10^6	9.2	640
	1.7×10^7	6.4	750
	2.3×10^7	5.1	820
7	1.9×10^7		490
	5.9×10^7	8.9	800
8	2.7×10^7		500
	3.6×10^7		520
	2.4×10^7	5.5	800
	2.9×10^7	7.8	820

potentials of the hydrocarbons **2**–**8**. (We are assuming that cyclohexane has only a minor stabilizing effect on molecular ions.) If the monophotonic photoionization model is accepted, we thus observe a drastic reduction of the energy requirement for ionization in condensed phase—from 7.8–9 eV for the hydrocarbons **2**–**8** in the gas phase to probably less than 5 eV in polar CH_3CN solution.

It is worth pointing out that preliminary photoionization experiments of **5** in CH_3CN (0.44 mM) by 10–20 mJ of 265-nm laser pulses resulted in the generation of the corresponding radical cation although the process is in many ways different from 249-nm irradiation. However, irradiation of hydrocarbons **2**–**8** by 20–30 mJ of 350-nm laser pulses resulted in no detectable radical cation formation.

Transient Blue–Green Absorption Band. The spectra in Figure 1 show that $2^{+\cdot}$ (shoulder), $3^{+\cdot}$, $4^{+\cdot}$, $7^{+\cdot}$, and $8^{+\cdot}$ absorb at 490–500 nm. All of these blue–green absorption bands, except the one for $2^{+\cdot}$, decay much more slowly than the absorptions in the red of the spectrum (see Table III). Following previous work,[6,16] and because of the synchronous decay of the bands at λ = 480, 700, and 750 nm (Figure 1a), the spectrum for **2** displayed in Figure 1 is assigned to the radical cation of **2** with the possible exception of the shoulder at 490 nm (see below). We conclude that for **3**, **4**, **7**, and **8** two kinetically distinguishable species are formed at the end of or shortly after the laser pulse. In addition, we observe that the absorbance (OD) around 500 nm is more than linearly dependent upon concentration; for example, in the case of $3^{+\cdot}$, OD_{490}/OD_{800} = 0.86 at 2.8 mM and 2.1 at 12.5 mM. Furthermore, in more concentrated solutions of **7** and **8** (about 10 mM), a very fast initial decay of the red absorption can be observed. This rapid decay, which is beyond the time resolution of the used apparatus, takes place in the first 10 ns after the end of the laser pulse and is followed by a slower second-order decay with the rate constants displayed in Table III. Dilution of the sample by a factor of 5 resulted in the suppression of the initial fast-decaying portion of the transient absorption in the red. Its fast initial loss was not matched by a corresponding sudden rise in absorption around 500 nm, the expected spectral region for product absorption (see below). We think that contributions to the photocurrent due to fluorescence or scattered light at λ ≤ 530 nm made an accurate measurement of fast rise time in this spectral region impossible. The possibility of the presence of $(CH_3CN)_2^{-\cdot}$, which absorbs weakly at 500 nm, could be discounted because this species could be observed only at low temperatures,[18] and, if present under our experimental conditions, we should have seen it in all cases. Radicals (benzhydryl) and carbocations (diphenylmethyl) are known to absorb below 360 and 450 nm. The available evidence points toward the presence of a dimer radical cation, which is responsible for the blue–green absorption and which is formed very rapidly with a diffusion-controlled rate constant ($k_f \simeq 2.0 \times 10^{10}$ M^{-1} s^{-1}) in CH_3CN in an exothermic reaction according to eq 4. The dimer

$$D^{+\cdot} + D \underset{k_d}{\overset{k_f}{\rightleftharpoons}} D_2^{+\cdot} \tag{4}$$

radical cation is thought to have a lower reactivity toward charge recombination or other reactions compared to its monomer. This difference in reactivity has been found previously[19] and has been ascribed to the difference in the hydrodynamic properties of $D_2^{+\cdot}$ vs $D^{+\cdot}$. Many aromatic $D^{+\cdot}/D_2^{+\cdot}$ systems absorb around 500 nm in a frozen matrix.[20] This absorption was attributed in many cases to $D_2^{+\cdot}$ and characterized as a charge resonance transition because it occurred in the same spectral region (~500 nm) regardless of the nature of the monomer (e.g., substituted benzene radical cation, naphthalene radical cation, $3^{+\cdot}$, $4^{+\cdot}$). The dimer radical cation formation in the case of **2** and biphenyl, which will serve as a model substance for **5** and **6** in the following considerations, is not accompanied by the appearance of an intense charge resonance band in the near-IR, so that there is a higher degree of uncertainty about the dimer radical cation absorption spectrum at 500 nm in both cases.[20,21] From previous experiments, it nevertheless seems certain that both $2^{+\cdot}$ and biphenyl radical cation dimerize in more concentrated solutions. Why then do we not observe transient absorptions for $5^{+\cdot}$ and $6^{+\cdot}$ around 500 nm? This fact could be explained by two reasons: (1) The dimer radical cations of **5** and **6**, if formed, do not absorb around 500 nm. (2) The dimer radical cations are not formed under our experimental conditions for reasons of ground-state depletion. A look at Table II reveals the fact that for **5** and **6** no ground-state molecules are found after irradiation with a 249-nm laser pulse of 30-mJ energy. Using the reaction system 5–9 with

