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High Mobility Solvent Holes in Methylcyclohexane†

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Using time-resolved dc photoconductivity, the migration patterns and reactions of solvent hole in liquid methylcyclohexane between 230 and 350 K have been studied. It is shown that solvent holes in liquid methylcyclohexane are reversibly scavenged by solutes whose liquid-state ionization potentials are 0.2−0.3 eV below that of the solvent. The reversible electron transfer is driven mainly by the reaction heat (60−90%); further decrease in the free energy is due to increase in entropy following the destruction of solvent structure around the hole. Between 133 and 360 K, the solvent hole diffuses with activation energy of 7.8 kJ/mol; the fastest electron-transfer reactions (ca. 8.7×10^{10} M^{-1} s^{-1} at 25 °C) have activation energies between 3.9 and 5.3 kJ/mol (250 to 350 K). Unusually large scavenging radii, 1.5−3 nm, were obtained for these charge-transfer reactions.

1. Introduction

Methylcyclohexane is one of several hydrocarbon liquids that can be studied under cryogenic conditions. It is the only such liquid that yields long-lived high-mobility solvent holes upon ionization. This unique combination of physical properties provides an opportunity to study hole migration over a sufficiently wide temperature range.

High mobility solvent holes in methylcyclohexane have not been studied as thoroughly as similar species in cyclohexane and *cis*- and *trans*-decalins.[1−5] A long-lived (∼1 μs), high mobility ($\mu_h \approx 2.6 \times 10^{-3}$ cm^2/(V s)) solvent hole in room-temperature methylcyclohexane was discovered by Warman.[1] Pulse radiolysis−time-resolved microwave conductivity was used to observe these holes. Later on, Bühler and co-workers[2,3] used pulse radiolysis−transient absorption spectroscopy to observe the holes in room-temperature and supercooled methylcyclohexane. From the analysis of recombination kinetics at 20 °C,[2] the sum $D_h + D_-$ of the diffusion coefficients for the solvent hole and the counteranion in N_2O-saturated methylcyclohexane was estimated to be 8.24×10^{-5} cm^2/s.[2] Using the molecular ion mobility of $\mu_i = \mu_+ + \mu_- \approx 9 \times 10^{-4}$ cm^2/(V s)[1] and assuming that the anion mobility $\mu_- \approx \mu_i/2$, this estimate yields $\mu_h \approx 2.8 \times 10^{-3}$ cm^2/(V s), in reasonable agreement with Warman's result.[1]

Bühler and co-workers also estimated the lifetime (>100 μs)[2,3] and mobility[2] of the solvent hole in supercooled methylcyclohexane (133−153 K). Over this temperature range, the activation energy for solvent hole diffusion was 7.6 ± 0.5 kJ/mol, which is lower than the activation energy for diffusion of molecular ions (10−13 kJ/mol).[5]

We have previously measured several reaction constants for methylcyclohexane$^{\bullet+}$ at 25 °C[4] and obtained temperature dependencies for hole migration and reactivity at 250−300 K.[5] In this temperature range, the activation energy of hole migration was 6 ± 1 kJ/mol[5] and the activation energy for hole scavenging by *trans*-decalin was 3.9 ± 0.2 kJ/mol.[5] Using our data on the hole scavenging constants,[4] and hole mobility determined by Warman[1] and Bühler and co-workers,[2,3] leads to reaction radii well over 1 nm. Since these reaction radii seemed to be too large, we speculated[4,5] that the hole mobility was underestimated. Indeed, as the solvent hole may not be the only cation generated by a radiolytic pulse (electronically excited holes fragment and thermalized holes react with radiolytic products in spurs yielding secondary ions in less than 1 ns),[6] one always obtains a *lower* limit for the solvent hole mobility. In this work, we revise both the kinetic and the mobility data for the solvent holes in methylcyclohexane.

