# Transient Absorption Spectroscopy of High-Mobility Ions in Decalin†

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Transient absorption spectroscopy is used to demonstrate that pulse radiolysis of a decalin mixture (63% *cis*-decalin + 37% *trans*-decalin) with 15 MeV electrons results in formation of high-mobility solvent holes. These radical cations react with perylene with a rate constant of $8.5 \times 10^{10}$ mol$^{-1}$ dm$^3$ s$^{-1}$. This scavenging is faster by an order of magnitude than ion-molecule reactions of normally diffusing ions (∼(5−7.5) × $10^9$ mol$^{-1}$ dm$^3$ s$^{-1}$). Under conditions of the experiment, the lifetime of the rapidly migrating solvent holes is ∼150 ns, which identifies them as the high-mobility cations observed by dc and microwave conductivity.

## Introduction

Ionization of cyclohexane,[1−5] methylcyclohexane,[5−7] *cis*-decalin, and *trans*-decalin[1,3,8−11] results in the generation of cations whose mobility and scavenging rates are greater by an order of magnitude than those of the normally -diffusing ions. Many researchers believe that these ions are solvent radical cations (holes) involved in rapid resonant charge transfer.[1] In this case, the solvent holes must be long-lived: in pure cyclohexane the conductivity signal from high-mobility ions (HMI) decays with a first-order rate constant ∼$2 \times 10^6$ s$^{-1}$; in pure decalins $3 \times 10^5$ s$^{-1}$.[3] Some of us have previously argued that low chemical stability of the solvent holes at room temperature contradicts the observed longevity, and we proposed that HMI are some secondary ions, for instance, the proton adducts of alkanes.[12]

Recently, we studied the formation kinetics of aromatic solute ions in cyclohexane and found that the lifetime of the mobile radical cation precursor is ∼30 ns.[13] In the subsequent study, we demonstrated that the dc conductivity kinetics observed in radiolysis and laser photolysis of cyclohexane are incompatible with the existence of a single HMI. It seems as if two HMI—a short-lived solvent radical cation (<30 ns) and a long-lived secondary ion (∼300 ns)—are needed to explain the results.[14] Yet it is unclear what mechanism other than resonant charge transfer could cause ultrafast migration of the ions. To solve this riddle, we speculated that in cyclohexane the mobile (chair form) radical cation is in equilibrium with a normally diffusing (twist-boat form) ion.[13,14] The twist conformer (∼$10^{-4}$ mol dm$^{-3}$) which has lower IP rapidly scavenges chair-form radical cations. Being endothermic, the backward transfer is relatively slow, and the equilibrium is reached in 20−30 ns. It was this process that was perceived as the fast decay of the solvent radical cations in our transient absorption experiments. After the equilibrium is reached, only ∼1/3 of the solvent holes exist in the chair form capable of rapid motion via resonant charge transfer. A thorough analysis of dc conductivity data shows that the observed kinetics does correspond to the postulated behavior.[14]

In conformationally frozen cycloalkanes, such as decalins and methylcyclohexane, the radical cations exist in a single form. Thus, a pattern different from that of cyclohexane must be seen. In agreement with this conclusion, the dc conductivity kinetics observed in decalins and their mixtures can indeed be accounted for by a single HMI.[14] In this letter, we demonstrate that the transient absorption kinetics in pulse radiolysis of decalin also implies that the solvent radical cation is highly reactive and relatively long-lived.