$$D \xrightarrow[249\ \mathrm{nm}]{h\nu} D^* \tag{5}$$

$$D^* \rightarrow D + h\nu \tag{6}$$

$$D^* \rightarrow {}^3D^* \tag{6a}$$

$$D^* \rightarrow D^{+\cdot} + e^{-\cdot} \tag{7}$$

$$D^+ + D \rightleftarrows D_2^{+\cdot} \tag{8}$$

$$D^+ + X^{-\cdot} \rightarrow D + X \tag{9}$$

D corresponding to **5** or **6**, where $k_6 = 1.0 \times 10^8$ s^{-1} (fluorescence (for **5**)), $k_{6_a} = 4.0 \times 10^8$ s^{-1} (intersystem crossing to T_1), $k_7 >> 10^8$ s^{-1} (ionization), $k_8 \sim 2 \times 10^{10}$ M^{-1} s^{-1} (dimerization), $k_9 = 7.7 \times 10^{10}$ M^{-1} s^{-1} (recombination), and X = negative species, and an estimated rate constant for reaction 8, we find that dimerization reaction 8 cannot compete with the recombination 9 shortly after irradiation because of the magnitude of the (measured, see below) rate constant k_9 and because of the low concen-

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(19) Kira, A.; Arai, Sh.; Imamura, M. *J. Chem. Phys.* **1971**, *54*, 4890; **1972**, *56*, 1777.

(20) Badger, B.; Brocklehurst, B. *Trans. Faraday Soc.* **1969**, *65*, 2582. Shida, T.; Hamill, W. H. *J. Chem. Phys.* **1966**, *44*, 2375, 4372. Shida, T.; Iwata, S. *J. Am. Chem. Soc.* **1973**, *95*, 3473.

(21) For many aromatic hydrocarbons, the fluorescence (ϕ_F) and triplet quantum yields are very similar in polar and nonpolar solution. Furthermore, $\phi_F + \phi_T = 1$, to a very good degree of approximation.

tration of D. The triplet quantum yield (Φ_T) of biphenyl (S_1)[21] has been measured as 0.81, such that a few tens of nanoseconds after the irradiation [D] has recovered to 20% of its original value by fluorescence emission less the amount of D which underwent ionization (~10%) for D = **5**. Using the rate parameters of reactions 8 and 9 in conjunction with the triplet quantum yield for biphenyl and the concentrations of Table II (for **5**), we arrive at the following comparison of the first-order rate constants for the two competing rate processes 8 and 9: $k_8^I = (2 \times 10^{10})(8.8 \times 10^{-5})(0.9) = 1.6 \times 10^6\ s^{-1}$, $k_9^I = (7.7 \times 10^{10})(4.4 \times 10^{-5}) = 3.4 \times 10^6\ s^{-1}$. The rate for dimerization is about a factor of 2 slower than the rate of recombination, and we think this line of reasoning can explain the lack of dimer formation for **5** and **6**, especially in view of the long lifetime of the triplet state for **5** (4 μs), whose deactivation will not contribute to the rate of dimerization.

We cannot unambiguously identify the nature of the 490-nm absorption (shoulder) for **2**, but it seems unlikely that it corresponds to the absorption of the dimer radical cation of **2**. The triplet quantum yield of **2** for the process $S_1 \rightarrow T_2$ in fluid solution at room temperature is ~0.95 leading to trans → cis isomerization in 95% and to fluorescence in the remaining 5% of the singlet excited molecules. Furthermore, it has been discovered that neither excited *cis*-stilbene not its analogous radical cation has the tendency to react with itself or **2** in condensed phase. In agreement with this fact, no excimer emission from (*cis*-stilbene)$_2^*$ and no absorptions due to (*cis*-stilbene–**2**)$^{+\cdot}$ or (*cis*-stilbene)$_2^{+\cdot}$ have been detected so far.[16]

Negative Species. Our experiments do not provide information as to the nature of the reducing species in CH_3CN solution. In pulse radiolysis experiments in CH_3CN, a transient absorption has been found at 1450 nm,[8] but the exact nature of this absorption (solvated electron or $CH_3CN^{-\cdot}$) still remains unresolved.