First, we demonstrate that some electron donor solutes that appeared to scavenge the solvent hole slowly[4,5] in fact exhibit biexponential hole scavenging kinetics indicative of a reversible reaction. High mobility solvent holes in liquid cyclohexane[6] and *cis*- and *trans*-decalins[8] are known to participate in two types of reversible scavenging reactions: (i) electron transfer[7] and (ii) metastable complex formation (the latter reaction is followed by proton transfer).[8] In this study, reversible reactions of the first type are shown to occur for methylcyclohexane$^{\bullet+}$. In such reactions, the forward electron-transfer proceeds as fast as that for low-IP aromatic solutes,[4,5] implying large reaction radii.

Second, using multiphoton laser ionization and hole injection[5] for "clean" generation of methylcyclohexane$^{\bullet+}$, we obtained more accurate estimates for the solvent hole mobility and its temperature dependence. Remarkably, our results are consistent with the previous estimates of the hole mobility in radiolytic experiments.[1,2,3] Thus, our data further support the case for large reaction radii for hole scavenging in methylcyclohexane.

2. Experimental Section

The methylcyclohexane obtained from Aldrich contained 0.042 vol % of toluene and 0.02 vol % of dimethylcyclohexane isomers along with many other hydrocarbon impurities (mainly, polymethylated cyclohexanes and cyclopentanes). Toluene and traces of olefins were removed by multiple passage of the solvent through activated silica gel. The solvent was further purified by multiple-stage fractional distillation. After this

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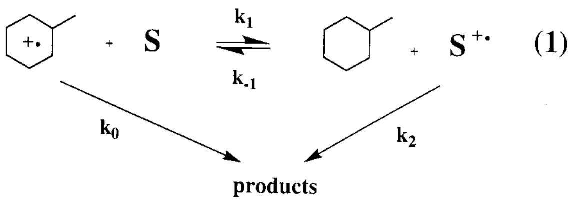
SCHEME 1



treatment, the impurity-limited lifetime of the solvent hole was 620 ns (at 25 °C).

The experimental setup was the same as that used in ref 8. The main improvement as compared to refs 4 and 5 is 10-fold increase in the flux of the 2.33 eV photons; this increase resulted in 5-fold improvement in the signal-to-noise ratio. Another improvement is that the temperature range has been increased by a factor of 2 (−120 °C to +85 °C).

Briefly, a 15 ns fwhm, 5 eV laser pulse (0.1 J/cm^2) was used to photoionize 10 μM triphenylene in CO$_2$-saturated methylcyclohexane. Triphenylene$^{\bullet+}$ was subsequently photoexcited using a 6 ns fwhm, 2.33 eV pulse from a second laser (0.2−2 J/cm^2) which was fired 2 μs after the 5 eV pulse. The dc conductivity traces σ_{on} and σ_{off} obtained with and without the second 2.33 eV pulse were subtracted and normalized by σ_{off}. The quantity $\chi = (\sigma_{on} - \sigma_{off})/\sigma_{off}$ is proportional to the product μ_h/μ_i [H], where [H] is the concentration of free solvent holes generated in oxidation of the solvent by photoexcited triphenylene$^{\bullet+}$ and μ_h/μ_i is the ratio of the solvent hole mobility and the sum μ_i of molecular cation (triphenylene$^{\bullet+}$) and anion (CO$_2^{\bullet-}$) mobilities. For more detail, see ref 8. Since triphenylene donates an electron to methylcyclohexane$^{\bullet+}$,[4] in 10 μM triphenylene solution the lifetime of the hole is shortened to ca. 300 ns.

The decay kinetics $\chi(t)$ of free solvent holes were exponential for some scavengers (such as aromatic hydrocarbons and aliphatic alcohols) and biexponential for others (e.g., bicycloalkanes). Biexponential kinetics were also observed above 50 °C in *neat* methylcyclohexane before the solvent was purified by fractional distillation. Gas chromatography analysis indicates that commercial solvent is contaminated with several mM of bi- and tricycloalkanes with high boiling points. Some of these compounds are capable of reversible trapping of the solvent hole on the microsecond time scale.

