Reactions of Photoexcited Aromatic Radical Cations with Polar Solvents[†]

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Reactions of electronically excited radical cations of various simple aromatic hydrocarbons (e.g., naphthalene, biphenyl, perylene) and amines (indole and L-tryptophan) with polar solvents (alcohols, ethers, and water) were studied. The radical cations were generated by biphotonic (248 nm) photoionization of aromatic solutes in oxygen-saturated solutions and subsequently excited by 2.3 eV photons from a Nd:YAG laser. The photobleaching is initiated by a transfer of the valence electron of the solvent to the solute radical cation ("hole injection"). In the polar liquids, a proton transfer occurs concurrently with this electron transfer and may occur in several ways. Hole injection is the general mechanism for decay of photoexcited radical cations, in both polar and nonpolar media. The efficiency of this process correlates with the ionization potential (IP) of the solute and optical absorbance of the corresponding radical cation. For high-IP solutes, the quantum yield of the photobleaching is 0.3−0.5. From scavenging of the photoexcited radical cations, it was found that while some of these states have the lifetimes below 1 ps, other have lifetimes of 10−40 ps (in acetonitrile).

1. Introduction

While the chemistry of lower excited states of aromatic molecules (ArH) has been extensively studied, little is known about reactions of photoexcited aromatic cations ($[\mathrm{ArH}^{\bullet+}]^*$) in common solvents. The interest in these energetic species is due to their mediation of highly exothermic electron-transfer reactions[1,2] and the crucial role that they play in radiolysis.[3] The photoreactions of organic radical cations that have been studied include fragmentation (e.g., dehalogenation of alkylhalides), rearrangements (e.g., ring opening of 1,3-cyclohexadiene$^{\bullet+}$ and benzidine rearrangement of tetraphenylhydrazine$^{\bullet+}$), *cis*−*trans* isomerization of polyenes and Decalins, radiative decay (e.g., for fluorobenzenes and acetylenes), and electron transfer from low-IP aromatic amines (see a review article by Haselbach and Bally).[1−5] These reactions were studied either in the gas phase or in low-temperature matrixes, such as frozen noble gases, halocarbons, and other high-IP solids. In this article we examine a class of photoreactions that is common to all of electronically excited radical cations in condensed matter—valence band (vb) electron transfer from the solvent.

The solvent oxidation reactions of photoexcited organic radical cations were first studied by Skvortsov and Alfimov in the 1970s,[6−10] though there may be earlier reports.[11] It was observed that the radical cations of aromatic amines stabilized in frozen organic solvents could be bleached with visible light.[6,7] The onset of bleaching occurred at a wavelength that corresponded to the onset of the radical cation absorption.[9] The quantum yield of the photobleaching increased with the photon energy and reached $\sim 2 \times 10^{-2}$.[8,9] The bleaching of the radical cations was shown to be a result of their reactions with the solvent rather than recombination with photodetached electrons.[1,6,7] In the toluene−ether mixture, the bleaching was caused by an electron transfer from toluene to radical cations of the amines.[9,10] A partial recovery of the absorbance bands from the neutral amines was observed,[6] and a hole transfer from toluene$^{\bullet+}$ to a second solute was demonstrated.[9] Skvortsov and Alfimov speculated that in all of these solids, both polar and nonpolar, the photobleaching of radical cations was due to electron transfer from the solvent. They called this mechanism "overcharging"; we refer to this reaction as "hole injection", a term borrowed from solid-state physics.[12]

In previous publications from this laboratory, we reported that in several cycloalkane liquids (cyclohexane, methylcyclohexane, and decalins) the excitation of polycyclic aromatic radical cations with a single 2.3 eV photon resulted in formation of solvent holes:[13]

$$[\mathrm{ArH}^{\bullet+}]^* + \mathrm{RH} \rightarrow \mathrm{ArH} + \mathrm{RH}^{\bullet+} \qquad (1)$$

The holes were observed using time-resolved dc conductivity. Due to rapid hopping of the solvent holes in these cycloalkanes, their mobility is 5−20 times greater than the mobility of other molecular ions, and these holes can be observed through the increased conductivity.[14] Due to fast scavenging of the solvent hole by aromatic solute and impurities, the conductivity signal recovers in 200−500 ns, indicating that all of the injected holes have converted to solute cations.[13] In other saturated hydrocarbons, the hopping of the solvent hole is not faster than Brownian diffusion, and the hole injection cannot be directly observed by means of transient dc conductivity. Nevertheless, our observations support the view that in nonpolar media the decay of photoexcited radical cations is due to hole injection.

The mechanism of the photobleaching in polar liquids is more complex, due to multiple reaction routes of photoexcited organic radical cations. These redox reactions appear to be similar to those observed in UV photolysis of transition-metal ions. One-electron oxidation of *ligand* water by $[\mathrm{Fe(OH_2)}]_6{}^{3+}$ upon 5 eV photoexcitation yields a free hydronium ion and hydroxyl

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radical[15a] (photooxidation of *outer-sphere* water by complexes of Co^{III} was also reported).[16] Several complexes of Fe^{III} exhibit outer-sphere photooxidation of alcohols in aqueous solutions.[15b] Similar reactions were observed for UO_2^{2+} in liquid alcohol solutions[17] and for Cu^{II},[18] Ce^{IV},[19a] Fe^{III},[19b,20] and $[PtCl_6]^{2-}$ [19c] in frozen alcohols. In these solid matrixes, the stable photoproducts (which are the corresponding olyl radicals and solvated proton) are from dissociated solvent holes. In some cases, other radical products are formed (e.g., methyl radical from solid *tert*-butanol),[19] but the overall scheme is that of concerted electron and proton transfers.

Previously, we studied photobleaching of solute radical cations that occurs upon 4−5 eV laser ionization of anthracene and other aromatic solutes in alcohols.[21] At high fluence of the UV photons, the optical absorbance from the $ArH^{\bullet+}$ was significantly lower than that expected from a biphotonic process producing a geminate electron−hole pair. This indicated that the radical cations were bleached during the laser pulse. We surmised that the bleaching was due to protonation of the solvent by excited radical cations. The aryl radical formed in this reaction should abstract hydrogen from the solvent. H/D exchange upon the photoionization of deuterated anthracene was observed, and this finding suggested that the proton transfer did indeed occur.[21]

In this work, the photoreactions of aromatic radical cations in polar solvents, such as mono- and polyhydroxy alcohols, ethers, and water, are studied in more detail, using two-pulse two-color photoexcitation in order to separate in time the generation of the $ArH^{\bullet+}$ cations by two-photon (248 nm) photoionization and their subsequent excitation with 2.3 eV photons. This study suggests that the photobleaching of aromatic radical cations is initiated by electron and not by proton transfer. Proton transfer follows this electron transfer and may involve more than a single mechanism. The photophysics of these reactions are examined, and various implications of our results are discussed.

2. Background

For photoexcited radical cations in polar solvents (ROH), several types of bleaching reactions may occur. The first possibility is an electron transfer followed by a proton transfer,

$$[ArH^{\bullet+}]^* + ROH \rightarrow ArH + ROH^{\bullet+} \qquad (2)$$

$$ROH^{\bullet+} + ROH \rightarrow RO^{\bullet} + ROH_2^{+} \qquad (3)$$

(Here $RO^{\bullet}$ denotes both the oxygen-centered and olyl radicals.) In polar media, the solvent holes are very short-lived (e.g., for H_2O^+ the lifetime is <0.1 ps),[22] and these two reactions may not be separable. Thus, the overall reaction is

$$[ArH^{\bullet+}]^* + 2ROH \rightarrow ArH + RO^{\bullet} + ROH_2^{+} \qquad (4)$$

A variant of reaction 4 may occur when the solute molecule is a better base than the solvent, as is the case with aromatic amines. In such a case, the solvent hole can protonate the molecule, and instead of reaction 4, the overall reaction would be hydrogen abstraction,

$$[ArH^{\bullet+}]^* + ROH \rightarrow ArH_2^{+} + RO^{\bullet} \qquad (5)$$

Another possibility is a photoprotonation of the solvent[21]

$$[ArH^{\bullet+}]^* + ROH \rightarrow Ar^{\bullet} + ROH_2^{+} \qquad (6)$$

With aromatic hydrocarbons, the aryl radicals formed in reaction 6 react with the H atom donors,

$$Ar^{\bullet} + ROH \rightarrow ArH + RO^{\bullet} \qquad (7)$$

The products formed after this abstraction are identical to those in reaction 4 (save for the H/D exchange in the ArD molecules).[21]

There is also a possibility that the solvent (ROH) attaches to the phenyl ring of aromatic radical cation yielding a distonic cation, which then yields a cyclohexadienyl-type adduct radical, $RO^{\bullet}ArH$, and a proton (similarly to reactions of the ground-state radical cations of methylated benzenes with water)[23]

$$[ArH^{\bullet+}]^* + ROH \rightarrow R(H)^{+}O^{\bullet}ArH \qquad (8a)$$

$$R(H)^{+}O^{\bullet}ArH + ROH \rightarrow RO^{\bullet}ArH + ROH_2^{+} \qquad (8b)$$

An addition reaction of the ground-state 9,10-dimethylanthracene$^{\bullet+}$ with cyclic amines, very similar to reaction 8a, has been reported recently.[24] In acidic water, cyclohexadienyl radical $HO^{\bullet}ArH$ rapidly transforms to $ArH^{\bullet+}$. An analogous reaction may occur in alcohols, and therefore, the bleaching reaction 8 can be reversed by addition of acid. For reasons given below we believe that the occurrence of reaction 8 is unlikely.

From the standpoint of product formation, the only difference between reactions 4, 5 and 6, 7 is the involvement of a short-lived aryl radical $Ar^{\bullet}$ (with aromatic hydrocarbons). Its observation (or the observation of products from this radical) would be definitive evidence in favor of reactions 6, 7 vs reactions 4, 5. The rate constants of hydrogen abstraction from ethanol and 2-propanol by phenyl radical are 5×10^5 and 4.1×10^5 M^{-1} s^{-1}, respectively, which reduces the lifetime of this radical in neat alcohols to 250 and 190 ns, respectively.[25,26] Lifetimes of other aryl radicals are similarly short.[27a] For instance, 4-methyl phenyl reacts with methanol with rate constant of 1.4×10^5 M^{-1} s^{-1}, so the lifetime is ca. 300 ns.[25] These lifetimes are further reduced in the presence of 0.01 M oxygen, which is used to shorten the lifetime of solvated electrons and triplets of aromatic solutes (see below). Phenyl radicals add to oxygen with rate constant of $(3-5) \times 10^9$ M^{-1} s^{-1}.[27a] Thus, the lifetime of aryl radicals in oxygenated solutions is 20−30 ns. Without the oxygen in solution, the unquenched triplets of aromatic solutes can be photoexcited, abstracting hydrogen from the solvent and yielding the same photoproducts as those from the aryl radicals.