## Results and Discussion

Because the neat *trans*- and *cis*-decalins of sufficient purity are costly and the minimization of the effects of radiolytic products which scavenge HMI requires the use of rapid flow of the sample without recirculation, we studied the less expensive decalin mixture available from Aldrich (63:37 cis-to-trans according to the GC analysis). In ref 14 we demonstrated that HMI were present in all decalin mixtures. It was shown that the decay of HMI is first-order, and the mobility of HMI and scavenging rates change linearly with the mole fraction of *trans*-decalin.[14] By analysis of dc conductivity kinetics, it was determined that the mobility of HMI in the 63:37 mixture is $(4.3 \pm 0.3) \times 10^{-3}$ cm$^2$/V s (vs $\mu_+ + \mu_- \approx 4.1 \times 10^{-4}$ cm$^2$/V s for normally diffusing ions) and that the scavenging of HMI by cyclohexene, triethylamine, toluene, and *n*-propanol proceeds with rate constants of 6.6, 5.8, 5.6, and 3.0 (±0.2) × $10^{10}$ mol$^{-1}$ dm$^3$ s$^{-1}$, respectively.[14] Due to the presence of impurity, the first-order decay rate of the HMI is ∼$1.5 \times 10^6$ s$^{-1}$ in the neat liquid photoionized under the same conditions. To estimate the rate constants of typical diffusion-limited reactions in the solvent, we measured the quenching constants of fluorescence from the $S_1$ states of pyrene and naphthalene (Table 1). The fastest quenching occurs via charge transfer with rate constants of (5−7.5) × $10^9$ mol$^{-1}$ dm$^3$ s$^{-1}$. These constants are close to the dimerization constant of perylene$^{•+}$, $(6.1 \pm 0.3) \times 10^9$ mol$^{-1}$ dm$^3$ s$^{-1}$, as found in radiolytic experiments. In our analysis of the scavenging kinetics, we assumed that the charge-transfer reactions of normally diffusing ions occur with rate constant of $7.5 \times 10^9$ mol$^{-1}$ dm$^3$ s$^{-1}$.

Transient absorption kinetics in the pulse radiolysis of $N_2O$-saturated decalin were observed at 310−650 nm (we used 30 ps pulses from the 15 MeV Argonne linac). The solution was flowed to minimize the accumulation of products in the irradiated zone. The absorption spectra (Figure 1a) are due to two cations: ion I, which absorbs in the visible region, and ion II, which absorbs in the UV. The shape of the decay kinetics does not change from 450 to 650 nm. At 400 nm the absorbance reaches a minimum and then peaks again at 300 nm. In the 300−400 nm region, the decay is much slower than in the 450−650 nm region and can be simulated as the weighted sum of

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**TABLE 1: Rate Constants $k_q$ of Fluorescence Quenching in Decalin[a] at 25 °C ($10^9$ mol$^{-1}$ dm$^3$ s$^{-1}$)**

| D* | A | $k_q$ | type[b] |
|---|---|---|---|
| pyrene | $CH_2I_2$ | 5.1 ± 0.1 | ET |
| | nitrobenzene | 5.45 ± 0.05 | ET |
| naphthalene | $CH_2I_2$ | 7.5 ± 0.1 | ET |
| | nitrobenzene | 6.5 ± 0.2 | ET |
| | triethylamine | 1.3 ± 0.03 | CF |
| | tributylamine | 2.1 ± 0.02 | CF |

[a] 63% *cis*-decalin, 37% *trans*-decalin. [b] ET = electron transfer, CF = complex formation.

