Hole Injection and Formation of Polarons in Cycloalkane Liquids[†]

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In several cycloalkanes, ionization of the solvent or photoexcitation of a solute radical cation results in the formation of rapidly hopping solvent holes. Here we report the temperature dependence of scavenging rate constants and conductivity signals (220 to 350 K) for the solvent holes in liquid cyclohexane, methylcyclohexane, and Decalins. Our results indicate that the hopping in Decalins and methylcyclohexane is thermally activated; the activation energies are of the same order as the energy of solvent reorganization. In cyclohexane, the hopping does not seem to be thermally activated. We discuss the hypothesis that the mobile solvent holes in cycloalkanes are small polarons migrating by phonon-assisted hopping.

Introduction

Ionization of a hydrocarbon liquid results in the formation of electron−hole pairs. The valence band (vb) hole rapidly thermalizes and yields molecular ions.[1] At room temperature, the mobility of these ions (self-trapped holes) is low (10^{-5}−10^{-3} cm^2/Vs), and their migration is controlled by diffusion of the solvent molecules.[2] There is, however, a striking exception to this rule.[3] In several cycloalkanes (cyclohexane,[3a] methylcyclohexane,[3b] and *cis*- and *trans*-Decalins[3d,e]), the cations observed 0.1−1 μs after the ionization event exhibit much higher mobility ($\sim 10^{-2}$ cm^2/Vs).[1−8] This high mobility excludes Brownian diffusion as possible migration mechanism. In scavenging reactions with solutes, these mobile carriers exhibit the properties of a radical cation[4,5] and have been identified as the solvent holes. From conductivity studies, it was found that the mobility of the holes has either zero or negative activation energy.[3b−e] On the basis of these observations it was speculated that the holes migrate by hopping between neighboring molecules.[1,2] In such a case, the residence time of the positive charge on a given molecule is 0.5−2 ps, which indicates a very efficient electron transfer.

In this paper we address the questions of the attributes of mobile solvent holes and the mechanism of their migration. Specifically, we consider the temperature dependences of conductivity and reactivity of the solvent holes in cycloalkane liquids. Our results suggest that these holes are small polarons and that the mechanism of their migration is phonon-assisted hopping.

Background

Radical Cations of Cycloalkanes. A solvent hole in a molecular liquid is thought of as a *radical cation* that is localized on a single solvent molecule. In such a case, the thermalization of the hole can be regarded as a change in the molecular geometry in response to the charge. Warman[2] suggested that the fast hopping of the solvent holes in cycloalkanes is due to
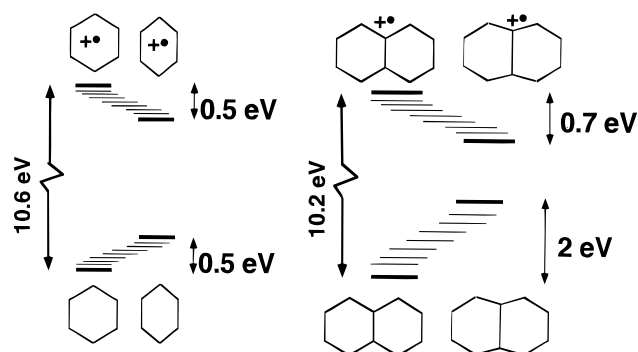

Figure 1. *Left:* The energy diagram for D_{3d} (chair) and C_{2h} (extended chair) forms of isolated cyclohexane and cyclohexane radical cations, as calculated using optimization with MINDO/3. The C_{2h} state is the lowest-energy state of the radical cation. Many more geometries exist for the molecule and the ion, which fill the gap between the chair and the extended chair states. *Right:* The same calculation, for *trans*-Decalin.

close geometries of the relaxed radical cations and parent molecules. This "close geometry" view, however, is not consistent with the data on the structure and energetics of the involved species.

Consider, for example, cyclohexane. Its lowest energy state, the chair form, has D_{3d} symmetry. Upon ionization, the chair form becomes unstable toward the ring distortions, due to the Jahn−Teller effect.[9] From electron paramagnetic resonance (EPR) spectroscopy and quantum chemistry calculations, it is known that the radical cation relaxes to the extended chair conformation with reduced symmetry.[9,10] Though the elongation of the C−C bonds is not >2%, this relaxation decreases the energy considerably. Semiempirical calculations indicate that the stabilization energy is ∼0.5 eV (Figure 1). This estimate is reasonable, because it is close to the width of the vb edge, as observed by photoelectron spectroscopy,[11] and to the difference between adiabatic and vertical ionization potential (IP), as determined by mass spectrometry.[12] The same calculation indicates that 0.4−0.5 eV is required to stretch the neutral chair form molecule to the extended chair configuration. Similar numbers were obtained for methylcyclohexane.

For *cis*- and *trans*-Decalins, the changes in the geometry are more pronounced. Upon ionization, the C−C bond that bridges two rings extends from 0.153−0.156 nm to 0.19−0.21 nm.[13]

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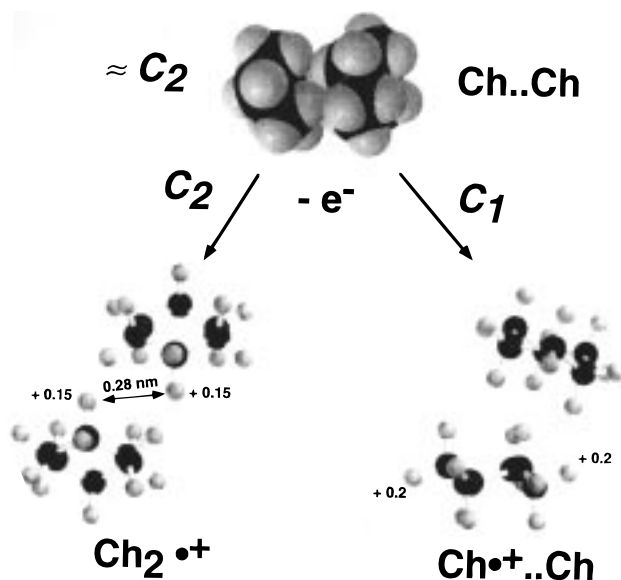‡ Permanent address: Institute of Low Energy Nuclear Physics, Beijing Normal University, Beijing, China.