3. Results and Discussion

The exothermicity of electron-transfer reaction 1 (Scheme 1) is given by the difference ΔIP_{liq} in the liquid-phase ionization potentials of the solvent and the electron donor solute S. Using the Born formula for polarization energy,

$$\Delta IP_{liq} \approx \Delta IP_g - {}^1/_2 e^2 (1 - {}^1/\epsilon)\,(1/r_{+,solvent} - 1/r_{+,solute}) \qquad (2)$$

where $\epsilon \approx 2$ is the dielectric constant, r_+ are the cation radii (that were equated with the molecular radii), and ΔIP_g is the difference in the corresponding adiabatic gas-phase ionization potentials. Using the gas-phase IP [9,10] and molecular volume data[11] in the literature, the estimate for ΔIP_{liq} is 0.23 eV for *iso*-propylcyclohexane, 0.28 eV for *trans*-decalin, 0.52 eV for benzene, and 0.86 eV for toluene. Solutes that exhibit biexponential scavenging kinetics are those with $\Delta IP_{liq} < 0.3$ eV: if the reaction is more exothermic, the backward transfer is too slow to result in biexponential scavenging kinetics on the microsecond time scale.

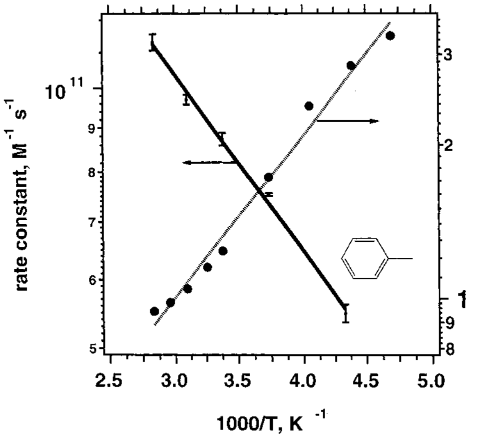


Figure 1. Arrhenius plots of the rate constant k_s (corrected for the thermal expansion of the solvent) for scavenging of methylcyclohexane hole by toluene; temperature dependence of the ratio χ is shown in the same plot (see the text).

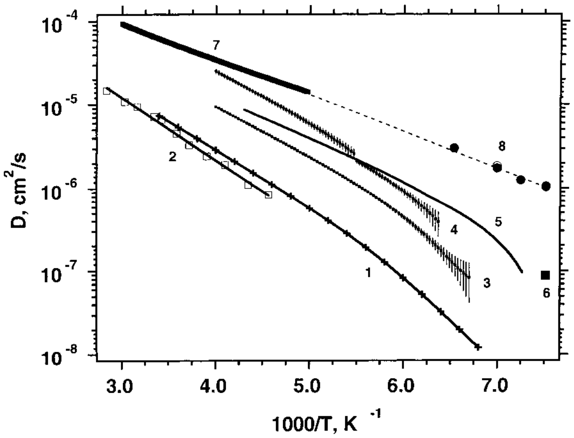


Figure 2. Diffusion coefficients for various species in liquid methylcyclohexane: (1) self-diffusion (calculated using the Stokes−Einstein formula from the viscosity data of ref 15); (2) triethylamine$^{\bullet+}$, from the time-of-flight conductivity data of ref 15; (3−5) the sums of diffusion coefficients of ^{1}pyrene* and CH$_2$I$_2$, I$_2$, and O$_2$, respectively (see the Supporting Information); (6) the sum of diffusion coefficients for norbornadiene$^{\bullet+}$ and O$^{\bullet-}$ at 133 K (ref 2); (7) D_h calculated from our conductivity data; (8) $D_h + D_-$ obtained in ref 2 (filled circles, N$_2$O-saturated; empty circles, CO$_2$-saturated methylcyclohexane).