Since the lifetime of the aryl radicals in oxygen-saturated alcohols is so short, a scavenging experiment is difficult. The concentration of radical cations upon laser ionization is low (<1 μM). To accumulate photoproducts to the level detectable by GC (10^{-5}−10^{-4} M), one needs 10−100 laser pulses, which makes it impossible to prevent secondary photolysis. Using GC-MS, it was found that upon 4−5 eV laser photolysis of d_{10}-anthracene in 2-propanol, some $d_{10}h$-anthracene was formed.[21] This result cannot be taken as an indication that reaction 6 has occurred since the H/D exchange might have occurred in other photoreactions, e.g., through cyclohexadienyl radicals formed in triplet photoreactions. More conclusive would be the observation of products specific for aryl radicals, such as adducts formed by reaction with double bonds. The problem is that such additions are slow (10^6−10^7 M^{-1} s^{-1}) while reaction 7 is fast.[27a] Thus, high concentration of unsaturated scavenger is needed (0.1−1 M). This makes the whole approach not feasible since such a scavenger would absorb the UV light and interfere with the 5 eV photoionization.[28] There are solutes—O_2, I_2, CBr_4, and 2-iodopropane—that scavenge aryl radicals very rapidly, with rate constants of $(1-5) \times 10^9$ M^{-1} s^{-1};[27a] all of these solutes are also good scavengers of solvated electrons.[29] Since the recombination of $ArH^{\bullet+}$ with the corresponding anions yields the same products as those formed upon scavenging of $Ar^{\bullet}$, these solutes cannot be used to distinguish between reactions 4, 5 and 6, 7.

This examination suggests other means of detecting the aryl radicals formed in reaction 6. One possibility is to convert them rapidly into other light-absorbing species and to use time-resolved optical spectroscopy to detect this species. Another approach may be to use primary and secondary aromatic amines instead of aromatic hydrocarbons. The aminyl radicals formed in reaction 6 cannot abstract hydrogen from alcohols and their reactions with oxygen are slow.

Thermochemistry. The gas-phase proton affinity, PA_g,[30] of aryl radicals can be estimated using the cycle

$$e^- + ArH^{\bullet+} \rightarrow ArH + IP_g(ArH) \tag{9}$$

$$ArH \rightarrow Ar^{\bullet} + {}^{\bullet}H - BDE(ArH) \tag{10}$$

$$H^{\bullet} \rightarrow e^- + H^+ - 13.6\ eV \tag{11}$$

where IP_g is the gas-phase ionization potential[31] and BDE is the bond dissociation energy, which is close to 4.7−4.8 eV.[32] Thus, $PA_g(Ar^{\bullet}) \approx 18.4\ eV - IP_g(ArH)$; the IP_g and PA_g for selected polar solvents and aromatic solutes are given in Tables 1 and 2. For the ground-state aromatic radical cation in 2-propanol, the reaction

$$ArH^{\bullet+} + ROH \rightarrow Ar^{\bullet} + ROH_2^{\ +} \tag{12}$$

is endothermic by

$$\Delta H = PA_g(ROH) - PA_g(Ar^{\bullet}) \approx 10.1\ eV - IP_g(ArH) \tag{13}$$

Equation 13 indicates that in the gas phase proton-transfer reaction 6 is exothermic for aromatic molecules with $IP_g > 7.8$ eV (for 2.3 eV excitation). The endothermicity of reaction 12 explains the stability of aromatic radical cations in alcohols. It means that the reverse reaction

$$Ar^{\bullet} + ROH_2^{\ +} \rightarrow ArH^{\bullet+} + ROH \tag{14}$$

is exothermic. There are examples of reaction 14, both in aqueous solution, for aminyl ($ArNH^{\bullet}$)[27b,33,34] and benzyl ($ArCH_2^{\bullet}$)[35] radicals. In both of these systems, deprotonation of radical cations occurs at neutral pH, while at lower pH reaction 14 takes place.[33−35] For methylated benzenes, log(k_{12}) is linear with IP_g, as may be expected from eq 13, and the protonation occurs only for radical cations of the molecules that have $IP_g > 8$ eV.[35] For benzyl radicals, the protonation (14) requires very low pH and is a slow reaction;[35] for aminyl radicals, $pK_a \approx 4-7$,[27b] and the protonation is diffusion-controlled.[34]

Reaction 14 has two consequences. First, a large fraction of geminate $\{Ar^{\bullet}..ROH_2^{+}\}$ pairs formed in reaction 6 can decay by backward proton transfer, drastically reducing the quantum efficiency of photobleaching. Second, addition of acids should lead to the recovery of $ArH^{\bullet+}$. Since no such recovery was observed experimentally (see below), it is concluded that the proton transfer does not occur.

Probably, reaction 6 does not occur (at least, for aromatic hydrocarbons) because it is less exothermic than reactions 4 and 5. Reaction 7 is exothermic by BDE(ArH) − BDE(ROH). Using bond dissociation energies from the literature,[32] the exothermicity of this reaction is 0.2 ± 0.1 eV. Thus, for aromatic hydrocarbons, reaction 4 is by 0.1−0.3 eV more exothermic than reaction 6. (This estimate is higher for secondary alcohols.) Most of this energy comes from reaction 3 while reaction 2 is endothermic by $IP_g(ROH) - [IP_g(ArH)+h\nu]$. For 2-propanol, gas-phase reaction 2 is exothermic for $IP_g(ArH) > 7.82$ eV.

TABLE 1: Gas-Phase Thermochemical Data for Several Solvents (Energies in eV)

solvent	IP_g	PE_{liq}	V_0[e]	IP_{liq}	PA_g[g]	IP_{liq} indole
cyclohexane	9.86[a]		+ 0.01	8.6[40] 8.72[41] 8.43[42]	7.33	
water	12.61[a]	10.06[c] 10.13[d]	−1.2	8.32, 8.4 8.7 ± 0.5[f]	7.15	4.35 4.5[h]
methanol	10.85[a] 10.94[b]	9.24[d]	−1.0	8.24	7.89	4.60
ethanol	10.47[a] 10.63[b]	9.19[d]	−0.65	8.54	8.17	4.85 6.4[i]
1-propanol	10.22[a] 10.45[b]	9.22[d]	−0.3	8.92	8.27	5.15
2-propanol	10.12[a]				8.29	
acetonitrile	12.19[a]				8.16	

[a] Reference 31. [b] Reference 59. [c] Reference 58. [d] The threshold energies were found from IP − Δ/2 where IP are the positions of the low-energy photoemission peaks and Δ are their half-width (Tables 1−6 in ref 59). [e] In liquid at 25 °C, refs 40 and 41. [f] Various estimates from ref 55. [g] Reference 30. [h] For L-tryptophan, ref 42. [i] For L-tryptophan, ref 38.

IP's in Liquid. The liquid-phase ionization potentials, IP_{liq}, are given by[36]

$$IP_{liq} = IP_g + P_+ + V_0 \tag{15}$$

where P_+ is the polarization energy of the radical cation (or the solvent hole) and V_0 is the energy of the excess electron (Table 1). These IP's are of particular interest to us since the thermal effect of the hole injection is given by the difference of the IP_{liq} of the solvent and the solute corrected by the photon energy. Only a handful of liquid-phase IP's have been reported. Several measurements have been made for *N*,*N*,*N′*,*N′*-tetramethyl-1,4-phenylenediamine (TMPD).[36−39] Due to its low IP_g of 6.7 eV, $TMPD^{\bullet+}$ does not bleach upon 2.3 eV photoexcitation, in both alcohols and cycloalkanes. Several IP's have been reported for indole ($IP_g = 7.76$ eV)[40,41] and L-tryptophan ($IP_g \approx 7.8$ eV);[37,38,42] see Table 1. For aromatic solutes other than TMPD, the data on IP_{liq} in hydrocarbons are sparse; we found several results for pyrene[43] and anthracene[44] and a single result for perylene in *n*-hexane.[39]

The IP_{liq} can be estimated using eq 15 with the P_+ found from the Born formula[36]

$$P_+ = -e^2(1 - \epsilon_{opt}^{\ -1})/2r_+ \tag{16}$$

where ϵ_{opt} is the optical dielectric constant and r_+ is the "effective" radius of the cation which was usually taken as the van der Waals radius of a neutral molecule.[45] We used eqs 15 and 16 with these "molecular radii" to estimate IP_{liq} for aromatic molecules in several solvents.

As for the liquid-phase IP's of the solvent molecules, these IP's have been determined for hydrocarbons, but not for polar liquids. For cyclohexane, Hiraoka gives an IP_{liq} of 8.6 eV;[46] this estimate is close to 8.72 eV given by Böttcher and

TABLE 2: Gas-Phase Ionization Potential (IP_g), Proton Affinity (PA_g), and Molar Extinction Coefficients ϵ_λ for Aromatic Radical Cations in Boric Acid Glass at Their Absorption Peaks (λ_{max}) and at 532 nm[a]

ArH	IP_g, eV	PA_g, eV	ϵ_λ[b] (λ_{max}) nm	λ_{532}[b]	λ, nm	Y_{exp} %	$\epsilon_{532}\phi$	$\phi \times 10^{-2}$
perylene	6.90	9.20	46 (547)	22	550	76	450	2.2
						95	(350)	(1.6)
pyrene	7.41	8.96	43 (452)	0.88	450	*48*	(65)	(7.3)
benz[*a*]anthracene	7.43		13.2 (874)	3.0	400	*29*	(72)	3.2
								(2.4)
acenaphthene	7.68	8.85	4.5 (680)	0.27	670	26	(80)	(30)
						61		
L-tryptophan[c]	~7.8, 7.76[d]		2.7 (580)	2.42	580	37.5	490	20
						45		
triphenylene	7.84		15.6 (410)	2.7	710	70	1240	46
			8.9 (700)			*100*	(1000)	(37)
biphenyl	7.95	8.53	10.2 (680)	0.87	390	44	265	30
			21.6 (390)			*70*	(235)	(27)
naphthalene	8.14	8.47	4.5[e] (680)	0.81	700	67	375	46
						92	(325)	(40)

[a] The wavelength λ for the observation of bleaching of the radical cations with 2.3 eV photons in oxygen-saturated 2-propanol at 25 °C, the bleaching efficiency Y_{exp} at 0.4 and 2.5 J/cm^2 (in italics), the product $\epsilon_{532}\phi$ and the quantum yield of bleaching ϕ as determined by numerical integration of eq A5 and using average fluences in the high-flux regime using eq A3 (in parentheses). [b] In 10^3 M^{-1} cm^{-1}. [c] In water. [d] For indole. [e] Reference 21.

Schmidt,[47] while Casanovas et al. estimated the IP_{liq} of cyclohexane as 8.43 eV.[48] For alcohols and water, no reliable data on IP_{liq} exist. This situation is partly due to the controversy[49−55] about the nature of low-energy photogeneration of electrons with thresholds of 6.05−6.5 eV for water[55−57] and ca. 4.7 eV for methanol.[51] For water, explanations suggested involve (i) electron transfer from H_2O^* to preexisting traps deep in the midgap[52,53] (with or without concerted dissociation of the $H_2O^{\bullet+}$ hole),[49,54] (ii) proton transfer from H_2O^* to another water molecule followed by electron transfer from $(OH^-)^*$ to the solvent,[51] and (iii) the OH bond dissociation followed by reaction of hot H atom with water[54] (see ref 55 for a recent review). What is agreed is that the low-energy process yields either localized or hydrated electrons; more energy is needed to eject the electron to the conduction band (cb). Bernas et al.[51,52,55] estimated this "bandgap" IP as $IP_{liq} = PE_{liq} + V_0$, where PE_{liq} is the threshold of the electron photoemission. For water (with a PE_{liq} of 10.06[58] or 10.13 eV[59]) this estimate gives $IP_{liq} \approx 8.4-8.9$ eV, which corresponds to the formation of a dry hole and a quasi-free electron (that is, an electron at the cb mobility edge).[55] The hydration energy of the electron is ca. 1.6 eV.[60] Thus, the threshold for formation of the dry hole and fully hydrated electron is ~8.5 eV.[55] Apparently, lower IP's can be obtained only when the hole is solvated or dissociated.[61] Given its very short lifetime,[22] dissociation is more likely, and we take the threshold of 6.5 eV as the onset for the formation of a localized (or hydrated) electron, a proton, and a hydroxyl radical.

