# High-Mobility Ions in Cyclohexane. A Transient Absorption Study<sup>†</sup>

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*Received: November 6, 1995; In Final Form: February 6, 1996*<sup>®</sup>

Transient absorption kinetics in radiolysis of N<sub>2</sub>O-saturated cyclohexane has been studied (0.1-100 ns; 300-800 nm). The spectra indicate the involvement of at least three cations (ions I, II, and III), only one of them having abnormally high mobility. Ion II is probably the cyclohexene radical cation, and ion III might be the dimer olefin ion. These two ions absorb as much as ion I at 450-500 nm. While ion II and ion III are scavenged by ethanol and triethylamine with a rate constant of  $\approx 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ , the scavenging of ion I proceeds with rate constants of  $\approx 9 \times 10^{10}$  and  $2.3 \times 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ , respectively. The spectrum of ion I is similar to the spectrum of the radical cation of cyclohexane isolated in low-temperature matrices. We were not able to observe the absorption from ion I at delay times longer than 50 ns. A corresponding fast growth of the absorption from solute radical cations of pyrene and perylene was observed. The data (simulated using continuum-diffusion and Monte Carlo approaches) indicate that the scavenging constant is  $\approx 4 \times 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ; the lifetime of the precursor of the aromatic radical cations is  $\approx 30 \text{ ns}$ . This short lifetime cannot be explained by a reaction with radiolytic products or by homogeneous recombination, and it seems to be incompatible with identification of the long-lived high-mobility ions observed in conductivity experiments as the radical cation of cyclohexane. A mechanism in which the mobile radical cation is in equilibrium with a normally-diffusing ion is examined in an attempt to resolve this conundrum.

# Introduction

On ionization, four cycloalkanes, cyclohexane, methylcyclohexane, *cis*-decalin, and *trans*-decalin, yield cations (high-mobility ions, HMI) whose mobility is 5–25 times greater than that of the normally-diffusing ions.<sup>1-6</sup> The mobility of HMI is independent of temperature over the entire liquid range of these four cycloalkanes; no HMI were found in crystalline or vitreous solids.<sup>3</sup> These ions are long-lived and can be detected using time-resolved conductivity techniques.<sup>2,3,6</sup> In pure cyclohexane the conductivity signal from HMI decays with a first-order rate constant (1.5–3) × 10<sup>6</sup> s<sup>-1,2,6</sup> Ion–molecule reactions of HMI are also very fast.<sup>1-6</sup> Scavenging rate constants  $\approx$ (2–3) × 10<sup>11</sup> mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup> have been reported for cyclohexane;<sup>3,6</sup> this is 20 times faster than a typical diffusion-controlled reaction, (1–1.5) × 10<sup>10</sup> mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>.<sup>1,4–6</sup>

Following the discovery of HMI,<sup>1</sup> it was proposed that these ions are the alkane radical cations (holes) involved in rapid resonant charge transfer.<sup>1,3</sup> Assuming that the transfer occurs between the neighboring molecules, it has been estimated that the residence time of the charge on an alkane molecule is  $\approx 1$ ps.<sup>3</sup> This short time scale suggests that no nuclear motions occur during the charge transfer. Therefore, such a rapid transfer may occur only when the geometries of radical cations and the parent molecules are close.<sup>3</sup> In most alkanes, the transfer is less efficient and the resulting migration is slower than diffusion. Recently, we have found HMI in squalane,  $C_{30}H_{62}$ , a viscous branched alkane.<sup>7</sup> These HMI were identified as the squalane radical cations. Due to their short lifetime (15-25 ns), the species were not observable by dc conductivity.<sup>7</sup> The residence time of the squalane holes is relatively long, 100-200 ps, but, due to the high viscosity of the liquid ( $\approx 20$  cP), the migration

of the holes is still 7 times faster than diffusion. Thus, in squalane the mobile ions *are* rapidly hopping alkane holes.

Over the years, this simple view has been challenged and the opinions as to the nature of the HMI in cycloalkanes diverged considerably. Warman, who pioneered the conductivity study on HMI, developed a concept of delocalized holes.<sup>3</sup> Some of us have argued that low chemical stability of alkane radical cations at room temperature seems to contradict the observed longevity of HMI.8 It was proposed that HMI are some secondary ions derived in the ionization event.8 Some support to this idea came from fluorescence studies which failed to indicate that the mobile holes are involved in the generation of delayed fluorescence from a scintillator.<sup>9</sup> The mobile holes were not observed with magnetic resonance techniques, such as fluorescence detected magnetic resonance (FDMR).<sup>10</sup> Even when the fast charge hopping was eliminated by dilution with high ionization potential (IP) alkanes, the radical cations of cyclohexane and trans-decalin were not observed.11 These observations indicated a short lifetime of the radical cation.

Other concerns arose from the picosecond pulse radiolysis experiments by Jonah and Le Motais.<sup>12</sup> No ultrafast scavenging of transient absorption from cyclohexane ion was found. These observations contradict the results of Menhert et al.<sup>5</sup> who observed such a behavior for several scavengers and of Hummel et al. and others<sup>1,4</sup> who observed fast generation of solute radical cations on scavenging. Interestingly, the earlier optical studies which lend support to the idea that HMI are the radical cation holes of cyclohexane gave no indication that the precursors of the solute radical cations were *long-lived*.<sup>4a</sup> Hummel *et al.* concluded that the lifetime of these precursors is  $\approx$ 50 ns.<sup>4a</sup> The lifetime of the conductivity signal from HMI is  $\sim 10$  times longer.<sup>3,6</sup> Warman *et al.* suggested that these discrepancies are due to the reactions of HMI with products and showed that the lifetime of HMI is decreased on continuous radiolysis of the solution.<sup>13</sup> As will be shown below, this is only a partial explanation.

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<sup>&</sup>lt;sup>†</sup> Work performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Science, US-DOE under Contract No. W-31-109-ENG-38.

<sup>&</sup>lt;sup>®</sup> Abstract published in Advance ACS Abstracts, April 1, 1996.

Two candidates for HMI in cyclohexane other than  $c-C_6H_{12}^{\bullet+}$  have been suggested: the proton adduct  $(c-C_6H_{13}^+)$  and the carbonium ion  $(c-C_6H_{11}^+)$ .<sup>8</sup> Proton and hydride transfers were suggested for the migration mechanism.<sup>8</sup> If the HMI *are not* the solvent holes, then one needs to explain how a transfer of H<sup>±</sup> (which involves a considerable rearrangement of the nuclei) can occur on the time scale of 1 ps and be a nonactivated process.

