2120 *J. Phys. Chem. A* **1997,** *101,* 2120−2123

Electron Transfer from Cyclohexane to Photoexcited Aromatic Ions. Generation and Kinetics of High-Mobility Solvent Holes[†]

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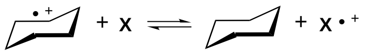
Received: August 14, 1996; In Final Form: November 25, 1996[⊗]

In cyclohexane solutions, aromatic radical cations are produced by two-photon (248 nm) photoionization of aromatic molecules. A novel excited state chemistry is observed; i.e., excitation of these radical cations with a 532 nm laser pulse, delayed by several microseconds, produces the high mobility cation of cyclohexane. The difference of the signals with and without the 532 nm pulse shows the decay of the cyclohexane radical cation free of complications from geminate ion recombination. The biexponential nature of this decay suggests an equilibrium involving the high mobility cation, such as was proposed to explain previous experimental results.

Introduction

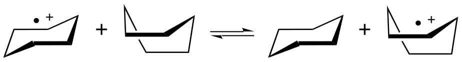
In a previous publication,[1] we reported that in 4 eV (308 nm) and 5 eV (248 nm) laser photolysis of $10^{-5}-10^{-6}$ mol dm^{-3} anthracene in cyclohexane the light flux dependence of the dc conductivity signal from solvent radical cation indicated that its production is a three-photon process. The first two photons, absorbed by the ground state of anthracene and the first excited singlet state, sequentially, result in ionization of anthracene. The third photon was proposed to be absorbed by the anthracene radical cation, resulting in production of cyclohexane$^{\bullet+}$ by electron transfer from the solvent to the aromatic ion. Due to extremely rapid hopping of the charge between the neighboring cyclohexane molecules, the solvent radical cation (also referred to as a high mobility ion, HMI) exhibits a mobility that is ca. 50 times greater than the mobility of other molecular ions in this liquid.[2−6] In high purity cyclohexane, the lifetime of the HMI is ∼500 ns and its mobility is $(1.6-1.8) \times 10^{-2}$ cm^2/(V s).[2] Thus, for cyclohexane, dc conductivity provides a sensitive method of detecting solvent radical cations in a solution that contains many other ions and excited molecules.[3]

In the present work, a second laser pulse was used to excite the aromatic ion with 2.3 eV (532 nm) photons several microseconds after the first 248 nm pulse, thereby producing the HMI. By determining the difference of the conductivity kinetics observed with and without the 532 nm pulse, it is possible to study the decay of the HMI in much detail. In previous experiments that did not use this “delayed pulse” technique, i.e., using just the excimer laser pulse, this decay is more difficult to study, even in the neat solvent, because the decay of HMI by geminate recombination and by homogeneous neutralization must be taken into account, and in addition, part of the conductivity is due to ions formed by the laser pulse that are secondary ions that do not have high mobility.[2] Still, multiparameter fitting was used to unravel this complex kinetics. These earlier computer fitting results showed that for decalins the decay kinetics of free HMI was pseudo-first-order, but for cyclohexane bimodal decay kinetics was required.[2] An explanation was proposed which involved an equilibrium between conformers of the cyclohexane radical cation. However, results obtained with the delayed 532 nm pulse indicate that the detailed nature of the observed biexponential decay is affected by the purity of the cyclohexane. Briefly, we observed that the decay of the signal induced by the 532 nm pulse depended on the time elapsed after the purification of the solvent. Most of the results were obtained with solvent for which more than a few days had elapsed. Freshly purified solvent was observed to result in slower decay of the conductivity. Analysis of these results indicates that an equilibrium is still required to explain the bimodal decay, but the equilibrium is required to involve an impurity, **X**, which acts as a shallow trap as shown in reaction (1). Because the effect of this impurity increases with time after purification, it is likely to be a result of a slow oxidation process. Attempts to identify it have so far been unsuccessful.