For liquid alcohols, some PE_{liq} have been measured for diols (8.65 eV for 1,5-pentanediol and 8.04 eV for ethylene glycol) and long-chain alcohols (8.76 eV for 2-ethyl-1-hexanol), but no data on V_0 for these solvents exist.[58] Recently, Faubel et al.[59] measured PE_{liq} for water and several monohydroxy alcohols in free microjets. (Their data are given in Table 1.) Using the V_0 given by Bernas et al.,[40,41] we obtained the "bandgap" IP_{liq} ranging from 8.24 eV (for methanol) to 8.92 eV (for 1-propanol). Since the solvation energies of electrons in alcohols are all less than in water, the threshold energies for formation of dry holes and solvated electrons are all in excess of 8 eV.

Due to these uncertainties, the energetics of hole injection cannot be estimated with accuracy. It is, however, safe to state that the occurrence of reaction 1 in cycloalkanes is compatible with the estimates of the IP_{liq}. For the $ArH^{\bullet+}$ cations which yield mobile solvent holes upon 2.3 eV photoexcitation in cyclohexane, reaction 1 is exothermic by at least 0.3−0.5 eV; in decalins this exothermicity is 0.7−0.9 eV.[13] The only exception is perylene, for which the IP_{liq} seems to be too low for reaction 1 to be exothermic. Pertinent to these estimates is the assumption that reaction 1 occurs faster than the electronic relaxation of the excited radical cation, which may not always be correct. In alcohols, the IP_{liq} of the aromatic hydrocarbons seem to be too low for reaction 2 to occur; i.e., only the concerted reactions 4 and 5 are expected to occur in these media.

3. Experimental Section

Flash Photolysis. Aromatic solutes (Aldrich) of the highest purity available were used as received. These solutes were chosen primarily for the ability of their radical cations to absorb 532 nm (2.3 eV) light. Thirty nanosecond fwhm pulses of 248 nm (5 eV) light from a Lambda Physik LPx-120i excimer laser were used to ionize 5×10^{-5} M to 10^{-3} M of the solute. The concentration depended on the absorbance of the solute at 248 nm. The 248 nm beam (20−50 mJ/pulse) was focused to a 0.33 cm × 1 cm aperture; a typical fluence of the UV photons was 0.1−0.2 J/cm^2. The 5 and 2.3 eV laser beams entered the cell through the same Suprasil window collinearly. The 2.3 eV pulse (second harmonic, 8 ns fwhm, 1−350 mJ/pulse) was produced by a Continuum model 8010 Nd:YAG laser at controlled delay times (0.01−10 μs) relative to the UV pulses. In several experiments, we used shorter 2.3 eV pulses using a different laser head (3 ns fwhm, 1−50 mJ/pulse) of the same Nd:YAG laser. Without focusing of the 2.3 eV beam, the maximum photon fluence through the aperture was 0.4−0.5 J/cm^2. In a variant of this experiment, the 2.3 eV beam was focused and both of the 5 and 2.3 eV beams passed through a 0.3 cm round aperture. This arrangement gave the maximum fluence of 2−3 J/cm^2. Both lasers were run at 1 Hz; the jitter between the two pulses was ±10 ns, which determines the time resolution of the kinetics presented here. The optical path of the beams was 1 mm. The analyzing light produced by a 70 W Xe arc lamp passed through the cell in a perpendicular direction to the laser beams; its optical path was 1 cm. Though collinear detection would have been more sensitive, it was impractical due to interference from the shock waves generated by the absorption of strong laser pulses.

The analyzing light was passed through a color glass filter and a monochromator and then detected using an R1913

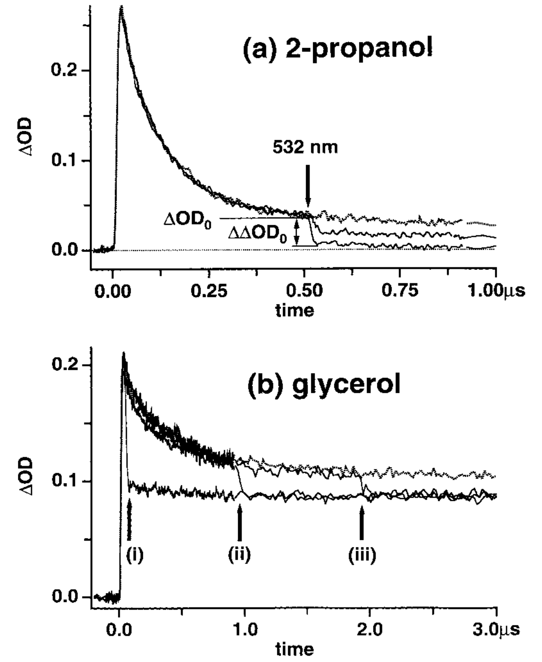

Figure 1. Transient absorbance (ΔOD) observed in two-color, two-pulse photolysis of 10^{-4} M triphenylene in O_2-saturated 2-propanol (a) and glycerol (b). The absorbance was detected at 710 nm where triphenylene$^{\bullet+}$ exhibits a peak (the visible spectrum is given in Figure 3b). The 248 nm laser pulse fired at $t = 0$ was used to generate the radical cations of triphenylene that were bleached by a delayed 532 nm laser pulse. The delay times of the 532 nm pulse were (a) 500 ns and (b) 50 ns (trace i), 800 ns (trace ii), and 1.8 μs (trace iii). The kinetics obtained with the 248 nm pulse only are shown by broken lines. The two solid traces in plot (a) are the kinetics obtained at fluences of 0.07 and 0.4 J/cm^2; the trace that exhibits more bleaching corresponds to higher fluence of the 532 nm photons. If not stated otherwise, the kinetics and spectra were obtained at 0.4 J/cm^2. In both solvents there is no recovery of the bleached absorbance as far as the ΔOD can be followed (150 μs in our experiment); this follows from the facts that the residual ΔOD signal decays in the same way as the signal obtained with the 248 nm pulse alone and that the ΔΔOD signal decay parallels the decay of the ΔOD signal (the latter can be seen in Figure 2a).

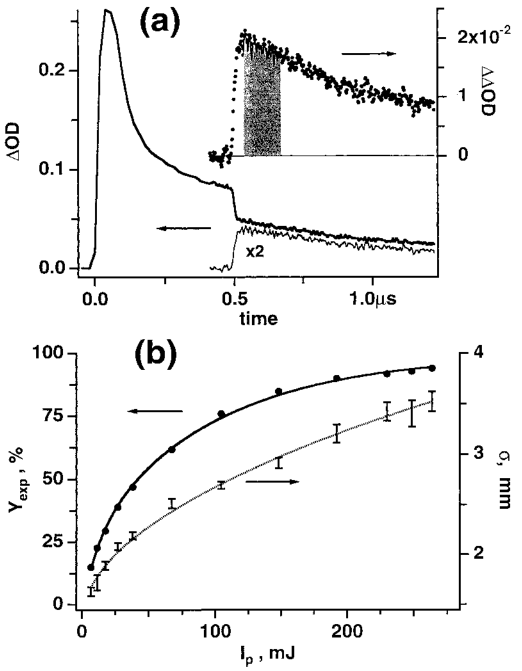

Figure 2. (a) Transient absorbance (580 nm) from the O_2-saturated aqueous solution of 3×10^{-4} M of L-tryptophan at pH ≈ 7. The 532 nm pulse was delayed by 500 ns relative to the 248 nm pulse. The difference trace (ΔΔOD) induced by the 532 nm pulse (also shown in the upper right corner) is normalized (×2) to demonstrate the similarity of the decay kinetics for the bleached and unbleached species. The darkened area under the ΔΔOD trace indicates typical range used for averaging of the signal in order to obtain the laser power dependence of the photobleaching efficiency Y_{exp}. (b) The dependence of Y_{exp} on the fluence of 532 nm photons for 10^{-4} M triphenylene in the O_2-saturated 2-propanol (710 nm detection). The total power (I_p) and radius (σ) for a Gaussian laser beam were determined as described in the Experimental Section. The broken line is the square root fit of σ. The solid line drawn through the experimental points was calculated using eqs A3 to A5; an estimate of $\epsilon_{532}\phi \approx 1250 \pm 50$ was obtained from this fit.

photomultiplier. For data collection, a Tektronix DSA-601 digital signal analyzer was triggered either by a portion of the 248 nm light (to observe the signal induced by it and the delayed signal induced by the 532 nm laser pulse) or by the 532 nm light (to observe the signal induced by the 532 nm photons). In the former case, the signal could be observed with just the 248 nm pulse, or with both pulses (the ΔOD traces in Figures 1 and 2a). In the latter case, a subtraction was done with the digitizer: the signal using just the 248 nm pulse (blocking the 532 nm pulse from the cell with a shutter) was subtracted from the signal obtained with both pulses (the ΔΔOD traces in Figure 2b). In some instances we needed to subtract the fluorescence from the solution and the scattered light coming from the 248 and 532 nm pulses. Each sample received 10−20 248 nm pulses and 5−10 532 nm pulses, the latter occurring after every second 248 nm pulse. Typical delay times of the 532 nm pulse relative to the 248 nm pulse were 300−500 ns. The absorption spectra shown in Figures 3 and 4 were obtained by integration of the ΔΔOD and ΔOD traces over a 50−100 ns wide time window.

The efficiency Y of bleaching was defined as $Y = 1 - [ArH^{\bullet+}]_{bl}/[ArH^{\bullet+}]_0$, where $[ArH^{\bullet+}]_0$ and $[ArH^{\bullet+}]_{bl}$ are the concentrations of the solute radical cations before and after the 2.3 eV excitation. In practice, it was the quantity $Y_{exp} = \Delta\Delta OD_0/\Delta OD_0$ that was determined experimentally, where ΔOD_0 is the transient absorbance before 532 nm photoexcitation and $\Delta\Delta OD_0$ is the change in the absorbance immediately after the 532 nm excitation (Figure 1a). These two quantities, Y and Y_{exp}, are equal when all of the absorbance at the time of the 532 nm excitation is from the radical cation.