Figure 2. Geometries of a neutral van der Waals complex of two cyclohexane molecules, Ch..Ch (with the C_2 symmetry and binding energy of 45 meV), and two of its charged states, a symmetric $Ch_2^{\bullet+}$ state and an asymmetric $Ch^{\bullet+}$..Ch state. The geometries where optimized using semiempirical AM1 calculation. The labels near axial hydrogens indicate their charge. In the $Ch_2^{\bullet+}$ state, the charge is shared between the inbound axial hydrogens that belong to different molecules; in the $Ch^{\bullet+}$..Ch state, the charge resides at the axial hydrogens of the $Ch^{\bullet+}$ fragment. The symmetric state is by 0.15 eV more energetic than the asymmetric state.

The stabilization energy of the radical cation is ∼0.7 eV; the neutral state that has the geometry of the radical cation is ∼2 eV above the ground state (Figure 1). These energies are considerably higher than the ones obtained for aromatic radical ions that undergo resonant charge transfer in solution (∼0.1−0.2 eV).

This brief consideration indicates that in the gas phase, a direct electron transfer from the ground-state molecule to the relaxed radical cation is endothermic by at least 1 eV. At room temperature, $kT \approx 25$ meV, and no thermal activation would make such an electron-transfer feasible. Thus, the "close geometry" argument is not acceptable.

In the gas phase, weakly exothermic charge transfer ($\Delta G° \approx -24$ meV)

$$c\text{-}C_6D_{12}^{\bullet+} + c\text{-}C_6H_{12} \rightarrow c\text{-}C_6D_{12} + c\text{-}C_6H_{12}^{\bullet+} \qquad (1)$$
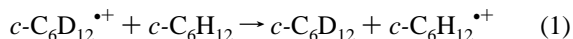
proceeds with the rate equal to ∼1/3 of the collision rate.[14] Lias et al.[14] explained this efficiency through the formation of a metastable collision complex (a dimer ion) in which the reactants have increased time to overcome the restrictive conditions through a concerted change in their geometry. This result implies a good coupling between the ion and the molecule in the collision complex and sharing of charge between the molecules in the complex.

To estimate this coupling, we studied the energetics of a van der Waals complex of two chair-form cyclohexane molecules, using a semiempirical AM1 method (Figure 2). The neutral Ch..Ch complex was found to have C_2 symmetry (or a slightly broken C_2 symmetry), with the energy of intermolecular interaction being ≈50 meV. Upon charging the complex, the initial C_2 symmetry can either be retained (in which case one obtains a state in which the charge is equally divided between the monomers, $Ch_2^{\bullet+}$) or broken (in which case one obtains a van der Waals complex of a monomer ion and a neutral
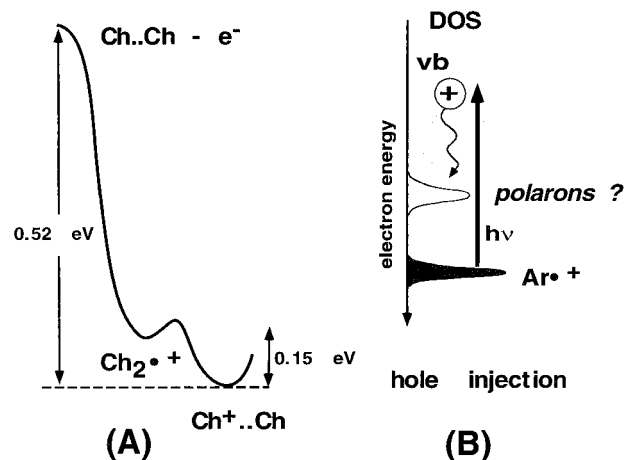

Figure 3. (A) Schematic energy diagram for the states of dimer ion shown in Figure 2. (B) A schematic representation of photoinduced hole injection. Photoexcitation of a solute radical cation (a defect state in the midgap) follows the electron transfer and formation of the hole in the upper valence band of the solvent (the density of states function is sketched).

molecule, $Ch^{\bullet+}$..Ch). We optimized the geometry for both of these states and found that the latter is lower than the former by ∼0.15 eV, whereas the stabilization energy of the $Ch^{\bullet+}$..Ch state is ∼0.52 eV (Figure 3a). For both of these states, the changes in the bond lengths, relative to those in a neutral molecule, are very small (<2%), and the difference in their energy comes from the way the positive charge is spread over the complex. In the $Ch^{\bullet+}$..Ch state, as in the monomer radical cation, the maximum charge is at axial hydrogens along the elongation coordinate (∼+ 0.2e); in the neutral monomer, the corresponding hydrogens have charges of + 0.05e. In the symmetric $Ch_2^{\bullet+}$ state, the inbound axial hydrogens have a charge of + 0.15e (Figure 2), and the outbound hydrogens have a charge of + 0.07e. Most of the excess energy of the $Ch_2^{\bullet+}$ state comes from the repulsion between these inbound hydrogens. In less symmetric states, intermediate to the $Ch^{\bullet+}$..Ch and $Ch_2^{\bullet+}$ states, this repulsion is decreased; apparently, one of these states mediates the electron transfer. Though we cannot indicate which state that is, our modeling suggests that there are states nearby the ground $Ch^{\bullet+}$..Ch state of the dimer ion in which there is a considerable partition of positive charge between the monomers. Fast electron transfer (1) is possible because such states exist.

Polaron Transport. Something quite similar occurs in larger clusters of cycloalkane molecules, in the liquid. In a cluster, there are many other solvent molecules with which to share a charge, so the solvent hole will exist as a *small polaron* − a charge that is coupled to the "lattice" and shared between several solvent molecules at once.[15] At no point is the hole localized on a single molecule as a molecular ion.

The idea that in liquid cycloalkanes the stabilization of solvent holes occurs through delocalization of charge has already been considered by Warman.[2] This idea was invoked to explain unusually large reaction radii of hole scavenging by low-IP solutes (such as aromatic molecules).[2,3c] Later, Sauer et al.[6,8] reconsidered these data and concluded that the scavenging radii do not exceed ∼1 nm, which is typical for electron tunneling reactions in liquid. We believe it unrealistic to assume that the hole is delocalized over >2−5 solvent molecules; such delocalization would have little effect on the scavenging radii. Still, the delocalization of the hole−the polaron − can be observed experimentally (vide infra).

The polaron migrates rapidly because only a fraction of the total charge resides at a given solvent molecule. A passage of this fractional charge to a neighboring molecule requires little structural or energy relaxation. Still, one would expect that it requires some relaxation. In the high-temperature regime, $T \gg \Theta_D/2$, where Θ_D is the Debye temperature (which for hydrocarbons is ~130 K),[16] *the migration of small polarons is thermally activated*, and the activation energy is ~1/2 of the lattice deformation energy.[15,17] In the liquid, the latter can be identified with the solvent reorganization energy (in the theory of Marcus).[18] In nonpolar media, this energy is usually ~50−100 meV.