(1)

The high mobility is due to rapid resonant charge transfer between the chair form radical cation and the chair form neutral molecule (which accounts for all but ≈10 ppm of the cyclohexane[9]). We cannot be certain that our previous suggestion that reaction 2 contributes to the bimodal decay is invalid, because if it occurs, its contribution would not be determinable unless we knew, and were able to vary, the concentration of impurity, **X**. In the purest samples, the combined concentrations of **X** and the twist/boat form of cyclohexane must be about 40 μM to explain the observed signal decay.



(2)

Before equilibrium is established, in several tens of nanoseconds, fast scavenging of HMI is observed. After the equilibrium is established, the effective scavenging constant falls by 2−3 times.[2,4] In this article we demonstrate how this complex scavenging kinetics can be investigated using two-color laser photoconductivity.

Experimental Section

The aromatic solutes were the highest purity available from Aldrich and were used as received. The cyclohexane (Baxter)

[†] Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, US-DOE, under Contract W-31-109-ENG-38.

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[⊗] Abstract published in *Advance ACS Abstracts,* February 15, 1997.

S1089-5639(96)02471-1 CCC: $14.00

was passed 4−5 times through a 1 m column of activated silica gel. The purity was checked by the UV absorption and the lifetime of HMI. Pulses of 248 nm photons (5 eV) from a Lambda Physik LPX 120i laser (≈20 ns fwhm, ≈30 mJ/pulse) were used to produce the HMI in CO_2-saturated solutions. CO_2 serves as an electron scavenger. The solutions were irradiated in a cylindrical 15 mL Suprasil cell with a 4 cm optical path. The cell has two rectangular 4 × 1.2 cm platinum electrodes separated by 0.65 cm, to which a dc voltage of 5 kV was applied. The signal due to the displacement current was amplified 100 times and acquired on a DSA-601 digitizing signal averager. Except for the use of a different excimer laser, the techniques related to the 248 nm excitation are the same as we have recently described.[2]

The 248 nm pulse entered the cell from one end; the optical system and apertures resulted in about 17 mJ per pulse over a 2 × 5 mm area throughout the length of the cell. A 3 ns fwhm, ≈60 mJ pulse of 532 nm light from a Continuum Model 8010 Nd:YAG laser entered the cell from the opposite end; the 532 nm beam is circular with a diameter of ∼5 mm. The zone irradiated by both lasers was exposed to ∼0.17 J cm^{-2} of 248 nm light and ∼0.3 J cm^{-2} of 532 nm light. Both lasers were run at 2 Hz; the jitter between the positions in time of the two pulses was ca. ±3 ns. This jitter determines the time resolution of the kinetics presented here. For data collection, the DSA-601 was triggered either by a portion of the light from the 248 nm pulse (to observe the signal induced by it and the delayed signal induced by the 532 nm pulse) or by the 532 nm light (to observe the signal induced by the 532 nm pulse). In the former case, the signal could be observed with just the 248 nm pulse or with both pulses. 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. Each difference signal presented here was obtained by averaging the results from three samples; each sample received 16−248 nm pulses and 8−532 nm pulses, the 532 nm pulses occurring at a predetermined delay after every second 248 nm pulse.

Results and Discussion

Photophysics. CO_2-saturated cyclohexane containing aromatic solutes whose radical cations have significant absorption at 532 nm,[7] such as triphenylene (Tp), biphenyl, fluoranthene, and anthracene, were pulsed with 248 nm light. The 532 nm pulse was introduced several microseconds later. At these delay times, most HMI generated by the first pulse from the excimer laser have been scavenged by the aromatic solute and impurity.[2] The geminate decay due to charge recombination with anions is also essentially completed.[2,5] The photoexcitation with the 2.3 eV light promotes the transfer of the valence band electron from the solvent to the aromatic ion; the photophysics and energetics of this process will be a subject of a future publication. We believe that, following the transfer, a short-lived highly mobile “intrinsic” hole with excess energy of at least a few tenths of an electronvolt is formed. From the magnitude of the signals observed, we estimate that less than 10% of the aromatic radical cations are converted to HMI at the highest 532 nm intensity used. For most solutes used, a single 2.3 eV photon can produce a hole with 0.5−1 eV excess energy. However, for perylene one photon should not be sufficient to ionize cyclohexane. The signal from all solutes is linear with and proportional to the light flux between 0.02 and 0.2 J cm^{-2}, within experimental error. Simulations have been made which show that if the production of HMI is a single-photon process, a quantum yield of just a few percent is required.