In preliminary experiments of 265-nm irradiation of **5**, no transient absorption was detected in the near-IR. In the case of the photoionization of **2** at 249 nm, the shoulder at 490 nm (Figure 1) could possibly be attributed to $2^{-\cdot}$, because in recent chloranil-sensitized ionic photodissociation and γ-ray ionization studies[16,20] in C_3H_7CN, only one absorption band at 480 nm was observed and assigned to $2^{+\cdot}$. Very similar UV/vis absorption spectra for the radical cations and analogous radical anions of alternant hydrocarbons, such as **2**, are expected on theoretical grounds. It is unlikely that the radical anions of **3** and **4** have been formed upon photoionization, because neither $3^{-\cdot}$ nor $4^{-\cdot}$ has been found to be stable in fluid solution despite several efforts to record their ESR spectra. However, radical anions of **5**, **6**, and **8** are stable in polar solution.[22] The absorption spectrum of $5^{-\cdot}$ in MTHF at 77 K reveals a broad band with maxima at λ = 640, 695, and 830 nm with the absolute maximum at 695 nm ($\epsilon = 8800\ M^{-1}\ cm^{-1}$), and Dorfman et al.[22] found absorption maxima for biphenyl radical anion at 620 nm in *i*-PrOH and at 630 nm in THF. It is possible that part of the broad band at 640 nm or the shoulder on the long-wavelength side of the 640-nm band of the photoionization spectrum of **5** and **6** (Figure 1, d and e) may be due to the presence of the corresponding radical anions, $5^{-\cdot}$ and $6^{-\cdot}$. However, this suggestion is somewhat inconsistent with the fast kinetics of disappearance of $5^{+\cdot}$ and $6^{+\cdot}$ by recombination (see below) with their corresponding radical anions, in which case one would expect a diffusion-limited rate constant for ionic recombination of $3.5 \times 10^{10}\ M^{-1}\ s^{-1}$ in CH_3CN.

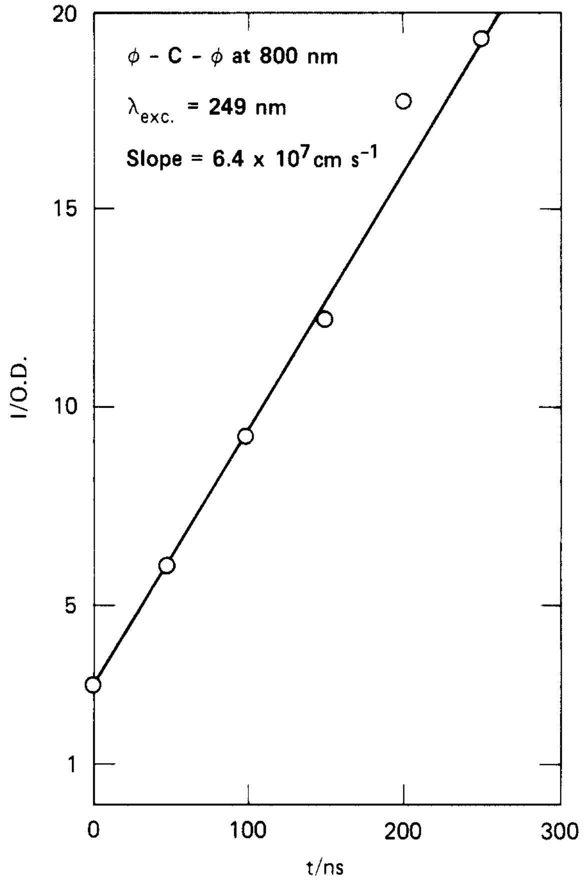

Figure 3. Second-order plot for the disappearance of diphenylmethane radical cation generated through photolysis at 249 nm.

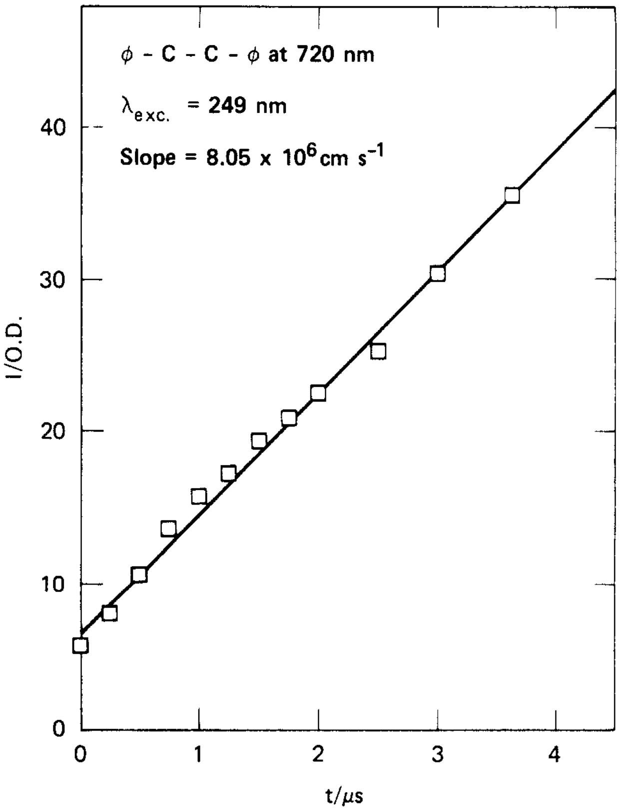

Figure 4. Second-order plot for the disappearance of bibenzyl radical cation generated through photolysis at 249 nm.