Laser Beam. Unlike the excimer laser, the Nd:YAG laser generates a beam that is very spatially inhomogeneous. This must be taken into account when the quantum yield of the photobleaching is determined. The radial dependence of the photon flux is given by $J_p(r) = I_p/\pi\sigma^2 \exp(-r^2/\sigma^2)$, where σ is the beam radius and I_p is the total energy of the pulse. For powerful laser beams used in this work, changing the power without changing the beam radius was difficult,[62] and we measured the spot sizes σ and I_p for every output power; the latter was varied by changing the delay time of the Q-switch. To determine σ, the laser beam was shaded by a blade translated in a direction perpendicular to the beam. The residual beam was expanded and its energy measured using a Gentec EM-1 power meter with an ED-500 probe head. The total power $I(x)$ of the shaded beam as a function of the off-center displacement x of the blade edge (50−75 points spaced by 300 μm) was fit by $I(x) = I_p/2 \operatorname{erfc}(-x/\sigma)$, and the best-choice parameters I_p and σ were used. A typical dependence is shown in Figure 2b; the spot size σ can be fit by $\sigma = c_0 + c_1\sqrt{I_p}$, where c_0 and c_1 are constants. For a beam centered in the middle of a rectangular aperture $a \times b$, the average fluence $\langle J_p\rangle$ through the aperture is given by $\langle J_p\rangle = (I_p/ab) \operatorname{erf}(a/2\sigma) \operatorname{erf}(b/2\sigma)$. Using our data on

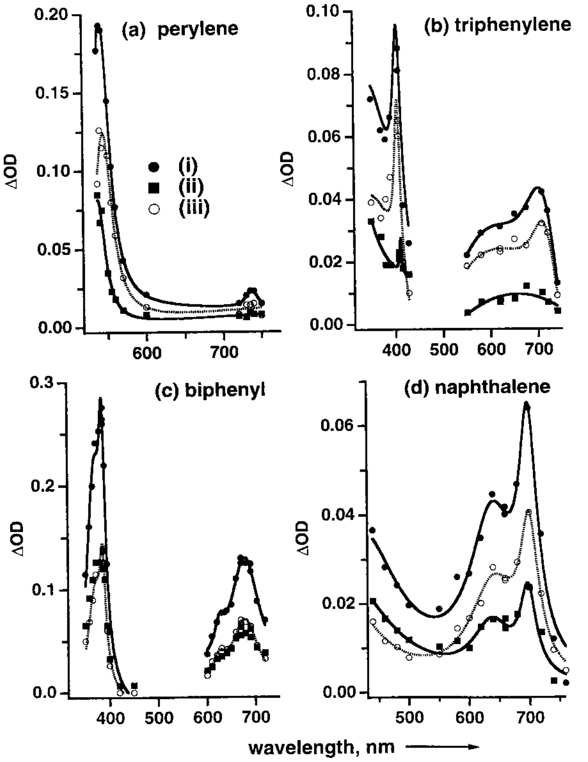

Figure 3. Transient absorbance spectra obtained from the O_2-saturated 2-propanol solutions of (a) 10^{-4} M perylene, (b) 10^{-4} M triphenylene, (c) 2×10^{-4} M biphenyl, and (d) 4.5×10^{-4} M naphthalene. The 532 nm pulse was delayed by 500 ns relative to the 248 nm pulse. Traces i were obtained before the 532 nm pulse, traces ii were obtained immediately after the pulse, traces iii are the difference (i.e., bleaching) spectra.

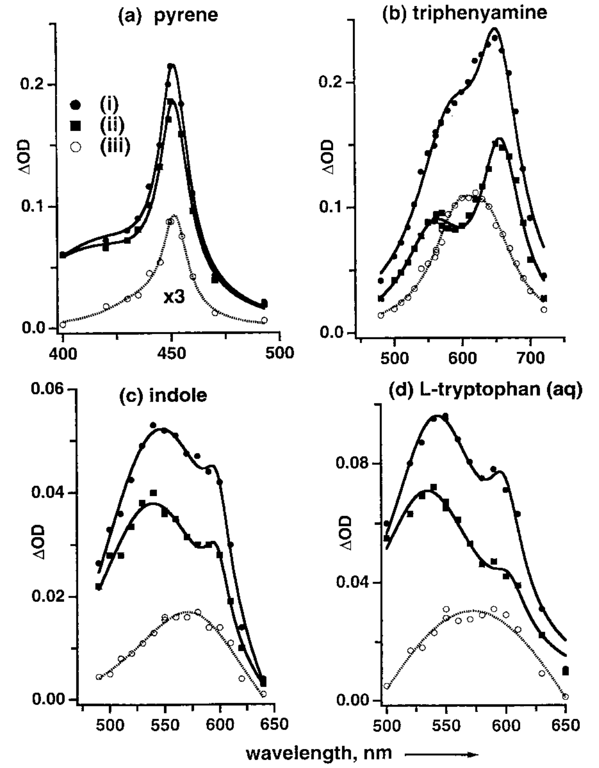

Figure 4. Transient absorbance spectra obtained from the O_2-saturated 2-propanol solutions of (a) 10^{-4} M pyrene, (b) 5×10^{-4} M triphenylamine, (c) 2×10^{-4} M indole and (d) aqueous solution of 3×10^{-4} M of L-tryptophan. The 532 nm pulse was delayed by 500 ns relative to the 248 nm pulse. Traces i were obtained before the 532 nm pulse, traces ii were obtained immediately after the pulse, and traces iii are the bleaching spectra.

σ and I_p and the known aperture dimensions, we found that $\langle J_p \rangle$ calculated using this formula was within 5% of the experimental value.

Extinction Coefficients. To determine the quantum yield ϕ of the 532 nm bleaching, one needs to know the extinction coefficient ϵ_{532} of the radical cations at this wavelength. Since for most of the radical cations such data are not available, we determined the coefficients ϵ_{532} using a technique originally developed by Benema et al.[63] and others[64] and modified by Gamy and Vanthey.[65] The radical cations were generated by laser photolysis of 10^{-5}−10^{-3} M solutions of aromatic solutes in the room-temperature boric acid glass. These solutions were prepared by addition of powdered solids to molten boric acid glass. A thin, 50−200 μm, 1 cm^2 film of the vitreous solution was cast by pressing the hot melt between two Suprasil plates. These films were irradiated with 5−10 pulses of the 5 eV light from an excimer laser (70 mJ/pulse). The conversion of ArH was monitored by the decrease of the UV absorbance of the neutral molecules and the appearance of the absorbance from $ArH^{•+}$ at 350−900 nm. Typically the conversion was 80−100%. Assuming that no other light-absorbing photoproducts were formed, the difference spectrum (before and after the UV irradiation) was taken as that of $ArH^{•+}$. These difference traces closely resembled the spectra of radical cations stabilized in γ-irradiated frozen butyl chloride and fumaronitrile, as observed by Shida.[66] The extinction coefficients ϵ_λ of the radical cations were determined using the known extinction coefficient of ArH at some reference wavelength λ' (taken from ref 67) and the changes in the absorbance at λ and λ' induced by the UV irradiation. (It was assumed that the absorption bands of ArH and $ArH^{•+}$ do not overlap.) For absorption peaks of the radical cations of biphenyl, perylene, and anthracene, this method gives ϵ_λ which are within 10−20% of the coefficients found in the literature.

To obtain an independent estimate of ϵ_{532} for triphenylene$^{•+}$, we used pulse radiolysis of 10^{-3} M of the solute in O_2-saturated n-hexane. Oxygen was used to scavenge electrons, aromatic triplets, and radical anions. Under the conditions of our experiment, no absorbances from aromatic species other than $ArH^{•+}$ were observed at delay times longer than 30 ns following a 4 ns electron pulse. It was assumed that the rates of hole scavenging and radical cation dimerization are similar for all aromatic solutes used. By comparing the transient absorbance spectra of two radical cations, the relative extinction coefficients were estimated. As a reference, we used the value of 2.4×10^4 M^{-1} cm^{-1} for the 450 nm band of pyrene$^{•+}$ [68a] (for the 8−10 nm band-pass of our setup; 4.5×10^4 M^{-1} cm^{-1} for 2 nm band-pass).[68b] From this experiment, we estimated that triphenylene$^{•+}$ has $\epsilon_{532} \approx 3.2 \times 10^3$ M^{-1} cm^{-1}. This estimate is close to 2.7×10^3 M^{-1} cm^{-1} obtained for triphenylene$^{•+}$ in boric acid glass.

4. Results

Photoionization. In polar solvents, photoexcitation of aromatic solutes with relatively long (∼30 ns) pulses of 248 nm light causes their biphotonic ionization mediated by the S_1 and T_1 states of the aromatic molecule.[21] With the high fluxes of the 248 nm light that was used in our experiment (0.1−0.2 J/cm^2) it was possible to bleach a substantial fraction (40−90%) of the S_0 and S_1 states. However, many triplet molecules were present in the solution during and immediately after the UV pulse. In many instances, these triplet states have UV−vis absorption spectra that closely resemble those of the corresponding radical cations or have overlapping bands. Furthermore, some of these triplet states absorb both the 248 nm photons (during the ionizing pulse) and 532 nm photons (during the second excitation pulse) and exhibit photochemistry such as abstraction of hydrogen from the solvent,

$$^{3}\mathrm{ArH} + h\nu \rightarrow {}^{3}\mathrm{ArH}^{*} \tag{17}$$

$$^{3}\mathrm{ArH}^{*} + \mathrm{ROH} \rightarrow {}^{\bullet}\mathrm{ArH}_2 + \mathrm{RO}^{\bullet} \tag{18}$$

For some triplets, such as ^{3}triphenylene*, reaction 18 is very vigorous.[69] To minimize the interference from these T_1 states and, to a lesser degree, the H adduct radicals $^{\bullet}ArH_2$ (which do not absorb at 532 nm), we found it necessary to saturate the solutions with O_2 and delay the 532 nm excitation pulse for 300−500 ns after the ionizing pulse. Given that in nonviscous liquids a typical rate of triplet quenching by oxygen is $\sim 10^9$ M^{-1} s^{-1} and the concentration of O_2 in oxygen-saturated solutions is ∼0.01 M,[70] less than 5% of these triplet states remained in the solution by the time of the 532 nm excitation. The addition of O_2 reduces the yield of radical cations: Since it accelerates intersystem crossing, shortening the lifetime of singlets, it decreases the yield of biphotonic ionization. In our experiments, this reduction was between 20% and 50%. Nevertheless, a typical yield of radical cations in O_2-saturated alcohols and acetonitrile was ∼1 μM, which is sufficient for optical detection with good signal-to-noise ratio. Another function of oxygen was to scavenge solvated electrons which strongly absorb in the visible[21] and, unlike the $O_2^{\bullet -}$ ions, can be excited by 532 nm light. The ground-state solvated electrons react with polycyclic aromatic solutes yielding their radical anions. Saturation of the solution with oxygen completely prevented the formation of these light-absorbing species. In some of our experiments (see below), the electrons were scavenged by 10^{-3}−10^{-2} M acid.

As was shown by Liu et al.,[21] the yield of radical cations upon laser ionization with 4 and 5 eV photons reaches a plateau for fluences of ca. 10^{17} photons absorbed per cm^3. Further increase in the fluence causes photobleaching of these radical cations. Though this effect reduces the efficiency of photogeneration of radical cations, it helps to achieve good shot-to-shot reproducibility for their yield, despite a considerable variation in the laser intensity (5−15% for our setup). This, in turn, makes it possible to study the photobleaching in a reproducible way. We stress that at the 532 nm photon fluences used (0.01−2.5 J/cm^2) no multiphoton ionization of aromatic solutes (except for rubrene, tetracene, and benzo[*g*,*h*,*i*]perylene) with the 532 nm pulses alone was observed.