Phonon-activated hopping is not the only mode of small polaron migration, though it is most frequently observed in *disordered* solids.[15] At low temperature ($T < \Theta_D/2$), the activation energy of hopping may decrease dramatically to a fraction of 1 meV[19] (Matyama and Funabashi[20] observed this behavior for electrons in glassy 3-methylpentane). At these low temperatures, the hopping may also become percolative[21] or distance dependent;[22] in this case, $\ln \mu \propto - 1/T^n$, where n is between 0.25 and 0.5.[23] Under certain conditions (e.g., weak coupling to the lattice), the polaron migrates as a quasiparticle. In this case, the drift mobility μ *decreases* with temperature because the scattering of the polaron wave function by phonons shortens the free path of the quasiparticle.[17] This band-type migration occurs in ionic crystals over a wide range of temperatures or in any perfect crystal at sufficiently low temperature. Due to potential fluctuations, this transport mechanism does not occur in disordered media.

In some solids, such as organic molecular crystals, the drift mobility of charge carriers decreases with temperature even for $T \gg \Theta_D$ (see chapters 5 and 7 in ref 24 for a review). The charge transport in these solids is of the tunneling type, but the details of the transport mechanism are not well understood. The models reviewed by Movaghar[25] and Kenkre and Dunlap[26] fall into two classes: (i) the band-type transport with a heavy quasiparticle and (ii) the "intermediate" small polaron. In *disordered* molecular solids (such as doped polymers), no such behavior has ever been observed. In the high-temperature regime, the drift mobility of the charge carriers is always activated. However, there are disordered solids that do not exhibit phonon-activated hopping: In some amorphous semiconductors (such as a-As₂Te₃) a "$\ln \mu \propto T$" behavior is observed.[28] Hurd[28] explained this behavior by tunneling of the polarons over a potential barrier whose width varies with lattice vibrations (this theory was criticized by Emin[29]). Another theory that predicts the decrease of μ with temperature at $T > \Theta_D$ is the model of *correlated* hopping in which the relaxation time of the lattice site visited by a polaron is longer than the hopping time.[30] In such a case, the polaron has higher probability to hop back to the previous site, which results in the higher rates of migration. Due to fast vibrational and rotational relaxation of molecules in liquid, such a regime cannot occur in cycloalkanes.

All of these theories were developed for solids, crystalline or disordered, which are poor reference systems for molecular liquids. The observations of thermally activated hole hopping in most amorphous solids suggest that this mode of polaron transport should also prevail in liquids. The known examples of small polarons in liquids (such as solvated electrons in water and alcohols) exhibit precisely this type of transport behavior. In nonpolar liquids, such as cycloalkanes, electron conduction is due to thermal activation of localized charges across the mobility edge to the conduction band.[2] For the solvent holes,

a similar process would require activation energies in excess of 0.5 eV (vide supra); that is, the modes of electron and hole hopping in cycloalkanes must be quite different.

When the interaction between the hole and the solvent is weak, the activation energy E_a of hopping may be so low that other hopping parameters, such as the site-to-site distance, coupling integral, etc., may have stronger temperature dependences than the exponential factor $\exp(-E_a/kT)$. In particular, thermal expansion of the liquid increases the average distance between the solvent molecules, which may result in higher rates of migration even if the hopping frequency stays the same. Thus, the temperature dependence of the drift mobility is of much importance, as it points to a class of the charge transport theories that can be applied to a given system.

Temperature Dependence of μ_h. Warman studied the temperature dependence of mobility (μ_h) of the solvent holes in cyclohexane and *trans*-Decalin, by using transient microwave conductivity − pulse radiolysis, and found that for both of these cycloalkanes, μ_h *has a negative activation energy of* 2−3 kJ/mol.[2,3b,3d] The problem with these measurements is that the quantity obtained is actually not the mobility μ_h by itself but the conductivity $\sigma_h \propto \mu_h C_h$, where C_h is the concentration of the solvent holes. Warman assumed that the C_h is equal to the total concentration of ions, implying that every ionization event results in the formation of a mobile solvent hole. This assumption may be incorrect, as suggested by later observations.[5−8] For example, in room-temperature radiolysis of cyclohexane and methylcyclohexane, the fraction ϕ_h of cations that are mobile solvent holes, is not >0.5.[5,6] If the fraction ϕ_h of the solvent holes in radiolysis is temperature dependent (e.g., due to a change in the efficiency of thermalization of the vb hole), the results on μ_h are flawed because it is the product of the yield *and* mobility that is measured in the conductivity experiments.

A recent transient absorption/pulse radiolysis study by Bühler and co-workers[31] points to such a possibility. They studied ion recombination from 130 to 150 K in methylcyclohexane.[31a] This recombination is part nonhomogeneous, part homogeneous. From the observed kinetics of recombination, the mobilities of the ions can be estimated. The diffusion coefficient D_h of the solvent holes was obtained by complex multiparameter fitting of the transient absorption kinetics at 570 nm, where methycyclohexane•⁺ is expected to absorb. Though it was not explicitly stated in the article, the fitting was done with the assumption of a long lifetime of the mobile solvent hole (>10 μs). This was not, however, elaborated upon. If the mobile solvent hole had a short (~1 μs) lifetime (as suggested by our own low-temperature dc photoconductivity data), the decay kinetics would not obey the equations used in ref 31a.

In their latest work, Bühler and Katsumura[31b] proposed a new kinetics scheme in which one of the cations derived from the solvent (methylcyclohexane) has a short lifetime of ~3 μs (at 143 K). They suggested that this cation is an excited solvent hole that either relaxes yielding the (high mobility) ground-state hole or fragments yielding methylcyclohexene•⁺. This relaxation is mediated by N₂O; the relative yields of the ground-state solvent hole to the olefin cation were determined as 3:2 in N₂O-saturated solution and 9:1 in argon-saturated solution.[31b] It is not clear how this new interpretation changes the results of ref 31a on the temperature dependence of D_h. From the data of refs 31a and 31b, it appears that there are at least three radical cations formed upon radiolysis of methylcyclohexane. We find it hard to accept the suggestion of Bühler and Katsumura that an electronically or vibrationally excited radical cation may live