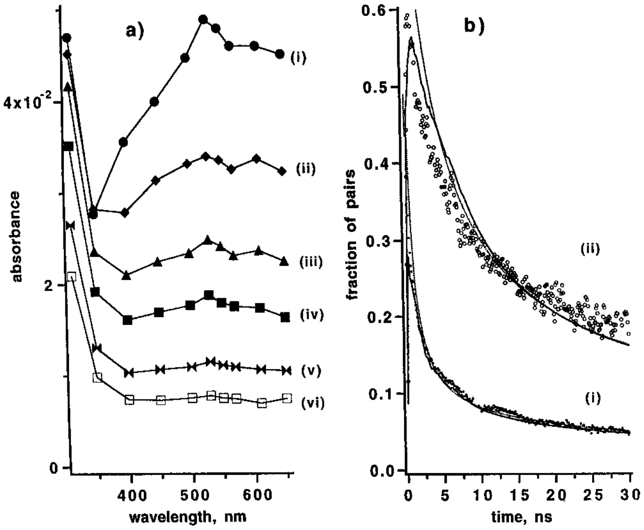

**Figure 1.** (a) Transient absorption spectra observed in radiolysis of the $N_2O$-saturated 63 *cis*-:37 *trans*-decalin mixture with 30 ps electron pulses (15 MeV, 60 Gy/pulse): (i) 0.2−1 ns, (ii) 1−2 ns, (iii) 2−4 ns, (iv) 4−8 ns, (v) 10−20 ns, and (vi) 20−50 ns. (b) Dots: normalized decay kinetics observed at (i) 500 nm (ion I) and (ii) 350 nm (ion II). The decay kinetics were simulated using a Monte Carlo model (dashed lines) and convoluted with the response function of the detection system (solid lines). The mobilities of ion I and ion II were taken as $4.2 \times 10^{-3}$ cm$^2$/V s and $1.3 \times 10^{-4}$ cm$^2$/V s, respectively; the mobility of anion was $2.8 \times 10^{-4}$ cm$^2$/V s.

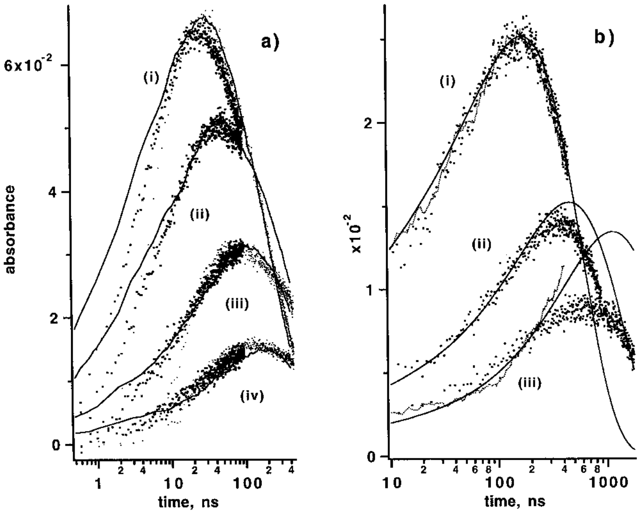

**Figure 2.** Formation of perylene$^{•+}$ in the $N_2O$-saturated decalin solution (63 *cis*-:37 *trans*-decalin mixture) with no (a) and 0.1 mol dm$^{-3}$ toluene (b). Concentrations of perylene are given in the units of $10^{-4}$ mol dm$^{-3}$: for (a) (i) 5.5, (ii) 2.8, (iii) 1.25, (iv) 0.44; for (b) (i) 5.7, (ii) 2.5, (iii) 1.1. Short time scale kinetics in (a) (solid dots) were obtained with 30 ps electron pulses, all other kinetics were obtained with 4 ns pulses (60−80 kGy/pulse). Solid lines in (a) are a Monte Carlo simulation for a HMI that lives 150 ns (see text). Solid lines in (b) represent a simulation using the continuum-diffusion model (compare with the dashed curves calculated with the Monte Carlo model). The discrepancy at $t > 0.5$ $\mu$s is due to homogeneous recombination, which was not included in the calculation.

the fast kinetics observed at $\lambda$ 450 nm and the slow kinetics observed at ≈313 nm. We believe that ion I is the high-mobility solvent radical cation, while ion II is a normally diffusing olefin ion(s), whose fast formation in radiolysis of decalins was observed by fluorescence-detected magnetic resonance.[15] Simulations shown in Figure 1b suggest that the fast kinetics observed at >400 nm is due to geminate decay of HMI; the slow kinetics is from geminate recombination (and, possibly, slow formation) of olefin ions.