One must also explain the fast formation of solute *radical* cations. It appears necessary to assume that there are two mobile ions: a short-lived one and a long-lived one. The short-lived ion is the alkane hole whose scavenging leads to the fast formation of the solute radical cations. The long-lived mobile ions (observed by conductivity) form no radical cations on scavenging.

The progress in the research on HMI in cyclohexane was stalled by the absence of reliable data on transient absorption. The use of 30 ps electron pulses from Argonne linac, fast detection, and extensive averaging allowed us to obtain kinetics much superior in quality to previous results. We have also carried out a new study on photoinduced and radiation-induced dc conductivity in cyclohexane (these results are discussed in the second paper of this series<sup>14</sup>). It was found that the scavenging constants reported by Warman et al.<sup>2,3</sup> and Schmidt and Sauer <sup>6a</sup> for the long-lived HMI were overestimated by 2-3 times. With the correct values, it is impossible to explain either the transient absorption kinetics<sup>4,5</sup> or the transient microwave conductivity<sup>2,3</sup> in cyclohexane radiolysis. It appears that two mobile ions are needed. We, however, wish to propose a different explanation: the mobile radical cation in cyclohexane is in equilibrium with a normally-diffusing ion.

### **Experimental Section**

**Materials.** Aromatic solutes, perylene (Pe) and pyrene (Py), were obtained from Aldrich and twice sublimed *in vacuo*. Absolute ethanol, cyclohexene, and triethylamine (TEA) were used as received from Aldrich. Cyclohexane (Baxter) was passed several times through activated silica gel. The purity of the cyclohexane was monitored by (i) its absorption at 200–240 nm and (ii) the lifetime of the HMI in the pure liquid (which was  $\sim 0.5-0.6 \ \mu$ s). Nitrous oxide (research grade, 99.999%) was from AGA.

The solutions were radiolyzed with 30 ps fwhm pulses from a 15 MeV Argonne linac. Usually, for transient absorption spectroscopy we used 6 krad pulses; in some experiments the dose was decreased to 0.8 krad/pulse. The beam irradiated the center 15% of a 8 mL, 2 cm long, suprasil cell. R1328U-02 and -03 photodiodes (Hamamatsu) were used for detection. The signals were sampled on a Tektronix 7250 digitizer with 20 ps resolution. A set of 5-20 traces was collected and averaged to improve signal-to-noise ratio. A set of interference filters with 7-12 nm bandpass at 310-630 nm and 40 nm bandpass at  $\lambda > 630$  nm was used for spectral resolution. The absorption was measured with the light pulse from a Hamamatsu L2416 flash lamp (10 W) used with a EG&G Electrooptics PS302 power supply (equipped with an extra 10  $\mu$ F high-voltage capacitor). The probing light entered the cell in the direction opposite to the linac beam. For kinetics longer than 100 ns we used a Photon Technology, Inc., arc lamp (75 W) with LPS-220 power supply and a Tektronix SCD 5000 digitizer. The kinetics were corrected by transient absorption from suprasil windows of the cell. The absorbance of the empty cell at 300-750 nm was  $(1-2.5) \times 10^{-3}$ . For aromatic solutes, the OD was corrected for fluorescence from the solution. Broad band cutoff filters were used to minimize excitation of the solute by the analyzing

flash lamp. The response function of the detection system was obtained by observing Cerenkov light emitted at 350 nm by air-saturated H<sub>2</sub>O. Alternatively, the absorption signal from solvated electron  $e_s^-$  at 500 nm was acquired and corrected by (i) the geminate decay of  $e_s^-$  [this decay was simulated as  $G(t) = 0.56 + 0.29 \exp(-t/\tau_1) + 0.16 \exp(-t/\tau_2)$  with  $\tau_1 = 9.5$  ns and  $\tau_2 = 1.2$  ns; this formula was suggested to us by C. D. Jonah (and based on new picosecond radiolysis work)] and (ii) the first-order decay of  $e_s^-$  in reactions with oxygen and impurities (ca.  $10^7 \text{ s}^{-1}$  under conditions of our experiment). The corrected absorption traces and integrated Čerenkov traces were similar. The fast component in the response function (90%) has a fall time of 180 ps; the slow component has a fall time of  $\approx 1.7$  ns.

During radiolysis, the solution was passed at a rate of 2-5 mL/pulse through the cell (but not recirculated) to decrease scavenging of HMI by reaction products. First, the solution was saturated with N<sub>2</sub>O for 10-15 min. Then, it was passed through the cell under a small excess pressure of the gas. All experiments were performed at room temperature, 23 °C. The details of the dc conductivity setups are given in ref 14.

# Results

Transient Spectra in Cyclohexane. Absorption spectra in the pulse radiolysis of neat cyclohexane have been reported by Menhert *et al.*<sup>5</sup> and by Jonah and LeMotais.<sup>12</sup> The latter results were obtained using picosecond pulse radiolysis. Menhert et al. used 20 ns pulses and a photomultiplier with response time of 2-5 ns.<sup>5</sup> The spectra observed by these two groups were markedly different. While the spectra obtained by Jonah and LeMotais were broad and featureless,<sup>12</sup> the spectra observed by Menhert *at al.* exhibited a sharp peak at 500 nm.<sup>5</sup> The latter spectrum somewhat resembles that of the matrix-stabilized radical cation of cyclohexane observed by Shida<sup>15</sup> (in CCl<sub>3</sub>F at 77 K). According to Menhert et al.,<sup>5</sup> a bell-shaped spectrum was also observed by Benz and Dunbar<sup>16</sup> who studied photodissociation of several alkanes. Our examination of the latter work, however, showed that the spectrum obtained by Benz and Dunbar,<sup>16</sup> in fact, is as broad and featureless as that obtained by Jonah and LeMotais.<sup>12</sup>

We used 30 ps electron beam pulses and a detection system with a response time  $\approx 180$  ps. Cyclohexane was saturated with  $0.12 \text{ mol } \text{dm}^{-3} \text{ of } N_2 \text{O}$  and passed through the cell continuously; the traces were corrected by the transient absorption signal from the cell windows. The latter signal comprised up to 20% of the total signal at t > 30 ns. Nitrous oxide scavenges  $e_s^-$  with a rate constant of  $3 \times 10^{12} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1.17}$  It also quenches the excited state of cyclohexane with a rate constant of 2.4  $\times$  $10^{10}$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup> (the actual decay is 1.8 times faster due to the time dependence of the rate constant).<sup>18</sup> In N<sub>2</sub>O-saturated solution,  $e_s^-$  and c-C<sub>6</sub>H<sub>12</sub>\* have lifetimes < 200 ps. At t > 0.5 ns, the signal must be only from cyclohexane ions. According to refs 2-4, the radical cation of cyclohexane accounts for >80% of all cations formed in radiolysis. The spectra observed in N<sub>2</sub>O-saturated cyclohexane are shown in Figure 1; the decay kinetics are shown in Figure 2. The spectra observed in the first 2 ns after the pulse are similar to those obtained by Jonah and LeMotais.<sup>12</sup> The spectra obtained at t> 50 ns are similar to those reported by Menhert *et al.* (Figure 1b).<sup>5</sup> In no time interval did we observe the end-of-pulse spectrum reported in ref 5 (Figure 3).