In the systems studied, the photobleaching is permanent. Although the residual signal decays, this decay simply follows the decay of the signal observed in the absence of the 532 nm excitation (Figure 1) and the ΔΔOD signal decay parallels the decay of the residual ΔOD signal (Figure 2a). When this decay is slow, as in glycerol (Figure 1b), no recovery is observed over the first 100 μs after the 532 nm pulse.

Bleaching Spectra (Figures 3 and 4). Using the optimum conditions examined above, we were able to prepare solutions of radical cations that contained either little or no other species that absorbed in the visible region and at 532 nm in particular. A notable exception was triphenylamine, which yielded a large quantity of the "600 nm transient" (Figure 4b). This absorbance is from a carbazole-like molecule formed by intramolecular electron transfer in the triplet states of N-substituted diphenylamines.[71] These species were bleached by the 532 nm light (with $\epsilon_{532}\phi \approx 2600$); the residual spectrum was from triphenylamine$^{\bullet +}$. For other aromatic amines—indole (Figure 4c), diphenylamine, aniline, and 2-aminonaphthalene (not shown)—the 248 nm photoexcitation yielded mainly the absorbance from their radical cations. Though the radical cations of the amines are known to deprotonate (reaction 12),[33] in alcohols the rate of this reaction is slow and the absorbance at $t < 1$ μs is from the radical cation. Almost identical spectra were obtained in the presence of 0.01−0.1 M sulfuric acid that was added to shift the equilibrium toward the radical cation form. For aqueous L-tryptophan (a naturally occurring amino acid derivative of indole, Figure 4d), the spectrum contains a large fraction of the "530 nm" absorbance from the aminyl radical (whose band can be seen more clearly at pH∼11−13).[34] The deprotonation rate of aqueous L-tryptophan$^{\bullet +}$ is 1.5×10^6 s^{-1},[34] and at the delay time of 400−500 ns more than 50% of these radical cations convert to the aminyl radicals. It appears that these radicals cannot be bleached with the 532 nm photons since the bleaching spectrum is that of the radical cation (Figure 4d).

Most of our studies were performed with triphenylene$^{\bullet +}$, which exhibits high efficiency of photobleaching with 532 nm photons (Figsures 1a, 2b, and 3b). The bleaching spectrum observed in photolyzed triphenylene solution is very similar to that of the radical cation stabilized in solid matrixes:[63,64,66,69] The overall shape is similar, and the ratio of the intensities of the 700 and 400 nm peaks is about 1:2. In the initial spectrum (before the 532 nm pulse) there is extra absorbance in the blue from the cyclohexadienyl-type radical formed in reaction 18; it is known to have a band centered at 400 nm and a broad shoulder in the UV.[69] Since this radical does not absorb at $\lambda > 450$ nm,[69] it is not bleached with the 532 nm photons and does not interfere with the detection of triphenylene$^{\bullet +}$ at 700 nm.

With the exception of triphenylamine, the bleaching spectra (ΔΔOD vs λ) obtained upon 532 nm excitation are those of radical cations. For several aromatic solutes (naphthalene, triphenylene, and perylene) the 500−700 nm absorption bands from their radical cations can be fully bleached provided that the 532 nm photon fluence exceeds 0.5 J/cm^2. For triphenylene (Figure 3b), the residual UV spectrum resembles that of the H-adduct radical. Without oxygen (or in viscous solvents), the residual spectrum is that of the T_1 state of triphenylene.[72] For biphenyl (Figure 3c), ca. 70% of the absorbance signal from biphenyl$^{\bullet +}$ in the 390 and 680 nm bands can be bleached at fluences >2 J/cm^2. Under the same conditions, 50% of the absorbance in the 450 nm band of pyrene$^{\bullet +}$ and 60% of the absorbance in the 670 nm band of acenaphthene$^{\bullet +}$ can be bleached. The nature of the residual absorbance varies from system to system. For some radical cations (pyrene$^{\bullet +}$, acetonaphthene$^{\bullet +}$, benz[*a*]anthracene$^{\bullet +}$, etc.) the product $\epsilon_{532}\phi$ is so small that even a photon flux of 1−3 J/cm^2 is insufficient to achieve complete bleaching. In these systems, the residual spectrum looks much like the bleaching spectrum (Figures 3c and 4a,c) and is mainly from radical cations. (A small fraction of the residual absorbance may be from unquenched triplets.) In other systems (indole, L-tryptophan) the residual absorbance is from other species, such as aminyl radicals, that cannot be bleached by 532 nm photons.

For aromatic amines—aniline, diphenylamine, and 2-aminonaphthalene—in alcohols no bleaching was observed at any fluence of the 532 nm photons. This is surprising, because Skvortsov and Alfimov observed efficient bleaching for aniline, diphenylamine, triphenylamine, and benzidine in frozen alcohols and ethers.[6−10] For aniline$^{\bullet +}$ and diphenylamine$^{\bullet +}$ the absorbance at 532 nm is quite low ($\epsilon_{532} \sim 100$ M^{-1} cm^{-1}). If the quantum efficiency ϕ of 532 nm bleaching for diphenylamine$^{\bullet+}$ is $\gg 10^{-2}$, as reported by Skvortsov and Alfimov,[8,9] the bleaching would be too small to observe under the conditions of our experiments. However, aniline has an IP$_g$ of 7.72 eV like aromatic solutes for which ϕ is 0.2−0.5 (see below). Furthermore, the radical cation of 2-aminonaphthalene (IP$_g$ = 7.10 eV) absorbs strongly at 532 nm and even if ϕ for this species is close to that of diphenylamine$^{\bullet+}$ (IP$_g$ = 7.16 eV), one would still expect to observe some bleaching. Therefore, it seems likely that these radical cations do not bleach in liquid solution at all. We also observed no bleaching for anthracene$^{\bullet+}$ and biphenylene$^{\bullet+}$ in 2-propanol and other alcohols, though both of these ions absorb at 532 nm and their parent molecules have high IP's; we cannot account for this behavior.

An interesting result was obtained for *all-trans*-1,6-diphenyl-1,3,5-hexatriene (t-DPH). This solute has fairly low IP$_g$ (a semiempirical AM1 calculation gave 7.38 eV for vertical and 7.07 eV for adiabatic IP$_g$ for C_{2h} geometry), but its radical cation absorbs strongly in the yellow and red, which makes photobleaching possible. In acetonitrile, the excited state of t-DPH$^{\bullet+}$ undergoes rapid *trans* to *cis* isomerization: The 590 nm absorption from t-DPH$^{\bullet+}$ decreases and the 625 nm absorption from its cis isomer (c-DPH$^{\bullet+}$) increases.[4] The reverse reaction, thermal isomerization of c-DPH$^{\bullet+}$ to t-DPH$^{\bullet+}$, occurs with a rate constant of 5×10^5 s^{-1}.[4] The fast photoisomerization provides an internal "clock" by which the rate of the bleaching reaction with the solvent can be estimated.

To photoexcite t-DPH$^{\bullet+}$, we used tightly focused 550 nm, 28 mJ pulses from a Magic Prism OPO stage (OPOTEK) pumped by 355 nm (third harmonic) pulses from a Nd:YAG laser. Upon the 550 nm photoexcitation of t-DPH$^{\bullet+}$ in 2-propanol, an extra absorption signal was produced at 625 nm. This signal decays with a rate constant of 4×10^5 s^{-1}, which is ca. 4 times faster than the decay of the 590 nm signal. This constant is close to the rate constant of thermal isomerization of c-DPH$^{\bullet+}$ to t-DPH$^{\bullet+}$ in acetonitrile.[4] Therefore, the 625 nm absorbance is from c-DPH$^{\bullet+}$, and the bleaching of the t-DPH$^{\bullet+}$ (observed at 590 nm) consists of two components: the irreversible bleaching (that was observed many microseconds after thermal isomerization of c-DPH$^{\bullet+}$) and reversible bleaching due to photoisomerization. To compete with each other, these reactions should have comparable rates. The fast recovery component comprises 10−20% of the total bleaching signal at 590 nm. Thus, the reaction with the solvent is 5−10 times faster than the rate of photoisomerization (the latter is expected to occur on the picosecond time scale).[1]

Solvent Effects. In this work, bleaching reactions of radical cations were studied mostly in 2-propanol. To get a broader picture, we studied 532 nm bleaching of triphenylene$^{\bullet+}$ in various polar solvents, e.g., water, mono- and polyhydroxy alcohols, nitriles, and ethers.

Several solvents demonstrated no bleaching, not only for triphenylene$^{\bullet+}$ but also for all other solute radical cations that were studied. In some of these solvents (aceto- and *n*-butyronitrile, 1,1,1,3,3,3-hexafluoro-2-propanol) the yield of radical cations was as high as in alcohols, and the lack of bleaching was due to photostability of ArH$^{\bullet+}$. The IP$_g$ of these solvents is greater than 12 eV. Apparently, the high IP prevents the occurrence of hole injection. In the solvents of intermediate polarity (cyclohexanol, tetrahydrofuran, 1,4-dioxane) the yield of free ions was too low to discern the absorbance of the aromatic radical cation because of the much stronger absorbances from triplets and radicals. Therefore, these solvents were mixed with nitriles to increase the polarity and enhance the yield of free ions. (We used 1:10 to 2:1 mixtures.) In such mixtures, the triphenylene$^{\bullet+}$ can be readily bleached, which indicates that [triphenylene$^{\bullet+}$]* reacts with the corresponding solvent molecules (e.g., ethers). By contrast, no bleaching was observed in water−acetonitrile mixtures and the mixtures of *n*-butyronitrile with saturated hydrocarbons (cyclohexane, decalin, squalane, and *n*-alkanes from C$_5$ to C$_{20}$). Apparently, due to lowering of the solute IP$_{liq}$ in the nitriles, [triphenylene$^{\bullet+}$]* does not have enough energy to react with water or with the alkanes.

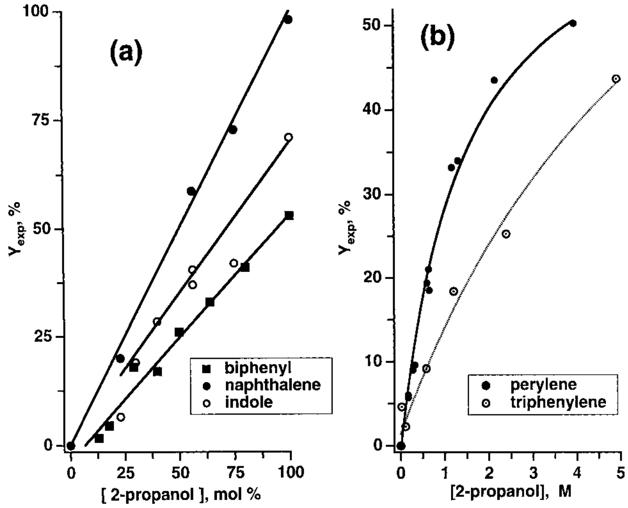

Figure 5. Efficiency Y_{exp} of the 532 nm bleaching as a function of the concentration of 2-propanol in O$_2$-saturated acetonitrile solutions of 2×10^{-4} M biphenyl (390 nm, 275 ns), 8×10^{-4} M indole (600 nm, 360 ns), 10^{-3} M naphthalene (700 nm, 275 ns), 5×10^{-5} M perylene (540 nm, 450 ns), and 10^{-4} M triphenylene (410 nm, 380 ns). The numbers in brackets are the detection wavelength and the delay time of the 532 nm pulse. Two types of the dependences were observed, linear (a) and curved (b). The latter can be fit using Stern−Volmer equation.