TABLE 1: Activation Energies of the Photoconductivity Signals and Mobilities of Excess Electrons, Solute Ions, and High Mobility Solvent Holes in Cycloalkanes[a]

activation energy, kJ/mol	*trans*-Decalin	*cis*-Decalin	methylcyclohexane	cyclohexane
electrons, σ_e	30 ± 1	15.7 ± 1	21.9 ± 0.5	20 ± 1
ions, σ_i	25 ± 0.5	23.1 ± 0.6	17.5 ± 0.5	22 ± 2
holes, $\Delta\sigma$	9.1 ± 0.3	11.3 ± 0.8	11.7 ± 0.5	4.4 ± 2
$\phi_h\mu_h/\mu_i$	−16 ± 0.5	−12 ± 1	−6 ± 1	−14.4 ± 1.5
μ_e	*19.6 ± 0.8*[b]	*11.4 ± 1.2*[c]	17 ± 1	*12.3*[b]
	14 ± 2[d]	**19 ± 3**[d]	~12	*11.6*[b]
μ_i	*10.3 ± 0.5*[b]			
μ_+	**13.7 ± 1**[e]	**21.2 ± 0.7**[e]	**11.9 ± 0.4**[e]	**11.4 ± 0.6**[e]
	13.2 ± 0.4[f]	*20.2 ± 0.7*[f]		*12.1 ± 0.2*[f]
$\phi_h\mu_h$[g]	**−3 ± 1**	7 ± 2	**6 ± 1**	−3 ± 2
	−2.6 ± 1.2[b]			*0 ± 2*[b]
Y_i[h]	10.4 ± 2[i]	4.3 ± 2.2[i]	5.5 ± 1	10 ± 1[i]
k_s	8.9 ± 1.2[j]	5.4 ± 0.5[j]	3.9 ± 0.2[k]	−1.5 ± 1.4[j,k]

[a] See figs 3, 4, and 5 for the temperature ranges; the error limits represent the standard deviation in the Arrhenius plot; data taken from the literature are in italics. [b] From Tables 3 and 4 in ref 2. [c] From the rate constants of electron scavenging by dinitrobenzene. [d] $E_a(\mu_i) = E_a(\sigma_i) - \{E_a(\sigma_e) - E_a(\mu_e)\}$. [e] From our time-of-flight photoconductivity measurements, Figure 3b. [f] From ref 20. [g] $E_a(\phi_h\mu_h) = E_a(\sigma_h) - E_a(Y_i)$. [h] $E_a(Y_i) = E_a(\sigma_i) - E_a(\mu_i)$. [i] In radiolysis of Decalins and cyclohexane, $E_a(Y_i)$ are 6.2 ± 0.2 kJ/mol and 10.3 ± 0.6 kJ/mol, respectively.[35] [j] Scavenging by triphenylene. [k] Scavenging by *trans*-Decalin.

for several microseconds. Most likely, the short-lived species is the solvent hole, and the "long-lived solvent hole" is a secondary cation other than methylcyclohexene•+. In such a case, the activation energy of D_h reported in ref 31a would be that for the diffusion of a molecular cation rather than the solvent hole. As shown next, this is indeed the case (Table 1). Using their old method, Bühler and co-workers[31a] estimated *that the diffusion of the holes is activated, with* $E_a \approx 9$ kJ/mol.

Because of the importance of this activation energy and uncertainties in the results of Warman and co-workers and Bühler and co-workers, we undertook more accurate and direct measurements over a wide temperature range. To this end we used a two-color laser experiment ("hole injection", Figure 3b) whose details have been discussed in refs 7 and 8.

Hole Injection. As was shown in ref 7, the 2.3 eV laser excitation of aromatic radical cations (Ar•+) results in hole injection, a transfer of the vb electron from the solvent to the excited cation [Ar•+]*. The quantum yield of free solvent holes is low (~5−10%), due either to inefficient electron transfer or due to poor separation of the solvent hole and the aromatic molecule (Ar) after the transfer.[32] The formation of the high-mobility solvent hole is induced by absorption of a single 2.3 eV photon. We estimate that the excess energy of the vb hole immediately after the forward transfer is ~0.3 eV for cyclohexane and methylcyclohexane[7] and ~0.9 eV for Decalins.[8] Apparently, this excess energy is sufficient for some holes to migrate away from the Ar molecule and avoid the backward transfer.

The injection results in an almost instantaneous generation of high-mobility solvent holes (on the time scale of a few picoseconds).[32] In ref 7, we reported the observations of the solvent holes in cyclohexane; in ref 8 and this work we extend these observations to methylcyclohexane and *cis*- and *trans*-Decalin. The latter three liquids are easier to use for temperature-dependence studies, because cyclohexane freezes at +6.5 °C and becomes too volatile 40−50 °C above room temperature.

The hole injection experiment is done as follows: A short pulse of 5 eV photons is used to photoionize 1−10 μM of aromatic solute in the cycloalkane solution. The solution is saturated with CO_2 to scavenge free electrons (whose lifetime under these conditions is <1 ns). A pulse of 2.3 eV light is applied at a delay time when the conductivity signal σ_i induced by the 5 eV light pulse has decayed to a plateau. At this delay time (~1 μs), the geminate ions are gone and the mobile solvent
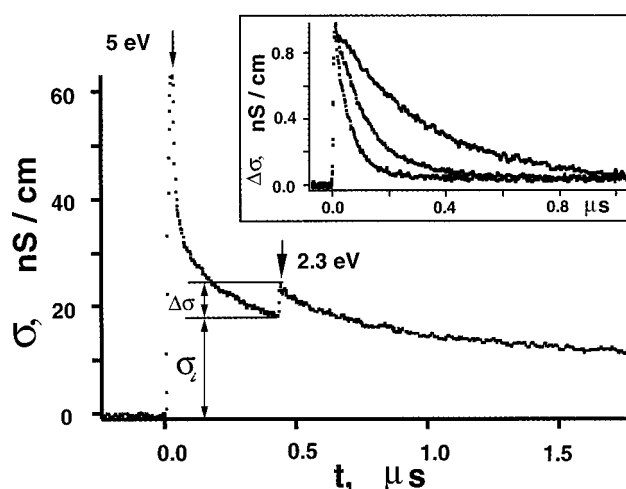

Figure 4. Conductivity signal, σ, observed in room-temperature CO_2-saturated methylcyclohexane solution containing 8 μM triphenylene. The delay time of the 2.3 eV light pulse is 0.5 μs after the 5-eV light pulse. The insert is the difference signal, $\Delta\sigma$, from the 2.3-eV laser excitation that shows the decay of the conductivity from the rapidly migrating solvent holes; the methylcyclohexane solution contained 4, 65, and 130 μM of the solvent hole scavenger (*trans*-Decalin).

holes (generated by three-photon excitation of the solute) have mostly been scavenged. The residual dc conductivity is due to ~10^{-8} M of long-lived solute ions, such as Ar•+, Ar₂•+, and CO_2•−, which slowly recombine over 1 to 10 ms. On the time scale of hole scavenging (0.1−1 μs), this recombination is negligible. At room temperature, the combined mobility $\mu_i = \mu_+ + \mu_-$ of molecular ions is (3−9) × 10^{-4} cm²/Vs (Table 4 in ref 2) and the anion makes a somewhat larger contribution to μ_i than the cation. The dc conductivity σ_i of the solution is equal to $\sigma_i \propto C_i \mu_i$, where C_i is the concentration of molecular ions.