It appears that at least three cations contribute to the transient absorption at 300-800 nm. We will call them ion I, ion II, and ion III. Absorption of ion I is centered at 450-500 nm. This ion reacts with scavengers much faster than the other two



**Figure 1.** (a) Time evolution of absorption spectra from N<sub>2</sub>O-saturated cyclohexane (30 ps pulse, 6 krad/pulse). Empty squares indicate the end-of-pulse spectrum obtained by LeMotais and Jonah.<sup>12</sup> (b) Comparison between the absorption spectra obtained at 1-2 and 40-80 ns in this work with normalized spectra obtained in similar time regimes in refs 5 and 12.



**Figure 2.** Broken lines: a Monte Carlo simulation of geminate decay for a high mobility (i,  $\mu_+ = 9.5 \times 10^{-2} \text{ cm}^2/\text{Vs}^3$ ) and a normally diffusing ion (ii,  $\mu_+ = 3.2 \times 10^{-4} \text{ cm}^2/\text{Vs}; \mu_- = 6 \times 10^{-4} \text{ cm}^2/\text{Vs}^3$ ). Dots: normalized transient absorption traces observed at (a) 450 and (b) 313 nm (30 ps pulse). Solid lines: convolution of curves i, ii with the response function of the detector system.

ions (see below). Ion II and ion III have normal reactivity. Ion II absorbs at  $\lambda < 400$  nm; ion III absorbs at  $\lambda > 550$  nm. It seems very likely that ion II is cyclohexene radical cation. Since this olefin ion does not absorb at  $\lambda > 500$  nm,<sup>19</sup> the absorption in red must be from another species. Proton adducts and carbonium ions of alkanes and the oxidation products generated in reactions with O<sup>•-</sup>, O<sub>2</sub><sup>•-</sup>, and HO<sup>-</sup> (formed on electron scavenging by N<sub>2</sub>O) are not known to absorb at 300–800 nm. The only ion derived from cyclohexane that we can think of,



Figure 3. Comparison between the difference spectra (i, ii) with absorption spectra of cyclohexane radical cation given in refs 5 and 15. Traces subtracted are (i) 2-4 and 1-2 ns and (ii) 4-6 ns and 2-4 ns.

which might absorb in red, is the dimer ion of cyclohexene radical cation.<sup>19</sup> The spectra obtained at 50-100 ns resemble those obtained in  $10^{-3}$  mol dm<sup>-3</sup> solution of cyclohexene. The fast generation of the dimer olefin ions is possible in multiple pair spurs (see below). Though cyclohexadienes also absorb in the red,<sup>19,20</sup> their fast formation seems to be unlikely.

Since ion I reacts faster than other ions, on addition of scavengers its absorption decays faster than those of ion II and ion III. These two ions are stable, and their decay follows the kinetics of geminate recombination for normally-diffusing ions. In terms of the spectral shape, the absorption signals from ion II and ion III do not evolve with time. Since the recombination of ion I is faster, the spectral evolution of the overall signal is due to the systematic decrease in ion I relative to ion II and ion III. Figure 2 shows simulated decay curves for mobile (trace i) and normally-diffusing ions (trace ii) convoluted with the response function of the detection system (solid lines in Figure 2a,b, respectively). In this calculation, ion I was assumed to be stable. For normally-diffusing ions, the simulated curve is similar to the trace obtained at 313 nm (Figure 2b). After correction for the response time of the setup, the decay curve for a normally-diffusing ion has a flat top at t < 3 ns, while the signal from mobile ion rapidly decreases in the first 5 ns (Figure 2). Reducing the spectrum observed at 1-2 ns by the spectrum observed at 2-3 ns, we enhanced the fraction of the signal from ion I at least 4 times (Figure 3). A qualitative similarity between the spectrum shown in Figure 3 and that of  $c-C_6H_{12}^{\bullet+}$  observed by Shida<sup>15</sup> suggests that ion I is indeed the radical cation of cyclohexane. Our analysis suggests that  $\sim$ 50% of the absorption at 450 nm is from this ion.

To establish the existence of ion I at later times, we used the fact that its scavenging is faster than that of the other two cations. Figure 4 shows the spectra observed in N<sub>2</sub>O-saturated cyclohexane containing 0,  $10^{-3}$ , and  $4.5 \times 10^{-3}$  mol dm<sup>-3</sup> of



**Figure 4.** Time evolution of spectra from N<sub>2</sub>O-saturated cyclohexane with (i) no, (ii)  $10^{-3}$  mol dm<sup>-3</sup>, and (iii)  $4.5 \times 10^{-3}$  mol dm<sup>-3</sup> of ethanol (30 ps pulse). Spectra ii and iii are normalized to spectrum i at  $\lambda =$  700 nm. Integration windows: (a) 1–2, (b) 2–5, (c) 5–10, and (d) 15-25 ns.

ethanol (the spectra are normalized at  $\lambda = 700$  nm). Ethanol scavenges ion I with rate constant of  $(0.9 \pm 0.1) \times 10^{11} \text{ mol}^{-1}$ dm<sup>3</sup> s<sup>-1</sup>. While the normalized end-of-pulse spectra are similar (Figure 4a), the spectra observed at 2-5 ns (Figure 4b) and 5-10 ns (Figure 4c) show rapid decay of absorption from ion I relative to that of normally-diffusing ion II and ion III. At t > 10 ns, no ion I is observable in the solutions containing  $> 10^{-3}$ mol dm<sup>-3</sup> of ethanol. At t > 10 ns, the absorption is from ion II and ion III and the spectral shape does not change any longer (the upper trace in Figure 4d). A comparison between the spectra in cyclohexane and in the ethanol solutions shows that even at t = 30-50 ns there is a weak absorption from ion I in cyclohexane (ca. 10% of that from ion III). At later times, the absorption from ion I is too weak to measure. The mobile ion observed in the conductivity experiments lives 300-600 ns.<sup>2,3,6,13</sup>

**Fast Scavenging Kinetics.** Convincing evidence that ion I and the ion observed by conductivity are the same species would be the similarity between their reaction constants.