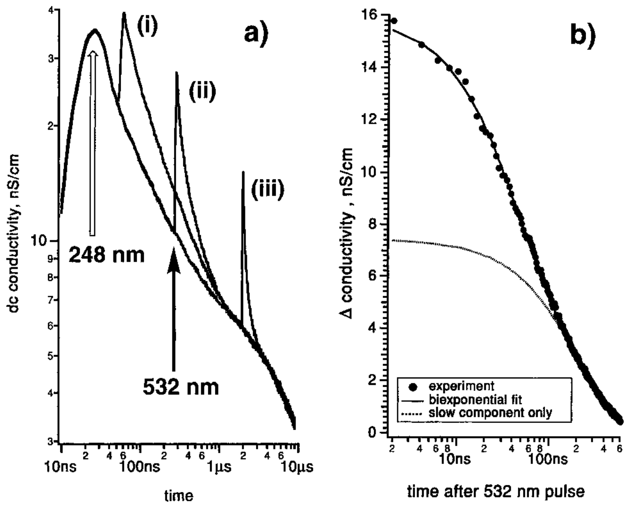


Figure 1. (a) Change in the conductivity induced by the 532 nm laser pulse (40 mJ) from a Nd:YAG laser in two-color photolysis of 8 × 10^{-6} mol dm^{-3} triphenylene in CO_2-saturated cyclohexane. A 20 ns pulse (248 nm, 30 mJ) occurred at time shown by a broad arrow; the 532 nm pulse was applied after (i) 30 ns, (ii) 270 ns (shown by an arrow), and (iii) 2 μs. The change in the conductivity is due to formation of HMI by photoexcitation of the triphenylene radical cation. (b) Trace iii from (a); the conductivity induced by the 248 nm pulse is subtracted. The difference trace (the decay kinetics of HMI) is fit by a sum of two exponentials. The slow component with a lifetime of 260 ns is given by the broken line; the fast component has a lifetime of 30 ns.

However, a two-photon process can also fit the observations if the lifetime of an intermediate state ($Ar_2^{\bullet+*}$) of the aromatic, produced by the first 532 nm photon , is about 4 ns, and if the quantum yield for producing HMI when this state absorbs the second 532 nm photon is about 0.01. This ambiguity arises mainly because of the high flux of 2.3 eV light relative to the concentration of the aromatic radical cation.

The HMI (solvent hole) produced by the 532 nm light by charge transfer from the excited aromatic radical cation migrates 2−3 nm away from the transfer site before thermalization. Upon thermalization (which occurs in 1−2 ps), the charge on the hole will sometimes return to the aromatic molecule formed in the transfer; this process results in the regeneration of the ions of the aromatic molecule. This geminate reaction is over in <1 ns.[8] Those HMI that escape this geminate recombination can eventually react homogeneously with aromatic solute and impurity (∼10^{-5} mol dm^{-3}). The concentration of free ions in our laser experiment (at the time of 532 nm laser pulse) is on the order of 10^{-8} mol dm^{-3}, and the second-order neutralization of HMI can be neglected.[2] In addition to the occurrence of “hole injection” in cyclohexane, we have observed, using the techniques described above, the same process in two other liquids, decalin and isooctane.

Decay Kinetics. Figure 1a shows typical kinetics obtained in the two-color experiment. The 532 nm light is absorbed by an aromatic ion created by the 248 nm pulse yielding a conductivity signal from HMI, which then “converges” to the conductivity from ions of the original mobility. The conductivity signal induced by the 532 nm laser pulse is a large fraction of the signal induced by the 248 nm pulse. The amplitude of the 532 nm signal correlates qualitatively with the absorbance expected for the aromatic radical cations that were produced from the aromatics listed earlier; this signal is linear with the photon flux. The 532 nm pulse alone was determined to produce no conductivity signal in any of the systems studied. The possibility exists that the 532 nm pulse could ionize a neutral product from the 248 nm pulse, for example, an aromatic singlet or triplet state. The occurrence of this can be ruled out