Oxygen and Solvent Effect. Two other observations, which help to elucidate the mechanism, can be cited.

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Excitation of the hydrocarbons in cyclohexane did not lead to any detectable transient absorption. Furthermore, saturation of the CH_3CN solution with O_2 had the same effect: after removal of O_2, the transient absorption was again detectable. The first observation confirms the ionic nature of the absorbing species found in CH_3CN, as ions are unlikely to be formed in nonpolar cyclohexane. On the basis of the O_2 effect, we believe that the observed ionization is the consequence of excitation to a singlet-excited state, which in cases of aromatic hydrocarbons has been shown to be effectively quenched by molecular oxygen with a diffusion-controlled rate constant.[23]

Kinetics of Disappearance. A fringe benefit of the quantitative assessment of the radical cation absorption properties is the measurement of their decay rates. All decay curves for the red and blue–green absorptions followed second-order kinetics over 1–1.5 order of magnitude of optical density. The second-order rate constants were relatively insensitive to the quality of the solvent, but very sensitive to the presence of photoproducts, so that fresh solutions were prepared every time that kinetic studies were undertaken. Figures 3 and 4 show typical results for **3** and **4**. In these cases, only the ratio k/ϵ could be deduced because the corresponding absorption coefficients ϵ are not known. The recombination kinetics for **5** and **6** were studied carefully because of the possible parallel recombination pathways 10 and 11. No indication of the

$$D^{+}\cdot + e^{-} \xrightarrow{\text{fast}} D \tag{10}$$

$$D^{+} + D^{-} \xrightarrow{\text{slow}} 2D \tag{11}$$

presence of a second, slower, recombination pathway was found from second-order plots, so that we conclude that the radical anion was not formed under our conditions. The results are listed in Table III in terms of the bimolecular rate constants in cases where ϵ could be measured and in terms of k/ϵ, where ϵ was unknown. From Table III it appears that the average bimolecular rate constant for the disappearance of the radical cation is $(7.7 \pm 1.1) \times 10^{10}\ M^{-1}\ s^{-1}$. This rate constant is considerably higher than the diffusional limit for neutral molecules ($k_{diff} = 1.8 \times 10^{10}\ M^{-1}\ s^{-1}$) or for ionic species ($k^{i}_{diff} = 3.5 \times 10^{10}\ M^{-1}\ s^{-1}$) in CH_3CN, and its absolute value indicates a charge recombination process between the radical cation and the negative species, with one species (presumably the negative one) being very mobile during our observation period ($\sim$1 μs). However, rate constants of similar magnitude have been found for the reactions $(C_6H_5)_2CH^{+} + Cl^{-}$ ($9.1 \times 10^{10}\ M^{-1}\ s^{-1}$) and $C_6H_5CH_2^{-} + Na^{+}$ ($1.5 \times 10^{11}\ M^{-1}\ s^{-1}$) in similar solvents.[24]

Conclusions

The results of our irradiation experiments of hydrocarbons in CH_3CN solutions with 5-eV photons (249 nm) lead us to the following conclusions:

(1) Transient absorption spectra from 600 to 840 nm reveal the presence of *radical cations* generated by photoionization of the parent hydrocarbon.

(2) Transient absorption spectra in the blue–green region (480–550 nm) indicate the presence of *dimer radical cations* ($D_2^{+}\cdot$) in solutions where bleaching of the parent hydrocarbon is not too strong.

(3) The photoionization process in solution is suggested to be monophotonic in nature and taking place from an excited singlet state. Furthermore, its efficiency based upon the number of excited parent molecules varies from 0.2% to 30%.

(4) The negative species appears to be a solvated electron or a species of similar hydrodynamic properties as revealed by its fast second-order recombination kinetics.

It appears that the energy requirement for ionization drops from 8–9 eV in the gas phase to (probably less than) 5.0 eV in polar solution because of the stabilizing effect that the solvent has on charged species. This simple method is well suited for the study of absorption properties and reactivities of these reactive species in condensed phase.

Acknowledgment. We thank the National Science Foundation, San Francisco Laser Center, for providing the opportunity to rent an excimer laser (Lumonics TE-860) with which a large portion of the experimental work was performed.

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