Menhert *et al.*<sup>5</sup> demonstrated that at  $\lambda = 500$  nm the absorption in the geminate spike was scavenged by TEA (and some other solutes) faster than in the "tail" of the decay (t > t20 ns). Jonah and LeMotais found that the absorption at 450 nm was scavenged by TEA with second-order rate constant  $\approx 10^{10} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ , typical for scavenging reactions of normally-diffusing ions.<sup>12</sup> Both of these experiments shared the same deficiency: the absorption from the solute ions was superimposed on the absorption from cyclohexane ions. Since the latter signal is very weak, even poor absorbers like TEA<sup>++</sup> can easily dominate the spectrum.<sup>20</sup> The growing signal from the solute ions compensates for the decay of absorption from cyclohexane ions. In the case of TEA, the fast formation of TEA<sup>•+</sup> is quite evident at 313 nm (Figure 5a). At  $\lambda = 750$  nm, where TEA++ does not absorb,<sup>20</sup> the fast scavenging of ion I can be observed without much interference (Figure 5b).

To measure the reaction rates of ion I we added a solute which does not yield light-absorbing ions on scavenging: ethanol (Figure 6). At  $\lambda < 370$  nm the absorption decayed with the diffusion-controlled rate (Figure 6a). At  $\lambda > 400$  nm the kinetics exhibited two components: a fast one and a slow one (Figure 6b). These curves were fit by biexponential dependences. The bimolecular rate constants corresponding to the slow component were taken from the fits to the 313 nm traces. The rate constants measured in this study are compiled in Table 1.



**Figure 5.** Formation of TEA<sup>++</sup> ((a)  $\lambda = 313$  nm) and decay ((b)  $\lambda = 750$  nm) of ions from cyclohexane observed on radiolysis of N<sub>2</sub>O-saturated cyclohexane containing no (dots),  $1.5 \times 10^{-3}$ ,  $3 \times 10^{-3}$ , and  $6 \times 10^{-3}$  mol dm<sup>-3</sup> of triethylamine. The arrows indicate the increase (a) and decrease (b) of the OD on addition of TEA.



**Figure 6.** Decay of optical absorption from cyclohexane ions on addition of ethanol to the N<sub>2</sub>O-saturated solution of cyclohexane, observed at  $\lambda = 313$  nm (a) and  $\lambda = 450$  nm (b). Dots: No ethanol added. Solid lines: with  $10^{-3}$  (traces b only)  $2.5 \times 10^{-3}$  and  $4.5 \times 10^{-3}$  mol dm<sup>-3</sup> of ethanol. The arrow indicates an artifact in our detector system.

These rate constants are close to the values given by Warman<sup>3</sup> and Schmidt and Sauer<sup>6a</sup> for the long-lived HMI observed by

TABLE 1: Rate Constants for Scavenging of Ion I and Ion II As Determined by Biexponential Analysis (See Text) vs Rate Constants for the Scavenging of HMI As Determined by Microwave and dc Conductivity ( $\times 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ )

scavenger	ion II	ion I	ref 3	ref 6a
triethylamine ethanol	$0.11^a \\ 0.096^b$	$2.2 \pm 0.1 \\ 0.9 \pm 0.1$	2.5 1.6	2.3 0.5

<sup>*a*</sup> From the tail of the 450 and the 750 nm kinetics. <sup>*b*</sup> From the 313 nm kinetics.



**Figure 7.** Formation of radical cations of (a) perylene (550 nm band) and (b) pyrene (450 nm band) in irradiated N<sub>2</sub>O-saturated cyclohexane solutions ([Pe] =  $3 \times 10^{-4}$  mol dm<sup>-3</sup>, [Py] =  $10^{-3}$  mol dm<sup>-3</sup>). In traces b, the peak at 410 nm is from triplet pyrene.

conductivity. Yet the formation kinetics of aromatic radical cations (see below) indicates that the lifetime of the mobile precursor is ca. 30 ns and that the rate constants of electron transfer are two times higher than the numbers given in Table 1.

**Formation of Aromatic Cations.** The fast formation of solute radical cations has been observed by several groups.<sup>1,4</sup> Unfortunately, the quality of data in these studies is insufficient for quantitative analysis. Particularly, it is not clear from those results whether the formation is fast due to rapid scavenging, fast transformation of ion I, or both.

In the latter studies, 10-50 ns electron pulses were used and either the end-of-pulse absorption or the decay on a submicrosecond time scale was analyzed. No correction for the absorption signal from cyclohexane derived ions was made. Hummel et al. used oxygen-saturated (0.01 mol  $dm^{-3}$ ) solutions of biphenyl, pyrene, dimethylaniline and tetramethyl p-phenylenediamine.<sup>4</sup> Radical cations and triplets of aromatic amines have nearly identical absorption spectra, which makes the results unreliable.<sup>21</sup> In oxygenated solutions, many aromatic anions and triplets are formed on radiolysis.<sup>4</sup> The absorption signals from these species strongly overlap with the absorption signal from the corresponding radical cations.<sup>20-23</sup> These complications were not taken into account. By simple analysis of the formation kinetics, Hummel et al. estimated that the rate constant of scavenging was  $(4-5) \times 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  and the lifetime of the precursor ions is  $<50 \text{ ns}.^{4a}$  Later, the Delft group reconsidered both of these estimates to accommodate the observations with microwave conductivity.<sup>2,3</sup>

We studied the formation kinetics of radical cations of perylene (Pe<sup>•+</sup>) and pyrene (Py<sup>•+</sup>) in N<sub>2</sub>O-saturated cyclohexane solutions. Our analysis fully supports the earlier estimates of Hummel *et al.*:<sup>4a</sup> we determined the rate constant as  $\approx 4 \times 10^{11}$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup> and the lifetime of the precursor ions as  $\approx 30$  ns.

**Perylene.** The absorption spectrum of  $\text{Pe}^{\bullet+}$  exhibits a sharp peak (fwhm 30 nm) at 550 nm (Figure 7).<sup>20</sup> To remove the absorption from cyclohexane ions (which have broad spectra), we subtracted from the trace observed at 550 nm a half-sum of

the traces observed at 530 and 570 nm:  $OD_{550} - \frac{1}{2}(OD_{530} + OD_{570})$ . <sup>3</sup>Pe, Pe<sub>2</sub>•<sup>+</sup>, and PeH<sup>+</sup> do not absorb at 530–570 nm.<sup>20,23,24</sup> Any signal whose spectrum in the 530–570 nm region can be approximated with a line is removed by this subtraction procedure.