The 2.3 eV photons absorbed by Ar•+ induce a dc conductivity signal due to the solvent hole. This signal can be observed over 1−2 μs, until the holes are scavenged by the solute or impurities, or otherwise converted to normally diffusing ions (Figure 4). Immediately after C_h of the Ar•+ ions are converted to the solvent holes, the dc conductivity difference signal ($\Delta\sigma$) is given by $\Delta\sigma \propto C_h (\mu_h - \mu_+) \approx C_h \mu_h$. Neglecting the increase in the rate of homogeneous ion recombination, the decay kinetics of $\Delta\sigma$ are given by the decay kinetics of the solvent holes, $C_h(t)$ (Figure 4, *window*). In cyclohexane, these kinetics are

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biexponential, due to a dynamic equilibrium between the solvent hole and $\sim 10^{-3}$ M of 1,1- and 1,2-dimethylcyclopentane impurities.[7,33] In methylcyclohexane and Decalins, the $\Delta\sigma(t)$ kinetics are pseudo first-order; $\Delta\sigma = \Delta\sigma_0 \exp(-k_1 t)$. This makes the measurement of the second-order scavenging constants k_s very simple. We used 5–10 concentrations of the scavenger $[(0.05-2.5) \times 10^{-4}$ M] to determine k_s from the slope of the k_1 versus [scavenger] plots. The initial jump in the conductivity $\Delta\sigma_0$ following the hole injection was determined by extrapolation of the least-squares exponential fit to $t = 0$.

Experimental Section

Purification of the solvents was discussed in refs 8 and 33. Thirty-nanosecond full width at half-maximum (fwhm) pulses of 5 eV photons from a Lambda Physik LPX 120i laser were used to ionize 10 μM of triphenylene in CO_2-saturated solutions. The measurements of the electron mobility were done in argon-saturated solutions. The solutions were photolyzed in a 3-mL cell with 1-cm optical path. The cell has two planar platinum electrodes spaced by 0.6 cm to which a voltage V of 5 kV was applied. The cell was placed in an aluminum jacket; cold *n*-hexane (down to 220 K) was circulated through the jacket using a FMS Systems model MC880A1 cryogenic bath equipped with a pump. Above room temperature (up to 350 K), hot water was circulated. The temperature inside the cell was calibrated with a thermocouple probe inserted between the electrodes; this probe was removed during the photoconductivity measurement; the readings in the cell were within ± 1 K of the temperature of the jacket. The 5-eV pulse entered the cell from one end; a 3-ns fwhm pulse of 2.3-eV photons from a Continuum model 8010 Nd:YAG laser entered it from the opposite end; both fluences were ~ 0.2 J/cm^2. The dc signal was amplified and recorded on a DSA-601 signal averager.

Time-of-flight conductivity was measured using a similar 2-cm path length cell in which the spacing between the electrodes was reduced to $L = 780$ μm (the maximum electric field, $E = V/L$, was 65 kV/cm). Due to their short lifetime (~ 0.2 μs), the solvent holes travel only 1–3 μm and their flight cannot be observed with our setup. The flight of (stable) solute ions with mobilities $\sim 10^{-5}-10^{-3}$ cm^2/Vs was observed on a time scale of milliseconds (Figure 5a). The ions were generated by photoionization of 0.7 mM triethylamine in CO_2-saturated cycloalkane. Triethylamine was chosen because (i) it has a low IP (it scavenges the impurity cations in several microseconds), (ii) its radical cation does not dimerize, and (iii) it has weak absorption at 248 nm, $\epsilon \approx 70$ M^{-1} cm^{-1} (the ions are formed uniformly along the optical path of the laser beam). The fluence of 5 eV light was $(1-3) \times 10^{-2}$ J/cm^2; the concentration of free ions, extrapolated to zero field, was 0.1–0.3 nM. Upon generation, the ions filled the space between the electrodes uniformly. Low ion concentration is required to reduce the effects of homogeneous recombination and space charge. The dc signal from the cell was terminated into 10 kΩ load resistor, amplified 10 times using a home-built low-noise preamplifier, and recorded using a Tektronix TDS-360 oscilloscope. Twenty to 50 traces were averaged to reduce the noise due to small dielectric breakdowns in the solution. The flight of triethylamine$^{\bullet+}$ was observed over 3–200 ms, depending on the temperature of photolyzate; the decay of $CO_2^{\bullet-}$ was 2–3 times faster. Typical traces, for 25 and 65 kV/cm fields are shown in Figure 5a. The cation mobility, μ_+, was determined from the time-of-flight τ using the equation $\mu_+ = L^2/\tau V$. The data on mobility of triethylamine$^{\bullet+}$ in different cycloalkanes are compiled in Figure 5b and Table 1. The mobility μ_- of anions (which is 2–3 times higher than μ_+) can also be determined
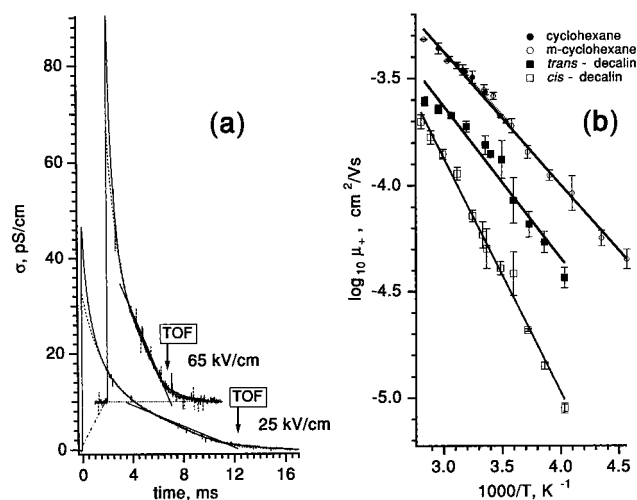