3.1. Second-Order Scavenging. Unlike *trans*-decalin, which was used in our previous study,[5] toluene is a sufficiently deep trap for the solvent hole to prohibit backward electron transfer on the microsecond time scale over the entire liquid range of the solvent. Figure 1 shows the Arrhenius plot for second-order scavenging constant k_s and ratio χ_0 (which is χ at $t = 0$ corrected by the decay of the hole during the 2.33 eV pulse). After the correction for thermal expansion of the solvent, the activation energy of hole scavenging by toluene is 3.92 ± 0.15 kJ/mol, close to our previous estimate.[5] Assuming that the quantum yield of photooxidation is temperature-independent (as determined for solvent holes in *trans*- and *cis*-decalin),[5,7] we obtain that the activation energy for the μ_h/μ_i ratio ($\propto \chi_0$) is − (6.1 ± 0.3) kJ/mol. Using the estimate of 11.9 ± 0.4 kJ/mol for activation energy for μ_i,[5] the activation energy of hole mobility is 5.8 ± 0.7 kJ/mol. When the hole mobility μ_h is converted to the diffusion coefficient $D_h = (kT/e)\mu_h$, one obtains the activation energy for D_h of 7.9 kJ/mol (Figure 2, trace 7), which is close to the activation energy for solvent hole diffusion in supercooled methylcyclohexane, 7.6 ± 0.5 kJ/mol (Figure 2, trace 8).[2]

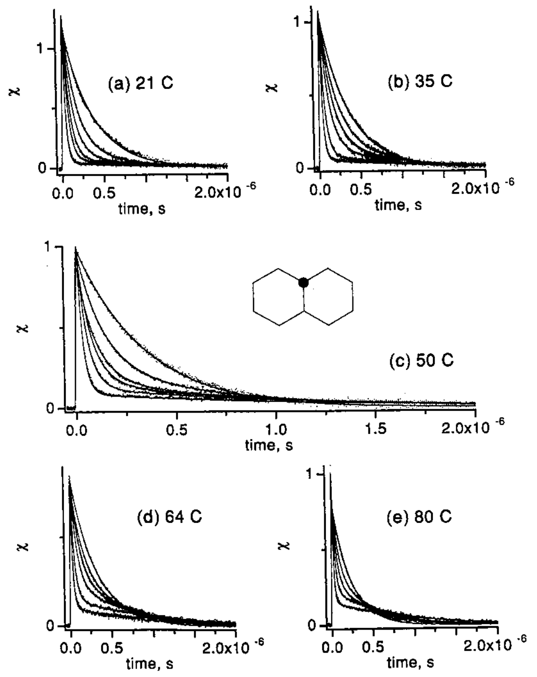


Figure 3. Decay kinetics of the 2.33 eV laser-induced photoconductivity (ratios ϰ are defined in the text) for scavenging the methylcyclohexane hole by *trans*-decalin at (a) 21 °C, (b) 35 °C, (c) 50 °C, (d) 64 °C, and (e) 80 °C. The solute concentrations are 0, 16 (shown for sets b and d only), 32, 63, 160, and 320 μM.

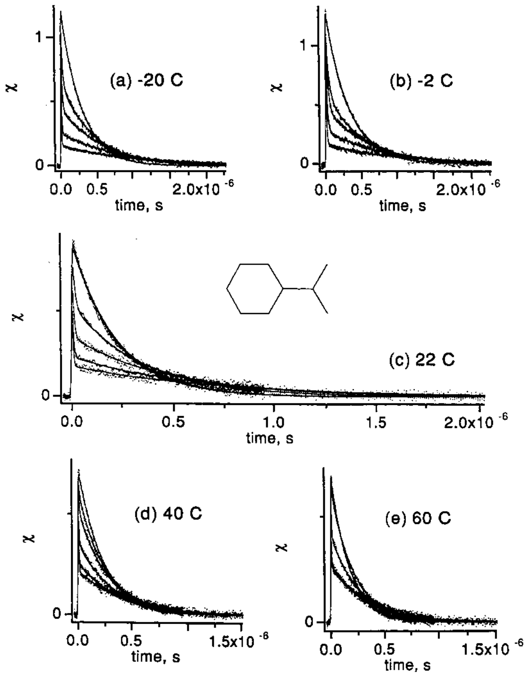


Figure 4. Decay kinetics of the 2.33 eV laser-induced photoconductivity for scavenging the methylcyclohexane hole by *iso*-propylcyclohexane at (a) −20 °C, (b) −2 °C, (c) 22 °C, (d) 40 °C, and (e) 60 °C. The solute concentrations are 0, 64 μM (not shown in e), 125, 320, 630, and 950 μM (not shown in b)). In set a, the solute concentrations were 0, 64 μM, 320 μM, 1.37 mM, and 3.2 mM.