The absorption spectrum of Pe$^{•+}$ exhibits a peak at 550 nm. $^3$Pe, Pe$_2^{•+}$, and PeH$^+$ do not absorb at 530−570 nm, the signal from Pe$^{•-}$ (centered at 580 nm) was eliminated because the solution was saturated with electron scavenger, $N_2O$.[13] Following refs 13 and 16, we removed the absorptions from decalin (and toluene) ions by subtracting a half-sum of the traces observed at 530 and 570 nm from the trace observed at 550 nm (Figure 2). To obtain the kinetics of scavenging of normally diffusing ions, we added 0.1 mol dm$^{-3}$ of toluene. Electron pulses of 4 ns duration were used in these experiments. At 0.1 mol dm$^{-3}$ toluene the lifetime of ion-I is < 0.2 ns,[8,14,17] so the slow kinetics observed at $t > 10$ ns is from scavenging of toluene$^{•+}$ by perylene. These kinetics are shown in Figure 2b. The lines drawn through the points are the kinetics simulated using the continuum-diffusion approach considered in ref 13. This model does not include reactions in multiple pair spurs and homogeneous recombination of ions. We assumed the following constants: $\mu_+ = 1.3 \times 10^{-4}$ cm$^2$/V s, $\mu_- = 2.8 \times 10^{-4}$ cm$^2$/V s (for O$^{•-}$ and $N_2O^{•-}$),[1] and $\epsilon = 2.175$[18] (calculated for an ideal solution). We used an $r^2$ Gaussian distribution of electrons with $b_G \approx 5.84$ nm, which corresponds to a free ion yield of 0.12−0.13 molecule/100 eV.[1,18] For $t < 0.5$ $\mu$s, the agreement between the experimental and theoretical curves is good. At later times, the agreement is less satisfactory due to second-order neutralization which is not included in the model.

The effect of perylene concentration with no toluene is shown in Figure 2a. Without toluene the formation of Pe$^{•+}$ is much faster and more Pe$^{•+}$ is formed, which indicates rapid scavenging of the precursor radical cation. To fit these kinetics we used a Monte Carlo program.[16] The curves shown in Figure 2 are not corrected for the response function of the photodiode, as the curves in Figure 1b were. The kinetics were fit assuming that the solvent radical cation transfers charge to perylene with a rate constant of $8.5 \times 10^{10}$ mol$^{-1}$ dm$^3$ s$^{-1}$ (consistent with scavenging constants observed for HMI by dc conductivity) and decays with rate constant ~ (6−7) × $10^6$ s$^{-1}$ in other reactions. The latter constant is 4−5 higher than that observed for the first-order decay of HMI in photoconductivity experiments. However, at our dose (~0.1 kGy/pulse) the lifetime of HMI must be reduced by recombination with free anions (~$10^{-6}$ mol dm$^{-3}$) which proceeds with rate constant ~$2.3 \times 10^{12}$ mol$^{-1}$ dm$^3$ s$^{-1}$ (estimated from the Debye equation[1]). Additionally, the lifetime of HMI is shortened by reactions with radiolytic products.[9] In oxygen-saturated *cis*-decalin, the yield of octalins and decalin dimers is 0.86 and 0.24 molecule/100 eV, respectively.[19] Assuming that the overall yield of these scavengers is ~1 molecule/100 eV and that the scavenging constant is ~(6−7) × $10^{10}$ mol$^{-1}$ dm$^3$ s$^{-1}$ we obtain the first-order constant ~(8−9) × $10^5$ s$^{-1}$. In sum, these reactions account for the decay constant ~$4.5 \times 10^6$ s$^{-1}$; the actual lifetime of HMI must be shorter since some geminate ions in overlapping spurs can also recombine.

## Conclusion

Fast optical spectroscopy was used to demonstrate that the long-lived high-mobility ions observed in conductivity experiments are indeed the solvent radical cations of decalins. Our result supports the view that high-mobility ions in cyclohexane are also the solvent radical cations whose behavior is complicated by the involvement of a conformer.[4,5]

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