Reversible Reactions of Cycloalkane Solvent Holes. 2. Scavenging of *cis-* and *trans-*Decalin•+ by Benzene

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Solvent holes in liquid *cis-* and *trans-*decalin form metastable complexes with benzene, which are probably solvation complexes of monomer radical cations of benzene. At 25 °C, the rate constants of formation of the complexes are, for *trans-* and *cis-*decalin respectively 1.1×10^{11} and 3.6×10^{10} M^{-1} s^{-1}, and the natural lifetime of the complex is 7 ns for *trans-* and 50 ns for *cis-*decalin. Thermodynamic potentials for the complexation are determined. The heat of the complex formation is ≈ -26 kJ/mol for *trans-* and ≈ -18 kJ/mol for *cis-*decalin. In *cis-*decalin, the complexes are more stable because of near-zero entropy of the complex formation. The complex decays by proton or H atom transfer with activation energy ≈ 10 kJ/mol (which yields a benzonium cation) or in a reactive encounter with a second benzene molecule (which yields a benzene dimer cation). Laser excitation of the dimer cation with a 1.165- or 2.33 eV photon causes valence band electron transfer and injection of a free solvent hole.

1. Introduction

The mixture of decalin (*cis-* and *trans-*decahydronaphthalene) with benzene is one of the benchmark systems in radiation chemistry of nonpolar solvents.[1,2] The S_1 states of these hydrocarbons are good fluorescers for which quantum and radiolytic yields are known with sufficient accuracy.[1] Furthermore, the S_1 states of decalins are uncommonly stable, which simplifies the kinetic and product analyses.[2] For some years, this binary system appeared uniquely suitable for studies of charge and energy transfer occurring in ionization of hydrocarbon liquids and was much studied. This suitability is now in doubt: recent studies suggest that at least two aspects of radiation-induced chemistry were overlooked by the previous workers.[3−7]

First, Lipsky et al.[3,4] showed that the sensitization of aromatic solute fluorescence by the transfer of energy from photoexcited solvents (cyclohexane, *n*-hexadecane, 2,3-dimethylbutane, and *cis-* and *trans-*decalins) can be explained only by the participation of *two* solvent excited states: the fluorescent S_1 state and a "dark" state. In *cis-*decalin containing 2×10^{-5} M of 2,5-diphenyloxazole, 70% of the solute luminescence is sensitized from this second state. Similar behavior was observed in decalin/benzene mixtures.[5] These dark states have a quantum yield of only a few percent of the S_1 states and do not yield these S_1 states upon deactivation.[3−5] It was suggested that the dark state is an exciplex-like species that migrates with a diffusion constant of 4×10^{-4} cm^2/s.[3]
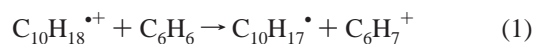
Second, Lipsky and co-workers concluded that on the time scale of a few picoseconds (which is the lifetime of the geminate electron−hole pair),[1] *trans-*decalin•+ reacts with benzene with a rate constant of 7.7×10^{10} M^{-1} s^{-1} [6,7] (a similar value was obtained for *cis-*decalin).[6] This constant is much higher than $(5−5.4) \times 10^9$ M^{-1} s^{-1} obtained in the time-resolved conductivity experiments of Warman et al.[8] and Sauer and co-workers.[9−11] To account for this discrepancy, the involvement of short-lived,

reactive excited holes has been suggested.[6,7] Thus, at least two short-lived exotic species, a dark state and an excited solvent hole, were postulated to account for the fluorescence data.

In this paper we demonstrate that the reactions of the solvent holes of *trans-* and *cis-*decalin with benzene produce metastable complexes, similar to the situation for alcohols as solutes.[11,12] We have obtained lifetimes of the complexes as large as 250 ns (*cis-*decalin at −19 °C). For *trans-*decalin, the reaction rate constant for the formation of the complex is higher ($\approx 1.1 \times 10^{11}$ M^{-1} s^{-1}) than previously determined values[8−11] (which are now realized to pertain to decay of the complex). A similar situation exists for *cis-*decalin. This new information makes the postulation of an excited solvent hole unnecessary.

2. Background

2.1. Energetics of Proton and Charge Transfers. As a scavenger, benzene may accept both the proton and positive charge from the solvent hole:

$$C_{10}H_{18}{}^{\bullet+} + C_6H_6 \rightarrow C_{10}H_{17}{}^{\bullet} + C_6H_7{}^{+} \tag{1}$$

$$C_{10}H_{18}{}^{\bullet+} + C_6H_6 \rightarrow C_{10}H_{18} + C_6H_6{}^{\bullet+} \tag{2}$$