Figure 5. (a) Time-of-flight dc conductivity observed upon 5-eV photoexcitation of 0.7 mM of triethylamine in CO_2-saturated (dashed lines) and N_2O-saturated (solid lines) cyclohexane at 25 °C. Under the conditions of our experiment, the initial concentration of free ions is 0.1–0.2 nM. The decay kinetics follow the flight of the ions and their neutralization at the electrodes. After rapid decay of anions ($CO_2^{\bullet-}$ and $O^{\bullet-}$, $\mu_- \approx 6 \times 10^{-4}$ cm^2/Vs), the conductivity signal is from slowly decaying solute cation(s) with $\mu_+ \approx 2.7 \times 10^{-4}$ cm^2/Vs; most of this signal must be from triethylamine$^{\bullet+}$. The time-of-flight (TOF) was determined by extrapolation of the linear part of the decay curve (as shown in the figure) and correlated with the electric field (indicated next to the traces). (b) Temperature dependence of μ_+ for cyclohexane, methycyclohexane, and Decalins. The mobility of the solute cation was determined by the time-of-flight photoconductivity. At 25 °C, the μ_+ are 2.7×10^{-4} cm^2/Vs (cyclohexane and methylcyclohexane), 1.55×10^{-4} cm^2/Vs (*trans*-Decalin), and 5×10^{-5} cm^2/Vs (*cis*-Decalin); the activation energies are given in Table 1.

from our time-of-flight data; however, these measurements are less accurate due to recombination of anions with cations during their flight. Therefore, rather involved fitting routines are needed to determine μ_-. From the computer simulations, we found that within the accuracy of our measurement, the temperature behavior of μ_- and μ_+ in cycloalkanes closely resembles each other, which is in full agreement with previous observations by Allen et al.[34] For this reason, we took the temperature dependence of μ_i as that of μ_+.

Results and Discussion

Temperature Dependence of the dc Conductivity. For $\mu_h \gg \mu_+$, the relative increase in the conductivity $\Delta\sigma/\sigma_i \approx C_h/C_i \{\mu_h/\mu_i\}$ (hereafter, we drop the index for $\Delta\sigma_0$). Because the C_h/C_i ratio is unknown, μ_h/μ_i cannot be determined directly. It is reasonable to assume that the quantum yield of hole injection is determined by the photophysics of electron transfer and is temperature independent, and that the relative yield of mobile holes ϕ_h can be temperature-dependent. With these assumptions, the temperature dependence of $\Delta\sigma/\sigma_i$ is the same as that of $\phi_h\mu_h/\mu_i$. Guided by the same logic, we can determine the temperature dependence of the ratio μ_e/μ_i of the electron and molecular ion mobilities from the ratio of the conductivity signals σ_e/σ_i because both σ_e and σ_i are proportional to the free ion yield, Y_i (which is independent of the mobility of the ions):[2]

$$\Delta\sigma \propto \phi_h\mu_h Y_i \qquad (2)$$

$$\sigma_i \propto \mu_i Y_i \qquad (3)$$

$$\sigma_e \propto \mu_e Y_i \qquad (4)$$

Provided that the temperature dependences of the mobilities μ_h, μ_i, and μ_e and the free ion yield Y_i exhibit Arrhenius behavior,
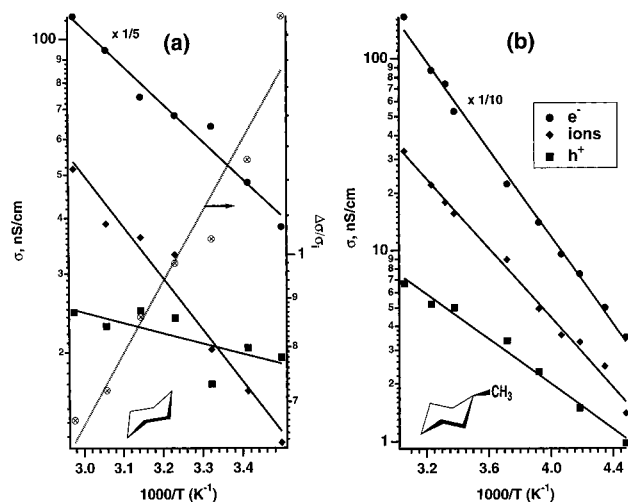
Figure 6. Temperature dependence of the dc conductivity signals σ_i (filled rombs), σ_e (filled circles), and $\Delta\sigma$ (filled squares) for (a) cyclohexane and (b) methylcyclohexane containing 8 μM of triphenylene. The signals were obtained under the same irradiation conditions. The electron signals σ_e were observed in Ar-saturated solution (these signals are scaled for convenience); σ_i and $\Delta\sigma$ were determined in CO_2-saturated solutions. All of these signals demonstrate Arrhenius behavior. For cyclohexane, the ratio $\Delta\sigma/\sigma_i$ is also plotted (open circles with crosses).
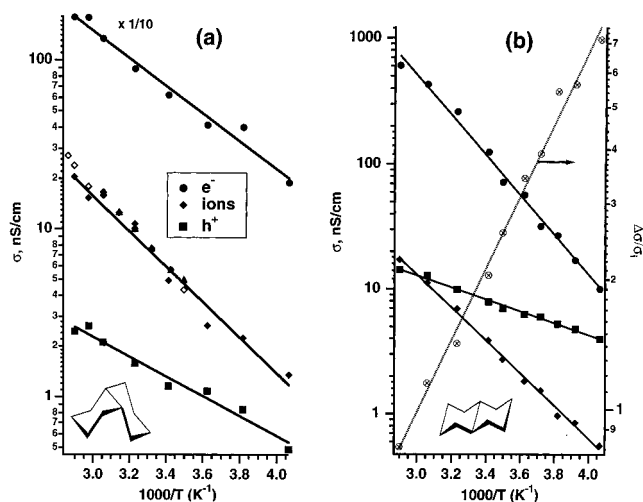

Figure 7. Temperature dependence of the dc conductivity signals σ_i, σ_e, and $\Delta\sigma$ for (a) *cis*- and (b) *trans*-Decalin (see caption to Figure 4). For *cis*-Decalin, σ_i determined in Ar-saturated (filled triangles) and N_2O-saturated (open rombs) solutions is shown along with the σ_i obtained in the CO_2-saturated solution.