The signal from Pe<sup>•-</sup> (centered at 580 nm)<sup>20</sup> was eliminated because the solution was saturated with N<sub>2</sub>O (0.12 mol dm<sup>-3 3a</sup>). In cyclohexane, aromatic solutes scavenge electrons with rate constants of  $(1-3) \times 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ,<sup>25</sup> which accounts for rapid generation of perylene radical anions. To suppress their formation, a high concentration of a second electron scavenger is required. Since the lines from Pe<sup>•+</sup> and Pe<sup>•-</sup> (as well as those from Py<sup>•+</sup> and Py<sup>•-</sup>) strongly overlap, the presence of Pe<sup>--</sup> substantially distorts the kinetics, even after being treated with our subtraction approach. A good test for the accuracy of the subtraction is to compare  $OD_{550} - \frac{1}{2}(OD_{530} + OD_{570})$  and  $OD_{550} - \frac{1}{2}(OD_{540} + OD_{560})$  traces. In our concentration regime ([Pe]  $< 5 \times 10^{-4} \text{ mol } \text{dm}^{-3}$ ; [Pe]/[N<sub>2</sub>O]  $< 4 \times 10^{-3}$ ) the two sets of curves were identical. With scavengers other than N<sub>2</sub>O we obtained less reliable results. Due to low concentration (0.01 mol dm<sup>-3 3a</sup>) and slow scavenging rate (5  $\times$  10<sup>10</sup> mol dm<sup>-3 26</sup>), O<sub>2</sub> competes insufficiently with the aromatic compounds. In oxygenated  $10^{-4}$  mol dm<sup>-3</sup> perylene solution, the signal observed from  $Pe^{-}$  at t = 1 ns is 2 times greater than the signal from Pe<sup>•+</sup>. We found that in oxygenated cyclohexane the signals from Pe<sup>•-</sup> and Py<sup>•-</sup> decayed with a half-lifetime  $\ll 10$  ns. This must be due to rapid electron transfer to O<sub>2</sub>:

$$\operatorname{Pe}^{\bullet-} + \operatorname{O}_2 \to \operatorname{Pe} + \operatorname{O}_2^{\bullet-} \tag{1}$$

After the first 10 ns, the formation kinetics of  $Pe^{+}$  obtained in  $O_2$  and  $N_2O$  saturated solutions using the subtraction technique are identical.

Planar aromatic radical cations yield sandwich dimers:<sup>27</sup>

$$\mathrm{Pe}^{\bullet+} + \mathrm{Pe} \to \mathrm{Pe}_2^{\bullet+} \tag{2}$$

which do not absorb in the spectral regions of monomer ions.<sup>28</sup> To measure the rate constant of reaction 2 we observed the decay of Pe<sup>•+</sup> on the time scale of  $0.1-5 \ \mu$ s. For Pe<sup>•+</sup> we found the rate constant  $1.25 \times 10^{10} \ \text{mol}^{-1} \ \text{dm}^3 \ \text{s}^{-1}$ ; for Py<sup>•+</sup> we obtained  $1.2 \times 10^{10} \ \text{mol}^{-1} \ \text{dm}^3 \ \text{s}^{-1}$ . Reaction 2 was included in all of our simulations.

To observe the kinetics of scavenging of normally-diffusing ions, we added 0.1 mol dm<sup>-3</sup> of cyclohexene. This olefin rapidly reacts with HMI.<sup>6a,13,14</sup> At this concentration the lifetime of ion I is less than 10 ps, so the observed kinetics is from scavenging of cyclohexene radical cation. The kinetics are shown in Figure 8a. The lines drawn through the points are the simulated kinetics (see below). The agreement between the experimental and theoretical results is very good.

The effect of perylene concentration with no cyclohexene is shown in Figure 8b. Without cyclohexene the formation of Pe<sup>•+</sup> is much faster. The maximum absorbance from Pe<sup>•+</sup> for a given concentration of perylene is 4–5 times greater. Both observations indicate fast scavenging of the precursor radical cation. However, the traces cannot be simulated with the assumption that the precursor ion is long-lived (Figure 8b). Assuming the scavenging rate  $k_{\rm HM} \approx 3 \times 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  (given as the maximum scavenging constant of HMI by Warman *et al.*<sup>2,3</sup>), we tried to fit the traces by varying  $\tau$ , the lifetime of mobile holes. Figure 9 shows two such simulations obtained in the assumption that HMI are transformed into normally-diffusing ions which (i) do or (ii) do not transfer charge to perylene. The kinetics were simulated using the continuum-diffusion model



**Figure 8.** Formation kinetics of Pe<sup>•+</sup> in N<sub>2</sub>O-saturated solution of (a) 1 vol % of cyclohexene in cyclohexane and (b) cyclohexane as a function of perylene concentration (OD<sub>550</sub> -  $^{1/2}$ (OD<sub>530</sub> + OD<sub>570</sub>), 30 ps pulse, 6 krad/pulse) Traces a (dots; *bottom to top*): [Pe] = 7.3 × 10<sup>-5</sup>, 1.4 × 10<sup>-4</sup>, and 5.4 × 10<sup>-4</sup> mol dm<sup>-3</sup>. Traces b: [Pe] = 2.8 × 10<sup>-5</sup>, 5.9 × 10<sup>-5</sup>, 1.1 × 10<sup>-4</sup>, 2.6 × 10<sup>-4</sup>, and 5 × 10<sup>-4</sup> mol dm<sup>-3</sup>. Solid lines: normalized simulated curves for (a) scavenging of normally diffusing ions and (b) scavenging of HMI with infinite natural lifetime ( $k_{\text{HM}} = 3 \times 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ).



**Figure 9.** Simulation of formation kinetics of  $Pe^{++}$  (dots: same as experimental curves in Figure 8b) with the assumption of a short-lived precursor of  $Pe^{++}$  (i.e., short-lived radical cation of cyclohexane) with decay time  $\tau = 33$  ns. Traces i are simulated with the assumption that this decay does not result in the formation of a radical cation; traces ii are simulated with the assumption that the product of the transformation is a radical cation.