For toluene and benzene, the scavenging constant k_s at 25 °C is $(8.7 \pm 0.15) \times 10^{10}$ M^{-1} s^{-1} and $(7.68 \pm 0.22) \times 10^{10}$ M^{-1} s^{-1}, respectively.[9] Proton donors are nearly as efficient scavengers as these low-IP hole acceptors: Higher aliphatic alcohols scavenge the hole approximately as rapidly as aromatic solutes ($(7.68 \pm 0.13) \times 10^{10}$ M^{-1} s^{-1} for *tert*-butanol), while lower alcohols scavenge twice slower ($(4.9 \pm 0.3) \times 10^{10}$ M^{-1} s^{-1} for 2-propanol and $(5 \pm 0.4) \times 10^{10}$ M^{-1} s^{-1} for ethanol; 25 °C). In other cycloalkane liquids, protonation of alcohols also occurred 30−50% slower as compared to the electron-transfer reactions.[4,7,8,12]

We also observed slow reactions of methylcyclohexane$^{\bullet+}$ with hydrocarbons with $\Delta IP_{liq} < 0.2$ eV, such as dimethylcyclohexanes (present in the solvent as impurity). For example, *cis*-1,3-dimethylcyclohexane scavenges the hole with rate constant $(1.28 \pm 0.08) \times 10^9$ M^{-1} s^{-1} at 25 °C (with activation energy ca. 5.1 kJ/mol); this corresponds to 1.5% of the diffusion-controlled rate. Similarly slow scavenging was observed for *trans*-1,2- and *trans*-1,3-dimethylcyclohexane; all of these rate constants are so low that it is likely that the scavenging is actually due to low-IP impurity in the solute.

3.2. Reversible Scavenging. For solutes with ΔIP_{liq} between 0.2 and 0.3 eV, scavenging kinetics were biexponential (e.g., Figures 3 and 4). *Trans*-decalin (Figure 3) and bicyclohexyl (not shown) have relatively low ionization potentials, and for these two solutes the biexponentiality becomes apparent only at elevated temperatures (e.g., traces (d) and (e)), whereas for *iso*-propylcyclohexane the kinetics are clearly biexponential even at −20 °C (Figure 4). These biexponential kinetics were simulated in terms of Scheme 1, in which k_1 and k_{-1} are the rate constants of forward and backward electron-transfer reaction 1, k_0 is the pseudo-first-order rate constant for reaction of the solvent hole with impurity in the solvent and k_2 is a similar rate constant for $S^{\bullet+}$. Figure 5 demonstrates Arrhenius plots for rate constants k_1 and k_{-1} and a van't Hoff plot for the equilibrium constants $K_{eq} = k_1/k_{-1}$; the activation energies and thermodynamic potentials are given in Table 1.

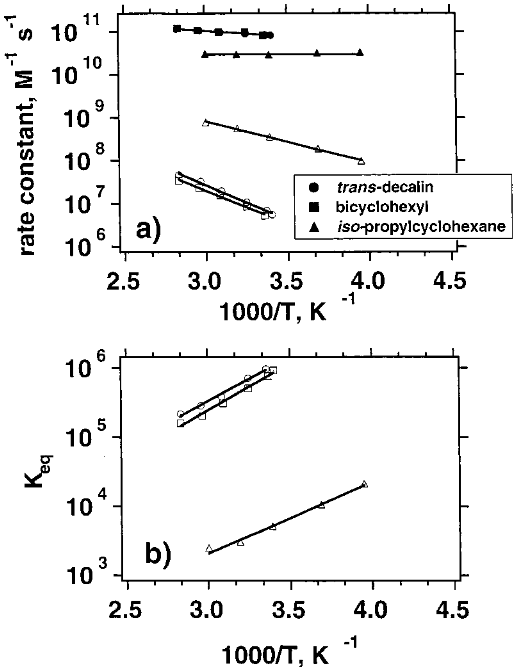


Figure 5. (a) Arrhenius plots for rate constants (solid symbols) k_1 and (empty symbols)k_{-1} for (circles) *trans*-decalin, (squares) bicyclohexyl, and (triangles) *iso*-propylcyclohexane. (b) van't Hoff plots for the equilibria constants $K = k_1/k_{-1}$ in the same scavenging reactions.