In mixtures of acetonitrile with 2-propanol, two types of behavior were observed (Figure 5). For perylene$^{\bullet+}$ and triphenylene$^{\bullet+}$, the concentration dependence of Y_{exp} is curved (Figure 5b). For [2-propanol]<5 M, this dependence can be fit with a Stern−Volmer plot. Assuming that [ArH$^{\bullet+}$]* reacts with 2-propanol with diffusion-controlled rate, 2×10^{10} M^{-1} s^{-1}, we estimated that the lifetimes of these species for triphenylene and perylene are 9.5 and 35 ps, respectively. The latter estimate is close to the lifetime of [perylene$^{\bullet+}$]* in boric acid glass (35 ± 5 ps) as determined by transient grating spectroscopy.[65] For biphenyl$^{\bullet+}$, naphthalene$^{\bullet+}$, pyrene$^{\bullet+}$, and acetonaphthene$^{\bullet+}$ the bleaching efficiency Y_{exp} is linearly proportional to the mole fraction of 2-propanol (Figure 5a). This linearity can be accounted for by the same Stern−Volmer dependence if the lifetimes of the corresponding excited radical cations are less than 1 ps. We conclude that while some of the excited radical cations of aromatic hydrocarbons have fairly long lifetimes in acetonitrile, other have the lifetimes shorter than 1 ps. Interestingly, there seems to be no correlation between the quantum yield of bleaching and this lifetime.

In alcohols, the bleaching efficiency Y_{exp} for triphenylene$^{\bullet+}$ correlated with the carbon number of the alcohol (Figure 6a). Y_{exp} is a maximum for C$_3$ and decreases for shorter and longer chain alcohols. Since [triphenylene$^{\bullet+}$]* is relatively long-lived, some of these variations could be due to changes in the molarity of neat solvents. As shown in Figure 6b, the ratio Y_{exp}/[ROH] depends on the carbon number in a more systematic way, steadily increasing with the length of the alkyl chain. The

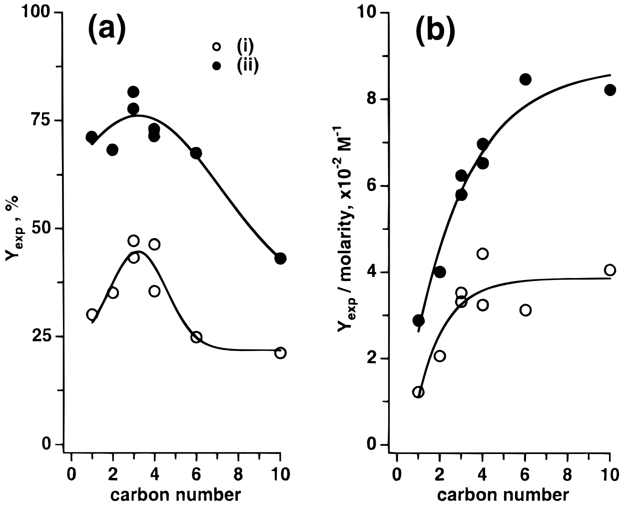

Figure 6. (a) Efficiency Y_{exp} of the 532 nm bleaching of triphenylene$^{\bullet+}$ in O_2-saturated 10^{-4} M alcohol solutions of triphenylene (710 nm detection, 530 ns delay time) as a function of the carbon number of the alcohols (methanol, ethanol, 1- and 2-propanol, 1- and 2- butanol, 1-hexanol, and 1-decanol). Traces i were obtained at the photon fluence of 0.1 J/cm^2 and traces ii at 0.35 J/cm^2. (b) Same plot for the ratio of Y_{exp} and the molarity of the neat solvent.

hydrogen bonding in the solvent and the difference in the IP_g of the solute and the solvent both decrease with the carbon number, making the higher alcohols poorer proton acceptors and better electron donors. This result is consistent with the view that the bleaching reaction is the hole injection. For other aromatic radical cations, Y_{exp} may depend on the carbon number in a more dramatic way. For example, for indole, the bleaching efficiency at 0.5 J/cm^2 in methanol and ethanol is ca. 8% while in 1- and 2-propanol it is ca. 40%. These changes seem to be due to an increase in the quantum efficiency ϕ of photobleaching rather than a change in the rate of deprotonation.

In polyhydroxy alcohols (glycols and glycerol) the bleaching of the 710 nm absorbance from triphenylene$^{\bullet+}$ is prominent (Figure 1b), but the fraction of the signal that can be bleached decreases with the solvent viscosity. This can be explained by the inefficiency of triplet and singlet quenching in viscous solutions. The residual absorption signals are apparently from triplets and radicals formed during 248 nm photoionization.

In aqueous solutions, we found only one solute whose radical cation demonstrated photobleaching upon 532 nm photoexcitation—a derivative of indole, L-tryptophan. Indole itself demonstrated no photobleaching, though it has a similar absorption spectrum (Figure 4c) and IP_g (Table 2) and is soluble in water. For most of the polycyclic aromatic solutes studied in this work, the solubility in water is so low that we were unable to generate sufficient concentration of their radical cations. However, even for naphthalene, which is more soluble ($\sim 6 \times 10^{-5}$ M) and whose radical cation can readily be observed in aqueous solutions, we found no photobleaching at 532 nm. The addition of water to alcohol solutions of naphthalene and other polycyclic aromatic solutes causes changes in the Y_{exp} that are similar to those observed upon addition of acetonitrile. The unique behavior of aqueous L-tryptophan$^{\bullet+}$ may indicate that this species photobleaches differently from other aromatic radical cations, due to the presence of a charged side branch.

Quantum Efficiency of 532 nm Bleaching. The bleaching efficiency Y_{exp} as a function of the laser power (Figures 2a and 7) was determined by integration of the $\Delta\Delta$OD kinetics within the first 100−200 ns following the 532 nm photoexcitation (Figure 2a). The products $\epsilon_{532}\phi$ were determined as discussed in the Appendix. The principal difficulty in these measurements is low absorbance at 532 nm for most of aromatic radical cations (Table 2): Only the radical cation of perylene has ϵ_{532} in excess of 10^4 M^{-1} cm^{-1}; for other radical cations studied here ϵ_{532} varied from 2×10^2 to 3×10^3 M^{-1} cm^{-1}. Thus, to observe saturation, photon fluxes of more than 1 J/cm^2 were needed in some cases (Figure 7b).

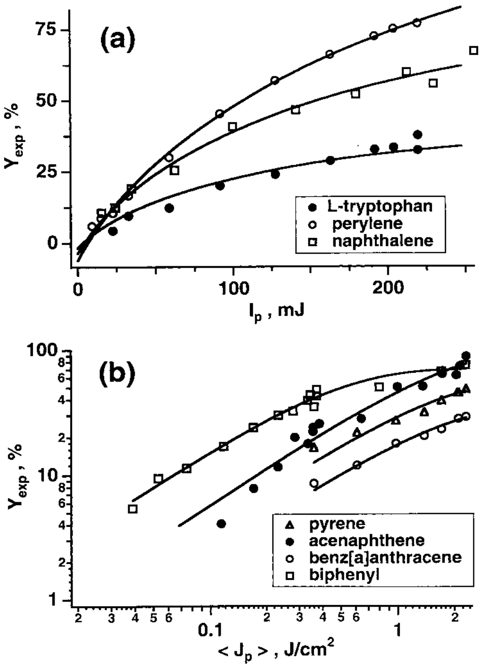

Figure 7. Power dependences of the bleaching efficiency Y_{exp} for radical cations of various aromatic solutes in O_2-saturated 2-propanol (except for L-tryptophan, which was in water). The 532 nm bleaching pulse was delayed 500 ns after the ionizing 248 nm pulse. The detection wavelengths are given in Table 2, and the solid lines were calculated using the equations given in the Appendix with the values of $\epsilon_{532}\phi$ given in Table 2. Traces a were simulated using eq A5, and traces b were simulated using eq A3 with the average fluences $\langle J_p \rangle$ determined experimentally.

Polycyclic aromatic radical cations tend to absorb either in the red or the blue.[60] Laser excitation in the blue causes multiphoton ionization of the solute which makes the results unreliable. In principle, it is possible to reduce the photon fluxes by excitation at the centers of the absorption bands of these radical cations in the yellow and the red, where ϵ_λ is $\sim$(1−4) $\times 10^4$ M^{-1} cm^{-1}. The problem is that one still needs photon fluxes of 0.1−0.5 J/cm^2 to reach the saturation level, and without doing that it is impossible to determine what fraction of the absorbance signal is from radical cations.

Using the data on $\epsilon_{532}\phi$ and the values of ϵ_{532} from Table 2, we determined the quantum yield ϕ of bleaching aromatic radical cations with 532 nm photons. The main uncertainty in these quantum yields is due to uncertainty in the extinction coefficients ϵ_{532}. Figure 8 demonstrates the linear correlation of log ϕ with the IP_g of the aromatic solute. For high-IP solutes ($IP_g > 7.7$ eV, such as triphenylene, acetonaphthene, biphenyl, and naphthalene), the quantum yield is high, 0.3−0.5. For medium-IP solutes (pyrene, benz[*a*]anthracene) the quantum yield is a few percent, and for the low-IP solute, perylene, the yield is less than 0.02. The latter estimate is close to the quantum yield of 532 nm photobleaching of radical cations for low-IP solutes diphenylamine and triphenylamine in solid diethyl ether[8] and ether−toluene mixtures[9] at 77 K. Figure 8 suggests that the main parameter controlling the efficiency of photobleaching is the IP_g of the solute. If one continues the line to higher IP's,

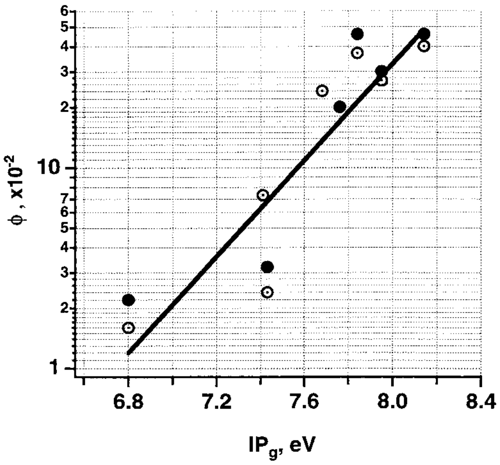

Figure 8. Correlation between the ionization potential IP_g of the aromatic solute in the gas phase and the quantum yield ϕ (Table 2) of the 532 nm bleaching of their radical cations in 2-propanol. Filled circles are the ϕ obtained using eq A5, and empty circles are the ϕ obtained with eq A3 using average fluences. Extrapolating from this plot, the quantum yield becomes unity at $IP_g \sim 8.4$ eV.

the quantum efficiency becomes unity at ca. 8.4 eV. Adding to that 2.3 eV, one obtains the threshold of 10.7 eV, which is close to IP_g of 2-propanol, 10.2 eV. As was shown above, these energetics are consistent with both electron and proton transfer occurring upon 532 nm photoexcitation.