TABLE 1: Rate Constants for Reaction of the Cyclohexane Radical Cation with Various Reactants at 296 K[a]

reactant, S	$k_{HM,S} \times 10^{11}$, $mol^{-1}\,dm^3\,s^{-1}$	reactant, S	$k_{HM,S} \times 10^{11}$, $mol^{-1}\,dm^3\,s^{-1}$
triphenylene[b]	4.2	decalin[c]	3.8
anthracene[b]	3.6	cyclohexene	2.3
biphenyl[b]	4.2	2-propanol	1.4
fluoranthene[b]	3.1	cyclohexene oxide	3.1
perylene[b]	3.3	triethylamine	1.8
benzene	3.0		

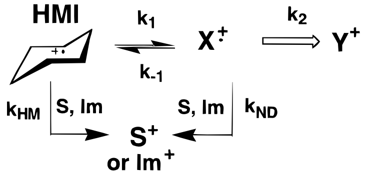
[a] Obtained by multitrace fitting of the scavenging kinetics using eq 7 with $k_{ND} = 1.5 \times 10^{10}$ mol^{-1} dm^3 s^{-1}. The estimated accuracy of these values is ≈±10%. The 532 nm pulse was delayed by 2−5 μs relative to the 248 nm pulse. [b] Was used both as a scavenger and a photosensitizer. [c] 67% cis, 33% trans.

because the decay of the difference signal does not exhibit the expected geminate decay (of $CO_2^{\bullet-}$ with the cation that would have to be produced) followed by second-order ion recombination; also, the 532 nm pulse produced no "permanent" change in conductivity, i.e., no net change in the free ion concentration resulted. Furthermore, the fact that the difference signal does not decrease appreciably when the delay between the pulses is changed from 10 ns to several microseconds rules out ionization of an aromatic singlet state. Involvement of aromatic triplet states was ruled out by experiments where the triplet quencher, O_2, was used instead of CO_2, and the difference signal for a 2−15 μs delay was not eliminated.

Figure 1b shows the difference trace obtained as described in the Experimental Section. The 532 nm pulse was applied 2 μs after the 248 nm pulse. Because the additional conductivity induced by the 532 nm photons is entirely due to the HMI (and is proportional to its concentration), the trace in Figure 1b represents the decay kinetics of HMI. This decay is not monoexponential, that is, the decay kinetics of HMI in cyclohexane is not, as was believed in the past,[5,6] pseudo-first-order. We found that the kinetics can be fit by a sum of two exponential functions, at any concentration of the aromatic sensitizer and added scavenger. For the data shown in Figure 1b for cyclohexane solution with 8×10^{-6} mol dm^{-3} of triphenylene, the fast component has a lifetime of ca. 30 ns (corresponding to reactions depleting HMI during the approach to equilibrium), and the slow component has the lifetime of 260 ns (corresponding to the disappearance of HMI after equilibrium is established). The latter lifetime is somewhat shorter than the lifetime of HMI in neat cyclohexane. This is expected, since the aromatic solutes are known to react with HMI in cyclohexane (our measurements give the scavenging constants ca. 4×10^{11} mol^{-1} dm^3 s^{-1} for low-IP aromatic solutes, Table 1). The fast component has a lifetime that is close to the lifetime, determined by transient absorption spectrophotometry, for charge transfer from HMI to aromatic solute molecules.[4] As is emphasized above, the fast component cannot result from the geminate reaction of HMI with the parent aromatic molecule, as this reaction is complete in 1 ns.[8] In refs 2 and 4, we argued that the lifetime of the fast component is close to the relaxation time of the equilibrium.