While for bicyclohexyl and *trans*-decalin the forward reaction 1 is as fast as that for toluene (and has slightly higher activation energy of 5.3 ± 1 kJ/mol), for *iso*-propylcyclohexane reaction 1 is 30% slower. This must be due to lower -ΔG° for electron transfer (Table 1). The relative decrease in the reaction heat (≈ 6 kJ/mol) is close to that estimated from ΔIP_{liq} (ca. 5 kJ/mol).

TABLE 1: Activation Energies and Standard Thermodynamic Potentials for Reaction 1 in Liquid Methylcyclohexane

solute	E_a (k_1)[a]	E_a (k_{-1})[a]	$-\Delta H^0$ [b]	$-\Delta G^0$ [b]	ΔS^0 [c]
iso-propyl cyclohexane	≅0	19.9 ± 1.8	20 ± 2	21 ± 3.5	4 ± 6
trans-decalin	5.3 ± 0.3	31.2 ± 1.1	26 ± 1.5	33.5 ± 2.5	25 ± 4
bicyclohexyl	5.3 ± 1	29.6 ± 1.3	24.4 ± 1.4	34 ± 3	32.5 ± 0.5

[a] Activation energy, kJ/mol. [b] Standard heat and driving force at 25 °C, kJ/mol. [c] Standard reaction entropy, J mol^{-1} K^{-1}.

Interestingly, for bicyclohexyl and *trans*-decalin, the electron transfer causes substantial increase in the entropy. A similar increase was observed in reactions of solvent holes in *cis*- and *trans*-decalin;[8] we explained it through disordering the solvent around a hole polaron after its neutralization.

3.3. Hole Mobility at 25 °C. Because laser photoionization, unlike pulse radiolysis, should yield very few prompt fragment and secondary cations, we used the single-pulse dc conductivity technique in ref 12 to obtain an independent estimate of μ_h. In this experiment, two-photon ionization of the solvent occurred using 5 eV photons (IP_{liq} is 8.8 eV).[13] At 25 °C, a mobility of $(2.30 \pm 0.16) \times 10^{-3}$ $\text{cm}^2/(\text{V s})$ for the solvent hole was obtained. This estimate compares favorably with those given in refs 1 and 2 suggesting that in room-temperature radiolysis of methylcyclohexane, the fragmentation of the hole is inefficient.

Still, there is a possibility that the fragmentation also occurs in photoionization. To obtain the *upper* estimate for μ_h, we used a method that does not require the knowledge of the solvent hole yield. After photoinjection, the solvent hole decays both in reaction with a scavenger and by recombination with negative ions. The latter reaction is $\nu = (\mu_h + \mu_-)/\mu_i$ times faster than recombination of normally diffusing cations. As described in ref 8a, the observed decay constant k_{obs} of the hole decay after hole injection can be approximated by $k_{\text{obs}} \approx k_s + 0.85\ \nu\ k_r$, where k_r is an “average” pseudo-first-order rate of molecular ion recombination (which may be determined from the dc conductivity data) and k_s is the rate of reaction with the scavenger. If both of these rate constants are varied in a controlled fashion, one can separate k_{obs} into two terms and determine ν.