presented in the Appendix; the calculations using the Monte Carlo model gave very similar results. We assumed the following parameters:  $b_{\rm G}$  for the  $r^2$ -Gaussian distribution  $p(r) = r^2 \exp(-[r/b_{\rm G}]^2)$  of thermalized electrons is 6.3 nm (corresponding to a free ion yield of 3%); recombination radius  $R \approx 1$  nm; permittivity  $\epsilon \approx 2.02$ ; electron mobility is 0.23 cm<sup>2</sup>/Vs;<sup>3</sup> the mobility of HMI is 9.5 × 10<sup>-2</sup> cm<sup>2</sup>/Vs;<sup>3</sup> mobilities of normally-diffusing ions of cyclohexane and radical cations and

anions of perylene are  $3.15 \times 10^{-4}$  cm<sup>2</sup>/Vs; mobility of O<sup>•-</sup> (and/or N<sub>2</sub>O<sup>•-</sup>) is  $6 \times 10^{-4}$  cm<sup>2</sup>/Vs;<sup>3</sup> the rate constant of electron transfer from perylene to olefin ions is  $k_{\text{ND}} = 1.5 \times 10^{10}$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup> (corresponding to the rate of a diffusion-controlled charge transfer reaction); the dimerization constant is  $1.25 \times 10^{10}$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>; the rate constant of electron scavenging is  $2.4 \times 10^{12}$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>;<sup>17</sup> and [N<sub>2</sub>O]<sub>sat</sub> = 0.12 mol dm<sup>-3</sup>.<sup>3</sup> The simulation (i) with  $\tau \approx 30$  ns fits the data best; the discrepancy could be due to formation of some normally-diffusing ions at t = 0. Simulation ii also fits the data reasonably well, so we cannot tell which route, (i) or (ii), is preferred.

Importantly, the shape of the formation kinetics is rather insensitive to the rate constant  $k_{\rm HM}$  once it exceeds  $\sim 10^{11}$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>. The only way to estimate  $k_{\rm HM}$  is to compare the kinetics obtained in cyclohexane and the cyclohexene solutions (Figure 8). Assuming that cyclohexene fully scavenges charge from the cyclohexane radical cation and fully transfers it to perylene, we obtained the maximum scavenging rate of 4 ×  $10^{11}$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>. If  $k_{\rm HM} \approx 3 \times 10^{11}$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>, one must assume that  $\approx 10\%$  of the charge is lost in side reactions of cyclohexene radical cation.

If the precursor of the solute radical cations and the longlived HMI observed by conductivity are the same species, the value we obtain for  $\tau$  cannot be explained without invoking a generation of radiolytic products which scavenge the HMI. Warman et al. found that the lifetime of the conductivity signal from HMI rapidly decreased with absorbed dose.<sup>13</sup> To test whether the mobile ions were scavenged by stable radiolytic products (such as cyclohexene and bicyclohexyl<sup>3,6a,13</sup>), we studied the formation of Pe+ in 10-4 mol dm-3 perylene solution. To decrease the buildup of the products, the flow rate was increased from 2 to 6 mL/pulse; the dose per pulse was decreased from 6 to 2 to 0.8 krad. In all of these experiments we observed no change in the shape of the formation kinetics of Pe<sup>•+</sup>. In another experiment, N<sub>2</sub>O-saturated cyclohexane was radiolyzed under our usual experimental conditions. An aliquot of  $2 \times 10^{-6}$  mol dm<sup>-3</sup> anthracene was added to the collected radiolyzate, and the resulting solution was photolyzed.<sup>6,14</sup> The lifetime of the HMI as determined by photoconductivity was not changed by the radiolysis. Furthermore, we directly measured the lifetime of the HMI under the conditions of our experiment using the pulse radiolysis dc conductivity setup described in ref 14. The dose in these experiments was varied from 0.7 to 3 krad/pulse (estimated from the collected charge). After the correction for second-order decay due to homogeneous ion recombination,<sup>14</sup> the lifetime of the HMI was determined to be 500–600 ns. Thus, the short lifetime  $\tau$  of ion I is not due to decay via homogeneous reaction with anions or radiolytic products.

**Pyrene.** Pyrene is more soluble than perylene which allows a wider concentration range to be used. The 450 nm absorption band of  $Py^{\bullet+}$  was used for detection.<sup>20</sup> For  $[Py] < 10^{-3}$  mol  $dm^{-3}$  the OD<sub>450</sub> -  $1/_2(OD_{430} + OD_{470})$  traces were collected; at higher concentrations the  $OD_{450} - \frac{1}{2}(OD_{440} + OD_{460})$  traces were collected (for the latter, we used normalization factor 1.58 determined for  $[Py] = 5 \times 10^{-4} \text{ mol dm}^{-3}$ ). In the higher concentration range, some Py<sup>--</sup> (500 nm band) and <sup>3</sup>Py (410 nm band) were formed even in N2O-saturated solutions. The formation kinetics obtained in  $(0.03-5) \times 10^{-3}$  mol dm<sup>-3</sup> pyrene solutions are shown in Figure 10. Once more, the simulations obtained in a model with  $\tau \sim 200-600$  ns did not account for the data. These results, however, can be simulated with the same parameters which were used to fit the Pe<sup>•+</sup> kinetics (Figure 10a). At [Py] > 5  $\times$  10<sup>-4</sup> mol dm<sup>-3</sup>, the agreement between the theoretical and experimental traces for t < 20 ns is poor.



**Figure 10.** Formation kinetics of Py<sup>++</sup> in N<sub>2</sub>O-saturated cyclohexane. Traces a (dots, *bottom to top*): [Py] =  $3.4 \times 10^{-5}$ ,  $6 \times 10^{-5}$ ,  $1.2 \times 10^{-4}$ ,  $2.5 \times 10^{-4}$ , and  $4.7 \times 10^{-4}$  mol dm<sup>-3</sup> (OD<sub>450</sub> -  $1/_2$ (OD<sub>430</sub> + OD<sub>470</sub>)). Traces b: [Py] =  $10^{-3}$ ,  $2.5 \times 10^{-3}$ , and  $5 \times 10^{-3}$  mol dm<sup>-3</sup> ( $1.58\{OD_{450} - 1/_2(OD_{430} + OD_{470})\}$ , 30 ps pulse, 6 krad/pulse). Solid lines (a,b): curves simulated for the given pyrene concentrations using  $k_{\text{HM}} = 3 \times 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$  and  $\tau = 33$  ns; the simulated traces in b were corrected for the response function of the detector system.

This is due to the response function of our detection system; if the latter is taken into account, the agreement is quite good (Figure 10b). Thus, the formation kinetics in both systems indicates a short natural lifetime of the mobile radical cations.

#### Discussion

Our results support the view that the *short-lived* mobile species in cyclohexane is indeed the radical cation (hole). This view is at least qualitatively consistent with the results on fluorescence<sup>9</sup> and FDMR.<sup>10,11</sup> Thus, the problem is the identity of the *long-lived* species observed in  $dc^6$  and microwave<sup>2,3</sup> conductivity experiments.