Effect of Acid. In an effort to discriminate between these two mechanisms, we studied the effect of acid on the recovery of the photobleached signals. As was argued in section 2, addition of extra protons to the solvent should convert the $Ar^\bullet$ radicals formed upon photoprotonation of the solvent back to radical cations. While for polycyclic aryl radicals the occurrence of reaction 14 is not documented, the protonation of aminyl radicals in aqueous solutions is well studied. For the aminyl radical of L-tryptophan in water, the rate of protonation is 3×10^{10} M^{-1} s^{-1}.[34] Thus, the lifetime of this radical changes from 300 μs at neutral pH = 7 to 3 ns at pH = 2. Assuming that the bleaching is due to photoprotonation, one should observe a gradual change from no recovery of L-tryptophan$^{\bullet+}$ at pH > 5 to complete recovery (the absence of bleaching) at pH ~2−3. In the intermediate region, the delayed recovery of L-tryptophan$^{\bullet+}$ on the time scale of 10^{-8}−10^{-6} s should be observed.

We performed this experiment varying pH from 7 down to 1, with and without oxygen in solution (which slowly scavenges the aminyl radicals). The bleaching at pH = 2 was no less efficient that at pH = 7, and no fast recovery of the L-tryptophan$^{\bullet+}$ for pH between 2 and 7 was observed (Figure 9). No bleaching was observed for pH < 1.5. This is due to the protonation of L-tryptophan that significantly changes the whole photophysics. The aminyl radical of L-tryptophan has a broad peak centered at 510 nm;[34] if it were formed upon photobleaching at pH ~ 7, one would observe a growth of this absorbance after 532 nm excitation. No such growth was observed (Figure 4d). Therefore, the aminyl radicals were not formed upon the photobleaching.

Similar results were obtained for indole$^{\bullet+}$ and other aromatic radical cations in alcohols. We conclude that the product of the bleaching reaction cannot be converted back to the radical cation by protonation. This result indicates that the bleaching reaction is not photoprotonation.

5. Discussion

Our results suggest that photobleaching of radical cations in polar solvents is due to concerted hole injection, reaction 4 or 5. The quantum yield ϕ of the photobleaching systematically increases with the IP_g of the parent molecule. For 2.3 eV photoexcitation in 2-propanol, the maximum quantum yields of 0.3−0.5 were observed for aromatic solutes with $IP_g > 7.7$ eV; this is close to the onset of exothermicity for electron transfer (2) in the gas phase. Assuming that the photobleaching is due to hole injection, one can estimate the energy of the excited radical cation and compare it with the IP_{liq} of the solvent molecules in liquid. Since practically none of these IP's are known well, we are limited to aqueous indole and L-tryptophan. For aqueous L-tryptophan, reported $IP_{liq} = 4.5$ eV,[42] which brings L-tryptophan$^{\bullet+}$ to 6.8 eV upon 2.3 eV photoexcitation. The onset of mono-[56] and bi-photonic[57] generation of hydrated electrons in pure water is ca. 6.5 eV (though threshold energies as low as 6.05 eV were reported).[55] The ionization of L-tryptophan was observed by measuring the yield of N_2 upon scavenging of hydrated electrons by N_2O.[42] (The concentration of N_2O in water is too low to scavenge dry electrons.) Thus, the reported IP_{liq} corresponds to that of the formation of a *hydrated* electron and L-tryptophan$^{\bullet+}$. The threshold of 6.5 eV is believed to be the energy for formation of a localized or hydrated electron and partially hydrated or *dissociated* hole.[54,55] (The formation of a hydrated electron and fully dissociated hole requires ca. 5.8 eV.[56]) For dry holes, the onset of ionization is above 8 eV. Thus, the photobleaching of L-tryptophan$^{\bullet+}$ at 2.3 eV is consistent with the occurrence of reaction 4. For indole, the IP_{liq} in water is 4.35 eV[40,41] (measured the same way as for L-tryptophan) which brings it to 6.65 eV after excitation. Probably, this energy is too close to the 6.5 eV threshold for reaction 4 to occur.

Another way to estimate these energetics is to compare the standard electrode potentials $E°$ for the involved redox reactions. The estimates of $E°$ (Trp$^{\bullet+}$/Trp) for L-tryptophan at pH ~ 7 range from 0.64 to 1.24 V; the latter estimate is close to the redox potential for aqueous indole.[73] Using this estimate and $E° = 2.85$ V for

$$HO^\bullet + H_3O^+ + e^- \rightarrow H_2O \qquad (19)$$

from ref 74, we obtain that the hole injection from the ground-state L-tryptophan$^{\bullet+}$ is endothermic by 1.6−1.8 eV. Thus, if

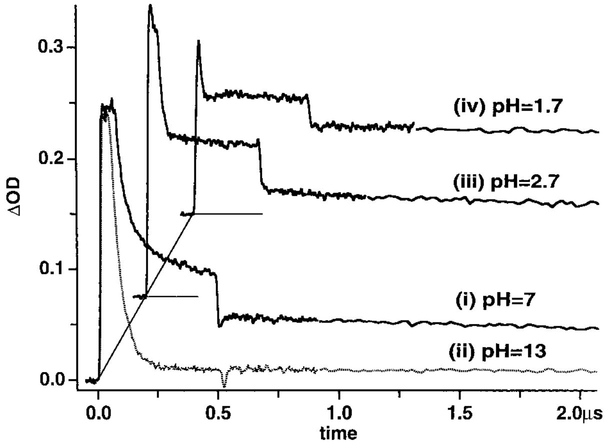

Figure 9. Effect of pH on the kinetics of transient absorbance from 2.5×10^{-4} M aqueous solutions of L-tryptophan (580 nm detection, 500 ns delay time of the 532 nm pulse). The pH is indicated next to the traces; traces i and ii were obtained in oxygen-saturated solutions and traces iii and iv in argon-saturated solutions. The rapid decay of the 580 nm absorbance at high pH is due to deprotonation of L-tryptophan$^{\bullet+}$.

the hydronium and hydroxyl radical are formed in their equilibrium states, reaction 4 is exothermic by at least 0.5−0.7 eV.

It becomes necessary to address the issue of the preference of reaction 4 over proton-transfer reaction 5. This is not the result of energetics. For aromatic amines, reaction 6 is endothermic by 0.9 eV, and therefore, reaction 5 is ca. 1 eV (!) more exothermic than reaction 4. Since the amines are better bases than alcohols, both in the gas phase (for aniline and its derivatives $PA_g > 9.3$ eV) [30] and in solution (pK_a for indole and pK_a(>NH) for L-tryptophan in water is ∼17),[75] reaction is ∼1 eV more exothermic than reaction 4. Thus, for aromatic amines, energetics of reactions 5 and 6 are comparable, while reaction 4 is much less exothermic than reactions 5 and 6. From this, one would expect that in polar solvents the course of the hole injection depends on the relative basicity of the solvent and the solute. The PA_g of polycyclic aromatic molecules is often higher than that of polar solvent molecules.[30] For example, the PA_g of perylene is 0.88 eV greater than the PA_g of 2-propanol and 1.02 eV greater than the PA_g of acetonitrile. In hydrogen-bonded liquids (water, alcohols), the liquid-phase PA is ca. 3 eV higher than the gas-phase PA,[76] which is likely to make reaction 4 a preferred route, unless the aromatic molecule is a strong base. In non-hydrogen-bonded solvents, or mixed solvents, reaction 5 would be preferred. Apart from these energetics, for aromatic amines reaction 5 is expected to be a preferred route by analogy: In liquid alcohols, the *ground-state* alkylaminium radicals slowly abstract hydrogen from the solvent (10^3-10^4 M^{-1} s^{-1} at 300 K).[27c]

Our results for indole and L-tryptophan do not contradict or support bleaching being due to reaction 5 rather than reaction 4. However, for aniline$^{\bullet+}$ and its derivatives in *solid* alcohols and ethers, the results of Skvortsov and Alfimov directly point to reaction 4.[6] In their first report, these authors observed a partial recovery of the UV bands of neutral amines upon photobleaching of the corresponding radical cations. Despite this claim, there is no evidence for such a recovery in the UV spectra reported in their later work.[8−10] (The absorption bands of protonated anilines shift to the blue relative to the bands of neutral amines (from 330 to 370 nm to 290 nm),[77] and in principle, reactions 4 and 5 can be distinguished spectroscopically.) Since in *liquid* alcohols no photobleaching was observed for these amines it could be that the proton-transfer (6) is preferred at higher temperature. In such a case, the low quantum yield of the photobleaching is due to rapid proton-transfer reaction 14 in the geminate pairs.

It should be stressed that our work does not provide a definitive proof that in polar solvents the photobleaching *is* due to reaction 4. In principle, a rearrangement or fragmentation of the excited radical cations may also cause their bleaching. For some of the radical cations studied in this work, such a rearrangement is possible. Breslin and Fox considered photocyclization of triarylaminium radicals similar to the cyclization of triplet triarylamines.[78] For [L-tryptophan$^{\bullet+}$]*, one can speculate on the occurrence of *internal* charge or proton transfers: Such reactions are known to occur in the T_1 state of L-tryptophan.[79] Our arguments in favor of hole injection are that (i) the photobleaching also occurs for polycyclic aromatic cations for which there are no obvious rearrangement or fragmentation channels, (ii) it is very fast and solvent-specific, (iii) its efficiency correlates with the difference in the IP's of the aromatic molecule and the solvent, (iv) in nonpolar solvents the photobleaching is shown to be due to the hole injection,[13] and (v) dissociative hole injection in hydrogen-bonded solvents is energetically feasible.

The fact that hole injection is preferred to the more exothermic proton or H atom transfer has a precedent in nonpolar media.[13] In cycloalkanes, solvent holes are formed even though the reactions analogous to (5) and (6) are 1−2 eV more exothermic than the electron-transfer reaction 1: The PA_g's of cyclohexane (7.34 eV) and cyclohexyl (7.87 eV) are lower than the PA_g of any aromatic molecule except for benzene.[30,31] This suggests that the proton transfer occurs neither upon hole injection nor immediately after it, even if these transfers are energetically favorable. Such a situation could only mean that the donor and acceptor of the proton are spatially separated or that there is a high potential barrier that prevents the occurrence of the transfer. In the absence of the proton transfer, hole injection yields a geminate pair of the solute molecule and the solvent hole. The backward charge/proton transfer in this pair is exothermic (and, in cycloalkanes, is diffusion-controlled),[13,14] and, therefore, these geminate pairs must recombine very rapidly. The observation of mobile solvent holes in the conductivity experiments[13] confirms that some of these holes (ca. 1−5%) escape geminate recombination. Since a typical reaction radius for scavenging of the solvent hole in cycloalkanes is ∼1 nm, this suggests that the geminate partners are initially separated by at least 0.5−0.6 nm (see comment 8 in ref 13).