To this end, we used a scavenger (triphenylene) that is a strong absorber of 5 eV photons: this solute serves both as a photosensitizer and an inner filter. By addition of 1−25 μM of triphenylene, the yield of free ions was varied over a factor of 3. In this concentration range, k_r changed linearly with [triphenylene] with a slope of 1.3×10^{10} M^{-1} s^{-1}, while k_{obs} changed with a slope of 1.56×10^{11} M^{-1} s^{-1}. The latter constant is much higher than scavenging constants obtained for low-IP solutes that are poor 5 eV light absorbers, such as benzene and toluene. Assuming that for triphenylene $k_s \approx 8.7 \times 10^{10}$ M^{-1} s^{-1} (as for toluene) we obtain $\nu \approx 6.3$ (at 25 °C). From that, an estimate of the *upper* limit for μ_h is 5.2×10^{-3} $\text{cm}^2/(\text{V s})$. Note that all other methods give an estimate of the *lower* limit for this quantity. If μ_h actually has a value near this upper limit, about half of the methyl cyclohexane holes fragment in both radiolysis and the photoionization experiments being discussed.

3.4. Reaction Radii. Using $\mu_h \approx 2.6 \times 10^{-3}$ $\text{cm}^2/(\text{V s})$,[1] we calculate that, at 25 °C, the reaction radii of proton transfer are 0.87 nm for ethanol, 0.85 nm for propanol, 1.33 nm for *tert*-butanol; the reaction radii of electron transfer are 1.51 nm for toluene and 1.35 nm for benzene. Since the activation energy for electron transfer is ≈ 2 times lower than that for D_h (see above), the latter two reaction radii are twice larger at lower temperature (scavenging constants for toluene are given in Figure 1, diffusion coefficients − in Figure 2). E.g., at −42 °C, the ratio $\chi = 2.7$ (vs $\chi° = 1.24$ at 25 °C), $k_s = (5.87 \pm 0.14) \times 10^{10}$ M^{-1} s^{-1}, and $\mu_+ = 5.6 \times 10^{-5}$ $\text{cm}^2/(\text{V s})$ (vs $\mu_+° = 2.65 \times 10^{-4}$ $\text{cm}^2/(\text{V s})$ at 25 °C).[5] Therefore, $\mu_h/\mu_h° = (\chi/\chi°)\ (\mu_i/\mu_i°) \approx 0.46$ and $\mu_h \approx 1.2 \times 10^{-3}$ $\text{cm}^2/(\text{V s})$, or $D_h \approx 2.3 \times 10^{-5}$ cm^2/s. Then, one obtains an electron-transfer radius $k_s/(4\pi D_h) \approx 3.3$ nm.

From the data in ref 11, van der Waals radii of ethanol, *tert*-butanol, and methylcyclohexane are, respectively, 0.322, 0.374, and 0.408 nm; therefore, the expected reaction radii of proton transfer are 0.73 to 0.78 nm, in a reasonable agreement with the experiment. However, the reaction radii of the fastest electron transfers are 2 to 4 times larger than the sum of the molecular radii. One way to account for this discrepancy is to assume a delocalization of the solvent hole, as previously suggested by Warman.[1]

Pilling and Rice[14] suggested a formula for the reaction radius of a diffusion-controlled electron transfer: $R = \lambda\ (1.15 + \ln [K_0\ /\ \text{D}\beta^2])$, where $K(r) = K_0 \exp(-\beta \text{r})$ is the distance dependence of the tunneling rate constant (typically, $\beta \sim 10$ nm^{-1}). Fitting this formula to our data over entire temperature range yields the optimum parameters $\beta^{-1} \approx 1.1 \pm 0.1$ nm and $K_0 \approx 10^{10}$ s^{-1}. If the hole mobility were twice larger (see above), the values would be $\beta^{-1} \approx 0.54$ nm and $K_0 \approx 4 \times 10^{10}$ s^{-1}. In the simplest formulation of the electron-tunneling theory, $\beta \approx (8\ m_e\ \Delta\ \text{E})^{1/2}/h$, where ΔE is the tunneling barrier.[14] If this formula were applicable, $\beta \approx 0.9$ nm^{-1} would be equivalent to the tunneling barrier of ≈8 meV.