From the standpoint of the transient absorption spectroscopy alone, the lifetime  $\tau$  of the precursors of the solute radical cations is too short to account for the conductivity signals observed as long as  $1-2 \mu s$  after ionization. Under the conditions of our experiment, no homogeneous reaction with radiolytic products and anions can explain the decay of mobile radical cations in 30 ns. Moreover, we directly observed the long-lived HMI in the same solution for the same dose using dc conductivity.<sup>14</sup> One could try to explain these results in terms of extreme scatter in the decay rates of the mobile holes. This might occur if the radiolytic products formed in multiple pairs scavenge most of the holes in spurs.<sup>29</sup> Only the holes which would escape these reactions (for example, the holes in the single-pair spurs) could be observed at t > 100 ns.

To test this idea, we simulated the multiple pair kinetics following the approaches of Bartzak and Hummel<sup>30</sup> and Brocklehurst.<sup>29</sup> The dynamics of ions, cyclohexyl radicals, and many radiolytic products was simulated using an elaborate Monte Carlo program. We included some 120 reactions

between the species; the spin conservation laws were rigorously enforced. The number of pairs in spurs was varied between 5 and 50, and different geometries (linear, cylindrical, spherical, random) were tried. We found that though the scavenging of cyclohexane radical cation by cyclohexene and cyclohexyl radical is quite efficient at t < 1 ns, the simulations consistently showed little effect of these ion-molecule reactions at t > 2ns, when most of the remaining mobile holes escape the Coulombic field of the anions.<sup>30</sup> Since such holes are wellseparated from the center of the spur (>20-30 nm), they react with the radiolytic products very slowly.

Furthermore, as shown in part II of this work,<sup>14</sup> the longlived HMI observed in dc conductivity experiments reacts with a typical scavenger with the rate constant of  $(0.5-1.6) \times 10^{11}$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>, which is 2–5 times slower than has been estimated previously. This discrepancy is related to the inability of a model with a single mobile ion to account for the dichotomy in the scavenging rates. Whereas at t < 100 ns the scavenging is very fast ( $\approx 4 \times 10^{11}$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>),<sup>3,6,13,14</sup> at t > 100 ns, it is 3–5 times slower.<sup>14</sup> When one fits the observed kinetics in terms of a monoexponential decay of a single HMI, the "rate constants" are quite similar to the numbers given by Warman<sup>3</sup> and Schmidt and Sauer<sup>6a</sup> (and Table 1). In other words, the short-lived and the long-lived HMI behave as two different species.

**Two Holes or an Equilibrium?** In the past, we considered a possibility that the long-lived HMI are the protons adduct of cyclohexane.<sup>8</sup> Our recent results indicate that it is unlikely to be the case.<sup>14</sup> At this stage, the identification of long-lived HMI as the solvent radical cations is the only way to account for their ultrafast diffusion.

In this work we suggest a different approach to the problem. We propose that (i) the radical cation of cyclohexane is the only HMI formed on ionization, and (ii) it is in equilibrium with a normally-diffusing ion. We assume that before the equilibrium is established, the scavenging constant is  $\approx 4 \times 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ . This estimate is consistent with the observed rate constants for the decay of microwave conductivity<sup>3,13</sup> and the formation kinetics of solute radical cations at t < 100 ns (see above). After the equilibrium is established (which is required to happen over several tens of nanoseconds), the effective scavenging constant  $k_{\text{eff}}$  is given by

$$k_{\rm eff} = (k_{\rm ND}K + k_{\rm HM})/(K+1)$$
 (3)

where *K* is the equilibrium constant. The bimodality of the decay of HMI in cyclohexane is established in ref 14. Using the experimental  $k_{\text{eff}} = 1.4 \times 10^{11} \text{ mol}^{-1}$ ,<sup>14</sup> we obtain  $K \approx 2$  (we address the reader to ref 14 for a more accurate treatment).

What could be the nature of such an equilibrium? It is wellknown that the chair form of cyclohexane is in equilibrium with the other two forms, the twist form and the boat form (0.22)and 0.3 eV above the chair form, respectively), the boat form being a transitory conformation.<sup>31</sup> The first-order rate constant for ring inversion is  $\sim 10^5$  s<sup>-1</sup> at 25 °C.<sup>31</sup> Thus, on the time scale of our experiments, liquid cyclohexane can be viewed as a binary mixture of the chair and twist forms. The equilibrium concentration of the twist form is  $\sim 10^{-4}$  mol dm<sup>-3</sup>.<sup>31</sup> On ionization, the majority of the radical cations are formed in the chair form and surrounded by the chair-form molecules. This situation is favorable for rapid resonant charge transfer.<sup>3,7</sup> At some point, the chair-form radical cation (the mobile ion) approaches a molecule in the twist form. Assuming that the latter reacts with the mobile ion with the rate constant  $\sim k_{\rm HM}$ , we obtain 25-30 ns for a lifetime of the chair-form radical cation. This estimate is similar to that obtained experimentally.

Thus, we postulate the equilibrium between different conformations of radical cation of cyclohexane [the idea that the conformation dynamics is involved in the chemistry of HMI has been considered by Hummel and Lutjens;<sup>32</sup> they suggested that reaction 4a transforms the mobile radical cation to a normally-diffusing one; kinetically, *irreversible* reaction 4a is equivalent to any other transformation of the solvent hole to a secondary radical cation; to cause the observed dichotomy in the reaction rates, the transformation must be *reversible*]:

$$c$$
-C<sub>6</sub>H<sub>12</sub><sup>•+</sup> (chair) +  $c$ -C<sub>6</sub>H<sub>12</sub> (twist) →  
 $c$ -C<sub>6</sub>H<sub>12</sub> (chair) +  $c$ -C<sub>6</sub>H<sub>12</sub><sup>•+</sup> (twist) (4a)

$$c-C_6H_{12}^{\bullet+}$$
 (twist)  $\rightarrow$  ?  $\rightarrow$   $c-C_6H_{12}^{\bullet+}$  (chair) (4b)

From the EPR studies by Iwasaki *et al.*<sup>33</sup> and Lund *et al.*,<sup>34</sup> it is known that in frozen matrices the lowest-energy conformations of cyclohexane radical cation are distorted chair forms (<140 K). The EPR spectra exhibit the reversible temperature changes typical for non-equivalent-site exchange.<sup>33</sup> Apparently, the media enforces site-specific Jahn–Teller distortions of the radical cations.<sup>33,34</sup> It is possible that in liquid cyclohexane, the twist form is actually lower in energy than the chair form. Once the charge is scavenged by the twist form, it does not transfer to the neighboring chair-form molecules until the radical cation transforms back to the chair form (in a spontaneous manner or by charge transfer).