Biexponential scavenging kinetics of HMI in cyclohexane can be understood quantitatively in terms of an equilibrium model similar to that suggested in refs 2−4. Bearing in mind that the concentrations of free ions in our experiments are ∼10^{-8} mol dm^{-3}, it may be seen that reaction 1 cannot change the concentration of **X** (or of the twist/boat cyclohexane molecule, if reaction 2 is involved) to an appreciable extent, because the concentration of **X** must be more than 2 orders of magnitude higher to give the observed decay kinetics. Therefore, equilibrium (1) can be reduced to that between the chair form (HMI) of the solvent radical cation and $\mathbf{X}^{\bullet+}$, a normally diffusing ion (Scheme 1). The evolution of their concentrations is given by

SCHEME 1: Scavenging Kinetics of Solvent Radical Cations in Cyclohexane



$$d[\mathrm{HMI}]/dt = -(k_1 + k_3)[\mathrm{HMI}] + k_{-1}[\mathbf{X}^{\bullet+}] \tag{3}$$

$$d[\mathbf{X}^{\bullet+}]/dt = k_1[\mathrm{HMI}] - (k_{-1} + k_4)[\mathbf{X}^{\bullet+}] \tag{4}$$

$$k_3 = k_{\mathrm{HM,S}}[\mathrm{S}] + k_{\mathrm{HM,Tp}}[\mathrm{Tp}] + k_5 \tag{5}$$

$$k_4 = k_2 + k_{\mathrm{ND}}([\mathrm{S}] + [\mathrm{Im}] + [\mathrm{Tp}]) \tag{6}$$

$$k_5 = k_{\mathrm{HM,Im}}[\mathrm{Im}] \tag{7}$$

where the three k_{HM}'s and k_{ND} are scavenging rate constants for high mobility and normally diffusing forms, respectively, with added scavenger, [S], any impurity, [Im] (which is a permanent trap for HMI, in contrast to **X**), and aromatic photosensitizer, [Tp]; k_2 is the rate of transformation of $\mathbf{X}^{\bullet+}$ to a normally diffusing ion that can no longer transfer charge to cyclohexane. For k_{ND} we assumed 1.5×10^{10} mol^{-1} dm^3 s^{-1}, typical for a diffusion-controlled scavenging reaction in cyclohexane.[2−6] Let us introduce $\tau = (k_1 + k_{-1})^{-1}$, the time constant of the equilibrium, and $K = k_1/k_{-1}$, the "equilibrium constant". Note that k_1 is actually $k_{HM,X}[\mathbf{X}]$, and therefore K and τ depend on [**X**] as we have observed in experiments where better purification, which reduces [**X**], causes the decay of the conductivity to be slower and thereby alters the values of K and τ. The solution of eqs 3 and 4 gives

$$[\mathrm{HMI}]/[\mathrm{HMI}]_{t=0} = \mathrm{const}\,\exp(-k_s t) + (1 - \mathrm{const})\,\exp(-k_f t) \tag{8}$$

where $k_{f,s} = (\tau^{-1} + k_3 + k_4 \pm r)/2$ are the rate constants of the fast and slow components, respectively, const $= (k_{-1} + k_4 - k_s)/r$, and

$$r = \{(\tau^{-1} + k_3 + k_4)^2 - 4(k_{-1}k_3 + k_1k_4 + k_3k_4)\}^{1/2} \tag{9}$$

Analysis of eq 7 shows that a family of decay curves for different scavenger concentrations [S] (see Figure 2) cannot be fit in a single way. While the scavenging constants $k_{HM,S}$ and $k_{HM,Tp}$ can be found unambiguously, the values of K and τ depend on [**X**], [Im], and the value of k_2. The scavenging of HMI by impurity Im shifts the equilibrium to the left side, while the transformation of $\mathbf{X}^{\bullet+}$ by k_2 shifts it to the right side. To compensate for these shifts, the equilibrium constant must be changed accordingly. Lower values of K result if $k_2 = 0$; higher values result if [Im] = 0. Because of the involvement of the impurity **X**, the significance of the experimental values of K and τ is diminished, and we give only values determined from results on scavenging of the HMI as a function of [triphenylene] to show the trends. Fixing $k_2 = 0$, the results of the fitting gave $K \sim 0.2$ and $\tau \sim 100$ ns for the higher purity solvent and $K \sim 0.4$ and $\tau \sim 50$ ns for the less pure solvent (smaller [**X**]). Fixing [Im] = 0, the results of the fitting gave $K \sim 1$ and $\tau \sim 120$ ns for the higher purity solvent and $K \sim 0.8$ and $\tau \sim 50$ ns for the lower purity.