the corresponding activation energies E_a can be calculated from

$$E_a(\Delta\sigma) = E_a(\phi_h\mu_h) + E_a(Y_i) \tag{5}$$

$$E_a(\sigma_i) = E_a(\mu_i) + E_a(Y_i) \tag{6}$$

$$E_a(\sigma_e) = E_a(\mu_e) + E_a(Y_i) \tag{7}$$

To estimate $E_a(\phi_h\mu_h)$, one needs to determine $E_a(\Delta\sigma)$ and use $E_a(Y_i)$ calculated from eq 8

$$E_a(Y_i) = E_a(\sigma_i) - E_a(\mu_i) = E_a(\sigma_e) - E_a(\mu_e) \tag{8}$$

Figures 6 and 7 show the temperature dependence of $\Delta\sigma/\sigma_i$ ratios and $\Delta\sigma$, σ_i, and σ_e signals in Decalins, cyclohexane, and methylcyclohexane. Each of these signals follows Arrhenius
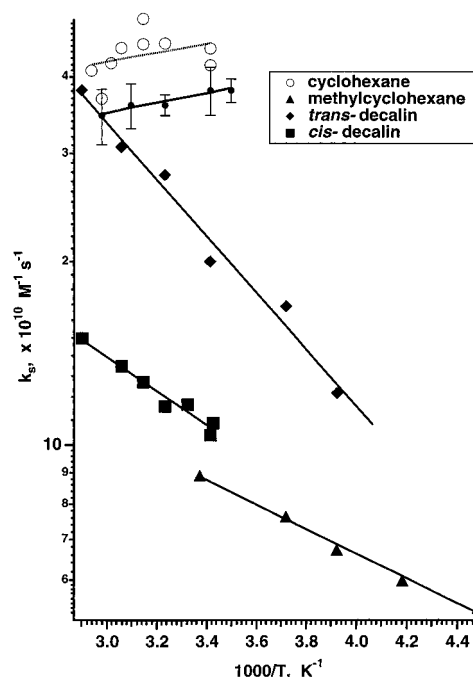

Figure 8. Temperature dependence of the scavenging rate constant k_s for solvent holes in cyclohexane (filled and open circles), *trans*-Decalin (filled rombs), *cis*-Decalin (filled squares), and methylcyclohexane (filled triangles). In Decalins, the holes were scavenged by triphenylene, in methylcyclohexane, the holes were scavenged by *trans*-Decalin (which exhibits the highest rate of scavenging observed in this solvent),[7] and in cyclohexane, the holes were scavenged by *trans*-Decalin (filled circles with error bars) and triphenylene (open circles).

behavior. These results allow accurate determination of the activation energies for μ_h, μ_i, and μ_e, providing that at least one of these energies is known.

Consider, for instance, *trans*-Decalin. In this solvent, σ_e increases with temperature with an activation energy of $\approx$30 kJ/mol (Table 1). Warman reported an activation energy for μ_e of 19.6 kJ/mol (Table 3 in ref 2). Hence, $E_a(Y_i) \approx 10.4$ kJ/mol. Using this and the activation energy for σ_i of 25 kJ/mol, we obtain $E_a(\mu_i) \approx 14$ kJ/mol. According to Warman, $E_a(\mu_i) \approx 10.3$ kJ/mol (Figure 10 in ref 2), whereas Gee and Freeman[35] give $\approx$13.2 kJ/mol (for μ_+ only). Our time-of-flight measurement over the studied temperature range gives $E_a(\mu_+) \approx 13.7 \pm 1$ kJ/mol; most of the uncertainty is due to deviations from Arrhenius behavior (Figure 5b). Given the uncertainties involved in these measurements, the agreement is reasonable. Because the $\Delta\sigma/\sigma_i$ ratio (which changes with temperature as $\phi_h\mu_h/\mu_i$) has an activation energy of -16 kJ/mol, $E_a(\phi_h\mu_h)$ is negative no matter which estimate for $E_a(\mu_i)$ is used. Using our estimate, we obtain $E_a(\phi_h\mu_h) \approx -2 \pm 1$ kJ/mol for *trans*-Decalin, which is close to $E(\sigma_h/Y_i) \approx -2.6 \pm 1.2$ kJ/mol given by Warman.[2,3e] Similar correspondence was observed for cyclohexane, also studied by Warman and co-workers.[2,3b,3c] Thus, both the light-induced hole injection and radiolysis yield the same temperature dependence for $\phi_h\mu_h$ for cyclohexane and *trans*-Decalin. Previously, we found that at room temperature, $\Delta\sigma/\sigma_i$ is linearly proportional to $\phi_h\mu_h/\mu_i$ as determined by pulse radiolysis—transient microwave conductivity experiments.[8] The coefficient of proportionality is the same for all four of the cycloalkane solvents. These two observations give us confidence to use our approach to estimate $E_a(\phi_h\mu_h)$ in methylcyclohexane and *cis*-Decalin (Table 1).

For methylcyclohexane, no activation energies for μ_i and μ_e have been reported. From our time-of-flight measurements, we estimated that $E_a(\mu_+)$ is $\sim$12 kJ/mol; this energy was used as

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an estimate for $E_a(\mu_i)$. Then, using Table 1 we obtain $E_a(\phi_h\mu_h)$ $\approx 5-6$ kJ/mol. For *cis*-Decalin, no data on $E_a(\mu_e)$ are available. To estimate this energy, we determined reaction constants k_e for scavenging of excess electrons by dinitrobenzene. Assuming that the reaction is diffusion-limited and the scavenging radius is temperature-independent (that is, $\mu_e \propto k_e/T$), an activation energy $E_a(\mu_e)$ of ≈ 11.5 kJ/mol was estimated. The $E_a(\mu_i)$ calculated with this $E_a(\mu_e)$ (from eqs 6−8) is close to the $E_a(\mu_+)$ as determined by conductivity measurements, which indicates the overall consistency.
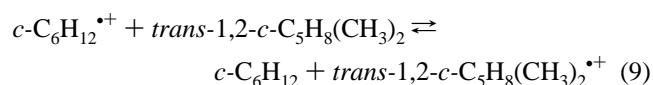
A surprising feature of Table 1 is that the activation energy $E_a(Y_i)$ for the free ion yield (determined with eq 8) is much different for different solvents, even for *cis*- and *trans*-Decalins. In radiolysis, the activation energies $E_a(Y_i)$ were the same for both Decalins (i.e., ~6 kJ/mol),[35] indicating the similarities in the distribution of the electron−hole pairs generated upon ionization. However, we cannot reconcile our data on σ_e, σ_i, and ion mobilities using this estimate or an assumption that $E_a(Y_i)$ for two Decalins is the same. Apparently, the distribution of electron−cation pairs upon photoionization of aromatic solutes is different from that in radiolysis, and more sensitive to the nature of the solvent.