Thus, the conclusion we can make is that the injected hole is separated from the neutralized radical cation. In ref 13, we speculated that this initial separation was due to high mobility of extended-state holes injected deep into the valence band, across the mobility edge. To approach these states, the solvent hole formed in reaction 1 should have considerable excess energy. While for some cycloalkanes this is not unreasonable (e.g., for decalins this excess energy is ∼1 eV), it is difficult to see how this mechanism can operate in high-IP liquids such as alcohols and cyclohexane, where the excess energy is probably less than 0.1−0.3 eV. It appears, therefore, that the hole is transferred to a localized state (a "preexisting *hole* trap") in the immediate vicinity of the radical cation.

A similar reaction (save for electrons instead of holes), electron photodetachment from aqueous halide anions, has recently been studied by ultrafast laser spectroscopy[80] and quantum molecular dynamics modeling.[81,82] It was shown that the injected electron rapidly localizes in a trap in the second solvation shell of the halide anion (within ∼50 fs)[81] and then drifts 0.3−0.4 nm away, forming a solvent-separated electron−atom pair (∼200 fs).[81,82] This pair dissociates on a picosecond time scale.[80,82] Although the reaction of hydrated electrons with halogen atoms in the solvent bulk is diffusion-controlled, the recombination of the geminate electron−atom pairs is relatively slow since the electron remains on the 4s/d potential surface isolated from the ground-state 4p surface by a large energy gap.[81,82] There are certain parallels between this reaction and hole injection in cycloalkanes: The injected charge rapidly localizes close to the geminate partner, the recombination in the geminate pairs seems to be much slower than in the solvent bulk, this recombination is highly exothermic, and the final state of the injected charge is a metastable polaron. An important insight from the calculations of Borgis and Staib[82] is that some of the initial electron traps are formed due to solvation of the ground-state halide anion; that is, the local concentration of suitable traps is higher than in the solvent bulk. *The "preexisting hole traps" could be solvent molecules disturbed by the presence of radical cations.*

The concept of "preexisting hole traps" can be applied to other classes of electron-transfer reactions with the solvent. Inorganic photochemists have long postulated that bonding between the metal ion complex and the polar solvent reduces the barrier of the charge-transfer-to-metal reactions.[15−20] According to EPR spectroscopy, ca. 70−80% of olyl radicals formed upon UV photooxidation of alcohol glasses by Cu^{II} and Fe^{III} complexes are bound to these complexes.[18,20] However, not all of these olyl radicals are in the outer coordination sphere, even at very low temperatures. As was shown by spin-echo EPR,[20] ca. 20% of the olyl radicals are separated from the reduced metal ion by more than 1.7 nm, and some radicals are found at distances in excess of 2 nm. Thus, at least some of the electron transfers involve the hole traps in the solvent bulk.

The participation of "preexisting *electron* traps" in ionization of polar liquids is widely acknowledged (e.g., ref 55 and references there in). However, such a possibility for the vb holes has never been considered. This omission is difficult to justify. In disordered solids, the existence of the band-tail hole states and their involvement in photoionization are well-established.[83] Furthermore, the Urbach tail in the UV spectra of neat polar liquids is from the tail states of *both* bands. For water, the estimates of the extension of the cb into the midgap[84,85] suggest that the cb tail states alone cannot account for the observed 5.9 eV onset of the one-photon absorbance.[86] It has been suggested that the low-energy transition (which is observed in both vapor and liquid) involves molecules with stretched OH bonds.[49,87] *Such molecules are hole traps that occupy the tail of the valence band.*

The hole states that are closest to the mobility edge (a demarcation energy that separates the extended and localized states) can be observed by UV photoemission spectroscopy (UPS).[83] In disordered solids, the density-of-state (DOS) function of the localized states is linear with energy near the vb mobility edge and decreases exponentially toward the midgap. This extended tail is difficult to resolve by UPS since the DOS falls by 1−2 orders of magnitude before it becomes exponential.[83] For liquids, the sensitivity of UPS is yet insufficient to resolve this tail, but the data allow one to estimate the width of the slowly decreasing section of the DOS function. Using a Gaussian fit, Faubel et al.[59] determined the following half-widths: 1.58 eV for water, 1.5 eV for methanol, and ca. 1 eV for ethanol and 1-propanol. Thus, the vb extends for more than 0.5 eV beyond the photoemission threshold; this is comparable to the extension of the cb band as estimated by Rossky and co-workers.[84]

The distance between a hole trap and the radical cation needs to be determined. In liquid the hole traps are short-lived, but in frozen glasses they could be stable. Skvortsov and Alfimov have studied the concentration dependence of quantum yield for 700 nm bleaching of diphenylamine$^{\bullet+}$ in solid mixtures of isooctane and toluene.[10] Due to the low IP of diphenylamine ($IP_g = 7.16$ eV), its radical cation cannot be bleached with 1.77 eV photons in isooctane ($IP_g = 9.9$ eV), and the decay was due to hole transfer to toluene (IP = 8.82 eV). Considering this transfer as a static scavenging reaction, a reaction radius of 0.52 nm was obtained.[10] This radius is obviously too short to account for the long-term stability of toluene holes close to diphenylamine. Given the tendency of aromatic solutes to aggregate in frozen solutions, the injected hole probably binds to more than one toluene molecule, hopping away from the solute, and this makes their result questionable. A better approach would be to study the geminate recombination of the $\{ArH\ RH^{\bullet+}\}$ pairs using ultrafast laser spectroscopy, a project that is currently in the progress in our laboratory.

6. Conclusion

Hole injection (oxidation of the solvent), with or without dissociation of the solvent hole, seems to be the general mechanism for decay of photoexcited radical cations, in both polar and nonpolar media, solid or liquid. The efficiency of this process correlates with the difference in the IP_g of the solvent and the solute corrected by the photon energy. For some high-IP liquids (e.g., acetonitrile) hole injection does not occur, but it readily occurs in common solvents, such as alcohols, alkanes, and ethers. For high-IP solutes, such as naphthalene, the quantum yield of photobleaching can be as high as 0.5. This quantum yield rapidly decreases with decreasing IP of the solute.

For basic solutes, such as aromatic amines, we cannot exclude the occurrence of the H atom transfer reaction 5 instead of reaction 4 or, in some cases, even the proton-transfer reaction 6. However, the majority of aromatic radical cations (whose basicity is lower than that of the polar solvent) photobleach via reaction 4. We argue that this reaction requires the existence of preformed "hole traps" some distance away from the excited radical cation. The existence of similar electron traps in the lower conduction band of water and other polar solvents has long been discussed by radiation chemists.

Our work is the first glimpse of an uncharted field—chemistry of excited polycyclic aromatic radical cations. Most of our conclusions are qualitative and may need further refinement. Two of these conclusions, however, are quite certain. First, there is common pattern in all these photoreactions. Hole injection provides the most reasonable mechanism which, in several instances, was verified directly. Second, the lifetime and reactivity of excited aromatic radical cations was found to vary strongly from species to species. While their reactivity follows the IP of the parent molecule, the lifetime in acetonitrile fits no obvious pattern. While some of the excited radical cations of aromatic hydrocarbons have the lifetimes below 1 ps, other (excited triphenylene$^{\bullet+}$ and perylene$^{\bullet+}$) are fairly long-lived, with the lifetime of several picoseconds or even several tens of picoseconds. The reason for this dichotomy is not yet clear.

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Appendix

In polar solvents with relatively low IP, photoexcitation of solute radical cations causes their permanent bleaching. The quantum yield ϕ of this bleaching can be determined by analysis of the photon flux dependence of the bleaching efficiency. Given that the lifetime of $[ArH^{\bullet+}]^*$ is much less than the length of the excitation pulse and practically no attenuation of the 532 nm light occurs on the passage through the reactive mixture (the corresponding optical density is less than 10^{-3}), the conversion of the ground-state radical cation upon single-photon excitation is given by

$$d[ArH^{\bullet+}]/dt = -w(t)[ArH^{\bullet+}] \qquad (A1)$$

where $w(t) = 2.3\epsilon_{532}\ \phi W_p(t)$ is the rate constant of photoconversion, $W_p(t)$ is the laser power in photons/(cm^2 s), ϵ_{532} is the extinction coefficient of $ArH^{\bullet+}$ at 532 nm, and ϕ is the quantum yield of photobleaching. Integrating over the duration of the laser pulse, one obtains that the bleaching efficiency

$$Y = 1 - \exp(-\beta J_p) \tag{A2}$$

where $\beta = 10^{-2}\epsilon_{532}\,\phi$; the extinction coefficient is in $M^{-1}\ cm^{-1}$, and J_p is the photon flux in J/cm^2. The important implication of eq. A2 is that the bleaching efficiency Y is independent of $[ArH^{\bullet+}]_0$. We found that varying $[ArH^{\bullet+}]_0$ by changing the flux of the 248 nm photons has no effect on the bleaching efficiency. The fact that Y is independent of the concentration gradients of $ArH^{\bullet+}$ is also important, since the optical density of solution at 248 nm is 0.01−0.1, and such gradients certainly exist. Assuming that the 248 nm beam has uniform cross section and the analyzing light probes all of the radical cations in the solution, the experimentally determined bleaching efficiency Y_{exp} (averaged over the rectangular aperture for the 5 and 2.3 eV beams) is given by

$$Y_{exp} = Y_{max}\{1 - \langle \exp(-\beta J_p)\rangle\} \approx Y_{max}\beta\langle J_p\rangle \tag{A3}$$

where $\langle J_p\rangle$ is the average photon flux through the aperture, and Y_{max} is the maximum bleaching efficiency (which can be less than unity due to the presence of other light-absorbing species). For a Gaussian beam from the Nd:YAG laser, the photon flux is given by

$$J_p(x,y) = I_p/\pi\sigma^2 \exp(-[x^2 + y^2]/\sigma^2) \tag{A4}$$

(Note that β changes with I_p due to thermal lensing in the laser rods, as discussed in the Experimental Section.) For a beam centered at the middle of a rectangular aperture $a \times b$,

$$\langle \exp(-\beta J_p)\rangle = \int_{-a/2}^{+a/2} dx \int_{-b/2}^{+b/2} dy \times \exp\{-\beta I_p/\pi\sigma^2 \exp(-[x^2 + y^2]/\sigma^2)\} \tag{A5}$$

This average was found by numerical integration. By fitting the experimental dependences of Y_{exp} vs laser power I_p with eqs A3 and A5 it is possible to determine β and the product $\epsilon_{532}\phi$. A less valid approach is to use $\langle J_p\rangle$ instead of J_p in eq A2. With the latter approach, β is underestimated by 20−30%. For radical cations with low absorbance at 532 nm or low quantum yield ϕ, β may be quite small, and we focused the 532 nm beam to obtain an average flux of 0.5−3 J/cm^2. Since for such a beam using accurate formulas is difficult, we used eq A2 with $\langle J_p\rangle$. The latter was determined experimentally. The high-fluence Y_{exp} was determined for all of the systems that showed incomplete bleaching at 0.5 J/cm^2; Y_{max} was determined by fitting these dependences with eq A3.

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