3.5. Comparison with Low-Temperature Pulse Radiolysis.[2,3] Supercooled methylcyclohexane studied in refs 2 and 3 was stabilized due to the cryoscopic effect of dissolved gases, CO_2 (0.07 M) and N_2O (0.118 M), which reduced the melting point of the solvent from 146 to 127 K and 133 K, respectively.[2,3] To estimate the diffusion coefficients D_i of molecular ions in this solvent, Bühler and co-workers used the Stokes−Einstein formula; the viscosity was extrapolated from the data in ref 15 for *pure* methylcyclohexane (Figure 2, trace 1). To better estimate D_i, we studied diffusion-controlled quenching of pyrene fluorescence with CH_2I_2, I_2, and O_2 in CO_2-saturated methylcyclohexane vs temperature (Figure 2, traces 3 to 5, respectively; for more detail, see the Supporting Information). Below 180 K, the diffusion of I_2 is 4.5 times faster; CH_2I_2, 1.8 times faster; and O_2, 6−15 times faster than that given by the Stokes−Einstein formula. The activation energies for diffusion of these fluorescence quenchers are 9.9 kJ/mol to 12.6 kJ/mol; these activation energies increase by 60−100% below 165 K. At 143 K, the sum of diffusion coefficients of ^{1}pyrene* and O_2 is ≈ 1.5×10^{-7} cm^2/s; Bühler and co-workers obtained $(0.88 \pm 0.07) \times 10^{-7}$ cm^2/s for the sum of diffusion coefficients of norbornadiene$^{\bullet+}$ and $\text{O}^{\bullet-}$ at 133 K. Though these diffusion coefficients are >10 times higher than calculated from the Stokes−Einstein formula, they are still 15−20 times lower than the diffusion coefficients D_h of the solvent hole.[2]

In Figure 2, we superimpose D_h calculated from our conductivity data (trace 7) obtained with assumption that $\mu_h \approx 2.6 \times 10^{-3}$ $\text{cm}^2/(\text{V s})$ at 25 °C, and the diffusion coefficients obtained in ref 2 (trace 8). It can be seen that extrapolation of the conductivity data below 150 K yields the diffusion coefficients obtained in refs 2 and 3.

Despite this good agreement, there are certain discrepancies between our results and those in refs 2 and 3. In particular, extrapolating from our data, the impurity-limited lifetime of the solvent hole at 140 K must be <4 μs. This estimate compares favorably with 3 μs obtained for the lifetime of an "excited" solvent hole identified in ref 3; however, as suggested by trace 8 of Figure 2, the long-lived "ground-state" hole[2,3] cannot be a secondary (impurity) cation, because it migrates too rapidly. It was estimated that at 133 K this long-lived hole is scavenged by norbornadiene with rate constant $(1.8 \pm 0.5) \times 10^8$ M^{-1} s^{-1} ($D_h \approx 1.1 \times 10^{-6}$ cm^2/s),[2] which yields a reaction radius of 0.22 nm. This radius is much shorter than 1.2 nm obtained for the same reaction of the solvent hole at 25 °C.[4] This dramatic decrease in the scavenging radius may account for the high stability of the solvent hole below 150 K.

4. Conclusion

We confirm previous estimates for the room-temperature mobility[1,2] and activation energies of diffusion[2,5] and scavenging of methylcyclohexane holes[5] and report the occurrence of reversible hole trapping in this solvent. It is shown that such reactions readily occur for electron donors with ΔIP_{liq} of 0.2−0.3 eV; the driving force is mainly determined by the reaction heat. In addition, the electron transfer to the solvent hole results in an increase in entropy, as was previously observed for the reactions of solvent holes in *cis*- and *trans*-decalin.[8]

Combining the conductivity measurements performed above 230 K (this work) and low-temperature study of Bühler and co-workers (133 to 153 K),[2] it is shown that the diffusion of the solvent hole exhibits Arrhenius behavior over the entire liquid range of the solvent (133−360 K). Between 300 and 230 K, the reaction radii of electron transfer are 1.5−3.3 nm. These large radii may indicate considerable spread of the electronic coupling between the solvent hole and electron donors (≈1 nm).

Supporting Information Available: Quenching of pyrene fluorescence in low-temperature methylcyclohexane. This material is available free of charge via the Internet at http://pubs.acs.org.

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