Scavenging Constants (Figure 8 and Table 1). For methylcyclohexane, within the accuracy of our measurement, the activation energies of the rate constant k_s of hole scavenging and diffusion coefficient D_h (the same as the activation energy of the product $T(\phi_h\mu_h)$, assuming that $\phi_h(T) =$ constant and remembering that $D_h = [kT/e] \mu_h$) are the same, as expected for diffusion-controlled reactions. This activation energy is two times lower than the one estimated by Bühler and co-workers.[31] We believe our estimate is more accurate, at least in the temperature range covered in this work. The same behavior was observed for *cis*-Decalin. Apparently, for these two solvents, ϕ_h is temperature-independent and migration of the mobile holes is thermally activated.

A different pattern was obtained for *trans*-Decalin. Although the activation energy for $\phi_h\mu_h$ (determined from the $\Delta\sigma/\sigma_i$ dependence) is ≈ -3 kJ/mol, k_s has positive activation energy of ~9 kJ/mol. To explain these results with $\phi_h \approx 1$ (a value which appears to be valid at room temperature, refs 6 and 8), at 80−100 °C the scavenging radii must increase to 1.5−2 nm, which is unrealistically large. It makes more sense to assume that the reaction radii are still ≈ 1 nm, as at room temperature, and that the hopping is thermally activated. If that is true, the negative temperature dependence of $\phi_h\mu_h$ obtained from the conductivity measurements requires a negative activation energy for ϕ_h (≈ -10 kJ/mol).

Cyclohexane. A completely different pattern was observed for cyclohexane. The activation energy for k_s is slightly negative (-1.5 ± 1.4 kJ/mol) and the temperature dependences of $\phi_h\mu_h$ and k_s/T are the same within the experimental error. This result confirms the earlier observation by Warman and co-workers that the hopping[2,3b] and scavenging[3c] of cyclohexane hole have slightly negative or zero activation energies.

In cyclohexane, the decay of the solvent hole is bimodal, due to reversible trapping by 10^{-4} to 10^{-3} M of 1,1- and 1,2-dimethylcyclopentane impurity present in the cyclohexane solvent even after extensive purification:[33]

$$c\text{-}C_6H_{12}{}^{\bullet+} + trans\text{-}1,2\text{-}c\text{-}C_5H_8(CH_3)_2 \rightleftharpoons$$
$$c\text{-}C_6H_{12} + trans\text{-}1,2\text{-}c\text{-}C_5H_8(CH_3)_2{}^{\bullet+} \quad (9)$$

with $\Delta G° \approx -0.25$ eV. *trans*-1,2-Dimethylcyclopentane scavenges the solvent holes with a rate constant of $\approx 10^{10}$ M^{-1}

s^{-1} (the activation energy of this reaction is ≈ 20 kJ/mol). Therefore, the rate of scavenging by $10^{-4}-10^{-3}$ M of the dimethylcyclopentanes is comparable to that by $(1-5) \times 10^{-5}$ M low-IP solutes (such as triphenylene). The backward charge transfer occurs on the same time scale (the equilibrium constant for reaction 9 at 25 °C is $\approx 10^4$).[33] The resulting kinetics is bimodal: before the equilibrium is established, the decay of the solvent holes is faster than afterward. Consequently, the temperature dependence of k_s, as determined by exponential fitting of the initial part of the decay kinetics, is tied to that of reaction 9. At higher temperatures, the equilibrium is approached more rapidly, and the effective rate of scavenging by a low-IP solute decreases even if the scavenging rate actually increases. Using the estimates of rate constants and activation energies for reaction 9 given in ref 33, we simulated the scavenging kinetics and found that negative $E_a(k_s)$ in cyclohexane is, probably, an artifact arising due to occurrence of reaction 9; the actual activation energy is slightly positive; that is, +-(1−2) kJ/mol.

Concluding Remarks

Our experiments indicate that (i) the hopping of solvent holes in cycloalkanes is thermally activated, with an activation energy 20−80 meV, and (ii) the thermalization of the vb holes does not yield the mobile solvent holes with 100% efficiency (see also ref 8). In *trans*-Decalin, this efficiency decreases with increasing temperature, which causes the observed negative activation energy for the conductivity signals.

Low (but positive!) activation energy of the hole transport in combination with high hopping rates suggests that the solvent holes in cycloalkanes are polarons migrating by phonon-assisted hopping. The activation energies are comparable to that of solvent reorganization. It seems reasonable that the yield of polarons at the initial stage of relaxation of the vb hole is temperature dependent because this very relaxation depends on the coupling of the charge to the solvent.

There is also some experimental evidence that the solvent holes are delocalized, as predicted by the polaron theory. In ref 33, we studied $\Delta\sigma(t)$ kinetics in cyclohexane−methylcyclohexane mixtures. Although the addition of <5−10 vol % of methylcyclohexane reduces both the $\Delta\sigma$ signal and its decay rate, further addition of methylcyclohexane yields little change in the $\Delta\sigma$ signal. These $\Delta\sigma$ kinetics are similar to those for the solvent holes in neat methylcyclohexane.

The initial reduction can be accounted for by reversible trapping of cyclohexane holes by methylcyclohexane, as explained in ref 33. Because the mobility of trapped holes must be normal, the $\Delta\sigma$ signal is from mobile cyclohexane holes only. Thus, both the $\Delta\sigma$ signal and its decay rate are proportional to the equilibrium concentration of cyclohexane holes. Although the trapping must occur at higher concentration of methylcyclohexane as readily, it does not lead to further reduction in the $\Delta\sigma$ signal or its decay rate. We must conclude that the migration rate of methylcyclohexane$^{\bullet+}$ ions in 5 vol % solution is similar to that of the mobile solvent holes in neat methylcyclohexane. When methylcyclohexane is diluted by *n*-hexane instead of cyclohexane, the $\Delta\sigma$ signal decreases proportionally to the fraction of *n*-hexane.[2,6] Thus, it was cyclohexane that made the difference.

This result suggests that methylcyclohexane holes are coupled to the solvent, forming a polaron and making resonant electron transfer as efficient as in neat methylcyclohexane. From the critical concentration of methylcyclohexane, we find that the reaction radius of the charge transfer is ~1 nm, or ~5 molecular diameters.

We conclude that our results strongly suggest that the mobile solvent holes in cycloalkanes are indeed small polarons.

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