Alternatively, the equilibrium can be due to a reversible proton transfer:

$$c-C_6H_{12}^{\bullet+} + c-C_6H_{12} \leftrightarrow c-C_6H_{13}^{+} + c-C_6H_{11}^{\bullet}$$
 (5)

The irreversible deprotonation is a typical reaction of alkane radical cations in liquid alkanes.<sup>8,11,35</sup> Though in the gas phase reaction 5 is endothermic by 0.42 eV,<sup>36</sup> in solid halocarbon solutions of cyclohexane the deprotonation can readily be observed by EPR above 100 K.<sup>33</sup>

Reversible reaction 5 could account for some peculiarities in chemical behavior of HMI as observed by dc photoconductivity.<sup>6a,14</sup> Particularly, alkyl halides<sup>6a</sup> and oxygen<sup>14</sup> were found to be weak scavengers of the conductivity signal from mobile ions (oxygen, for example, scavenges the conductivity with rate constant of  $3 \times 10^8$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup><sup>14</sup>). Both of these scavengers have higher gas-phase IP<sup>37</sup> and lower proton affinities<sup>38</sup> than cyclohexane, and therefore are not expected to react with cyclohexane radical cation at all. On the other hand, their reactivity toward alkyl radicals is well-known.

The problem with reaction 5 is that it requires too large a value of the pseudo-first-order rate constant for the reverse reaction ( $\sim 10^7 \text{ s}^{-1}$ ). If the diffusion-controlled reaction between the radical and the proton adduct were homogeneous, it would be equivalent to a steady-state concentration of cyclohexyl radicals  $\sim 10^{-3}$  mol dm<sup>-3</sup>, while in our experiments it was  $10^{-6}-10^{-5}$  mol dm<sup>-3</sup>. This argument, however, is incomplete: the proton adduct and the radical are formed as a geminate pair and, therefore, have unity probability to recombine if one neglects the side reactions of these species.<sup>39</sup> Still, only 5–10% of these geminate recombinations should occur on the time scale of 100 ns. Thus, we believe that the equilibrium due to reaction 4 is more realistic.

Reactions 4 and 5 cover all possible types of equilibria (the one between the two isomeric radical cations and the one between the radical cation and a radical *and* cation). Though one can envisage some other reversible transformations (for example, an equilibrium between the doublet and the quartet

states of cyclohexane radical cation), from the standpoint of the scavenging kinetics these processes are equivalent to either reaction 4 or reaction 5.

# Conclusion

We report observations of fast scavenging kinetics in reactions of radical cations of cyclohexane with various solutes. Both fast decay of the absorption from the solvent radical cations and the fast growth of the absorption from solute radical cations have been observed. Our data indicate that the scavenging constant is ca.  $4 \times 10^{11}$  mol<sup>-1</sup> dm<sup>3</sup> s<sup>-1</sup>; the lifetime of the mobile radical cation is ca. 30 ns. This short lifetime cannot be explained by a reaction with radiolytic products or by homogeneous recombination. Our results cast strong doubts on identification of the long-lived HMI observed in conductivity experiments as radical cations of cyclohexane. Yet the latter appears to be the only ion capable of fast motion via resonant charge transfer.

To resolve this dichotomy, we propose that the mobile radical cation is in equilibrium with a normally-diffusing ion. Two such equilibria were examined: the one between the conformers of the radical cation and the one due to reversible deprotonation. This hypothesis will be considered further in ref 14.

**Acknowledgment.** We thank Mr. D. Ficht for operating of the linac and Mr. J. Yan for technical assistance. We also thank Drs. C. D. Jonah and D. M. Bartels for many useful discussions.

# **Appendix: Continuum-Diffusion Model**

Diffusion equations were solved for an isolated geminate pair. We introduce  $C_{\alpha}(r;t)$ , the concentration of the  $\alpha$ th pair, where *r* is the distance between the radical ion partners. For this pair

$$\partial C_{\alpha} / \partial t = \nabla J_{\alpha} + \sum_{\beta} \mathbf{K}_{\alpha\beta} C_{\beta}$$
(A1)

$$J_{\alpha} = D_{\alpha} [\nabla C_{\alpha} + C_{\alpha} \nabla u]$$
 (A2)

where  $J_{\alpha}$  is the diffusion flux through the reaction zone,  $\mathbf{K}_{\alpha\beta}$  is the matrix of chemical transformations,  $D_{\alpha}$  is the diffusion coefficient for the given pair,  $u(r) = -R_{ons}/r$ , and  $R_{ons} \approx 27.9$ nm is the Onsager radius. Equation A1 is complemented with two boundary conditions,  $C_{\alpha}(r \rightarrow \infty;t) = C_{\alpha}(r=R;t) = 0$ , where  $R \approx 1$  nm is the recombination radius. The initial condition is  $C_{\alpha}(r,t=0) = \operatorname{conc}^{\circ}{}_{\alpha}p(r)$ , where p(r) is the charge distribution function,  $p(r) = (\text{norm}) \exp(-[r/b_G]^2)$ , and  $\operatorname{conc}^{\circ}{}_{\alpha}$  are the initial concentrations corrected by static (Perrin) scavenging. Introducing

$$\operatorname{conc}_{\alpha}(t) = \int_{R}^{\infty} \mathrm{d}r \, 4\pi r^{2} C_{\alpha}(r,t) \tag{A3}$$

$$c_{\alpha}(r;s) = \int_{0}^{\infty} \mathrm{d}t \ C_{\alpha}(r,t) \mathrm{e}^{-st}$$
(A4)

$$\operatorname{conc}_{\alpha}(s) = \int_{0}^{\infty} \mathrm{d}t \operatorname{conc}_{\alpha}(t) \mathrm{e}^{-st}$$
 (A5)

$$J_{\alpha}(s) = \int_{0}^{\infty} \mathrm{d}t \, J_{\alpha}(R,t) \mathrm{e}^{-st} \tag{A6}$$

we obtain

$$-\operatorname{conc}_{\alpha}^{\circ} p(R/x) = D_{\alpha}/R^{2} x^{4} \left( \partial c_{\alpha}/\partial x \right) y(x)^{-1} \left( \partial [c_{\alpha}y(x)]/\partial x \right) - \sum_{\beta} [s \delta_{\alpha\beta} - K_{\alpha\beta}] c_{\beta}$$
(A7)

$$J_{\alpha}(s) - (\text{norm})(\text{conc}^{\circ}_{\alpha}) = \sum_{\beta} [s\delta_{\alpha\beta} - K_{\alpha\beta}] \text{conc}_{\beta}$$
(A8)

where x = R/r and  $y(x) = \exp(-R_{ons}x/R)$ . Concentrations  $\operatorname{conc}_{\alpha}(t)$  were found by inverse Laplace transform of  $\operatorname{conc}_{\alpha}(s)$ . Equations A7 and A8 were solved numerically.

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JP953255L