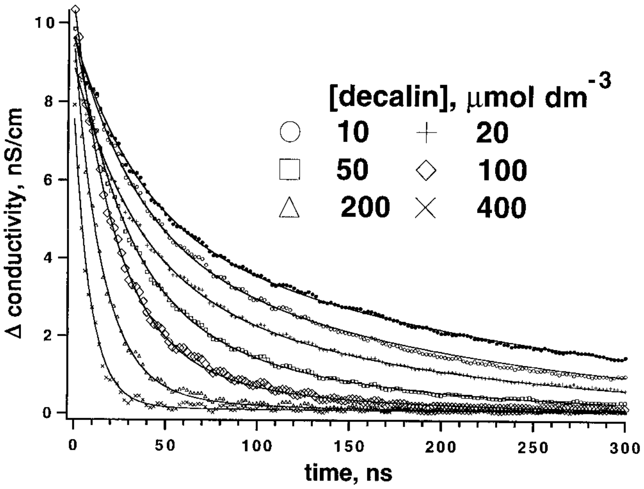


Figure 2. Multitrace fitting of the scavenging kinetics using eq 7, for a family of difference traces obtained by 532 nm photolysis of 8×10^{-6} mol dm^{-3} triphenylene with variable amounts of decalin, a good scavenger of HMI, in cyclohexane. The 532 nm pulse was applied 2 μs after the 248 nm pulse. The decay curve obtained for a solution without decalin is given by the filled circles (the top trace). The bimodality of the scavenging kinetics is well distinguished: in the first 50 ns the scavenging rates are notably higher than at the later times.

Table 1 summarizes the results of least-squares fits using eq 7 on multitrace data sets such as those shown in Figure 2, for several scavengers. The rate constants of scavenging of HMI by the photosensitizers and scavengers were determined by varying their concentrations. Importantly, the values of K and τ obtained from the least-squares fitting were independent of the scavenger, despite the 3-fold spread in scavenging rate constants (see Table 1). We believe that the values of $k_{HM,S}$ given in Table 1 are, so far, the most accurate HMI reaction rate constants obtained.

Conclusion

This work provides definitive evidence for the occurrence of “hole injection”, the transfer of the valence band electron from the solvent to a photoexcited solute ion, and is an interesting example of new chemistry of highly excited radical cations of aromatic molecules. The quantum yield of the process is only a few percent or less; if this low yield is due to a high probability of recombination, rather than to an inefficiency in the electron transfer, one can be estimate that the mean separation between the solvent hole and the aromatic molecule need be only somewhat less than a nanometer. Presumably, this separation could result from movement of the hole while it still has some excess energy. On the other hand, if the inefficiency is entirely due to the electron transfer, the separation would have to be several nanometers.

The biexponential decay of the conductivity signal from the high mobility cyclohexane cation is shown to be consistent with the existence of an equilibrium between this cation and an ion of a shallow hole trap (impurity ion or a conformer ion). Establishment of this equilibrium is responsible for a fast component in the decay of the high mobility ion, as we proposed on the basis of observations on the pulse radiolysis of cyclohexane solutions.[4]

Acknowledgment. We acknowledge stimulating discussions with Drs. J. M. Warman, M. P. de Haas, and W. F. Schmidt.

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(8) In the asymptotic limit ($t > \tau_D$) the decay kinetics of HMI in the geminate pairs with aromatic molecules is given by $P(t) = P_\infty\{1 + (\tau_D/\pi t)^{1/2}\}$, where P_∞ is the escape probability, $\tau_D = R^2/D \sim 30$ ps, R is the scavenging radius ($\approx$0.9 nm), [2] D is the diffusion coefficient of HMI ($\sim 3 \times 10^{-4}$ cm^2/s).[11] If the space distribution of HMI around the aromatic solute immediately after thermalization of the hole is Gaussian, $p(r) \propto r^2 \exp(-[r/b]^2)$, the escape probability can be estimated as $P_\infty = \mathrm{erfc}\,(R/b)$. For $b \sim 2-3$ nm, $P_\infty \sim 0.5-0.65$; a value of P_∞ only $\approx$0.1 or greater is needed to explain the observed yield of HMI.

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