Reaction (1) yields a benzonium cation, $C_6H_7{}^+$, and a decalyl radical, while reaction (2) yields the benzene monomer cation $C_6H_6{}^{\bullet+}$. The standard heat of reaction (2) is equal to the difference $\Delta IP_{liq} = IP_{Bz} - IP_{solvent}$ between the liquid-phase ionization potentials (IP) of $C_{10}H_{18}$ and C_6H_6. Gas-phase adiabatic IP's of decalins and benzene are both close to 9.25 eV,[13] and non-zero ΔIP_{liq} is due to the difference in their polarization energies in solution. In the dielectric continuum model, $\Delta IP_{liq} \approx \frac{1}{2}e^2(1-\epsilon)$ $[1/r_{h+} - 1/r_{b+}]$, where ϵ is the dielectric constant (Table 1) and r_{h+} and r_{b+} are the solvation radii for the solvent hole and $C_6H_6{}^{\bullet+}$, respectively. Estimating these radii from gas-phase molecular volumes (Table 1), we obtain that reaction (2) is exothermic by 0.25 eV for *trans-*decalin and 0.27 eV for *cis-*decalin (Table 1 and Figure 1).

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TABLE 1: Some Parameters for Solvent Holes in *trans*- and *cis*-Decalins

parameter	*trans*-decalin	*cis*-decalin
μ_h, $\times 10^{-7}$ m^2 V^{-1} s^{-1} [a]	8.7 ± 0.2	1.7 ± 0.1
μ_i, $\times 10^{-7}$ m^2 V^{-1} s^{-1} [b]	0.52	0.34
$E(\mu_h)$, kJ/mol[c]	-3 ± 1	6 ± 1
$E(\mu_i)$, kJ/mol[c]	13.7 ± 1	21.2 ± 0.7
$E(k_{et})$, kJ/mol[d]	0.94 ± 0.1	6.7 ± 0.4
r_{h+}, nm[e]	0.471	0.482
ϵ[f]	2.15	2.19
ΔIP_{liq}, eV[g]	-0.25	-0.27
[C$_{10}$H$_{18}$], M[h]	6.29	6.49

[a] Mobility of solvent holes at 25 °C, ref 9. [b] Mobility $\mu_i = \mu_+ + \mu_-$ of molecular ions at 25 °C, ref 28. [c] Activation energy of migration, ref 27. [d] Activation energy of charge transfer to triphenylene, ref 12. [e] "Hole" radius estimated from the molecular volume in the van der Waals isotherm, ref 29; for the monomer radical cation of benzene, $r_{B+} \approx 0.361$ nm. [f] Dielectric constant at 25 °C, ref 30. [g] Estimated heat of reaction (2). [h] Solvent molarity at 25 °C.
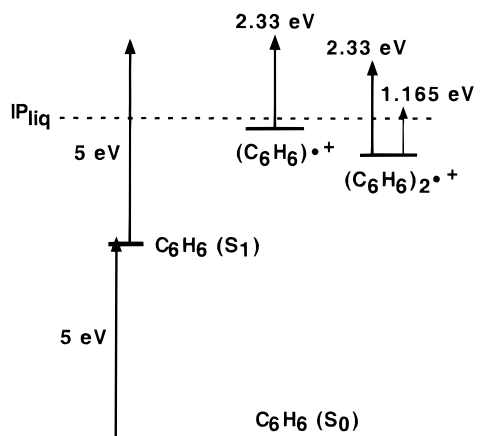
Figure 1. Energy diagram for benzene monomer and dimer cations in *trans*-decalin (see the text). IP$_{liq}$ is the liquid-phase ionization potential.

SCHEME 1
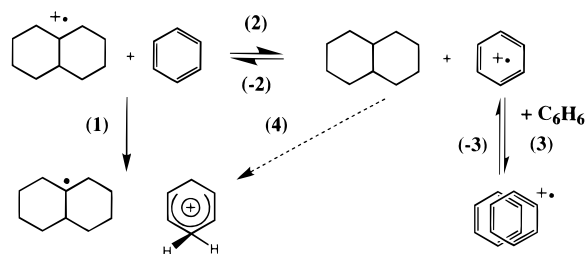
SCHEME 2
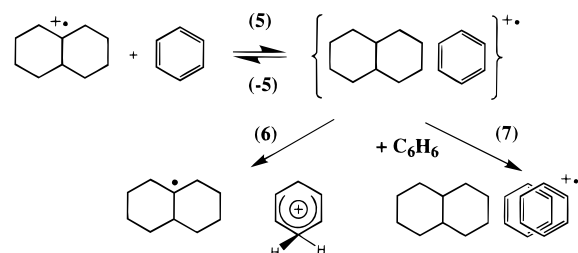
Reaction Schemes 1 and 2 delineate further details relating to reactions (1) and (2).

The energetics of reaction (1) is more difficult to estimate because the gas-phase proton affinity of decalyl radicals is not known. In ref 12, we estimated it as 7.9 eV for the 9-decalyl radical and 8.25 eV for other decalyl radicals (in *trans*-decalin)
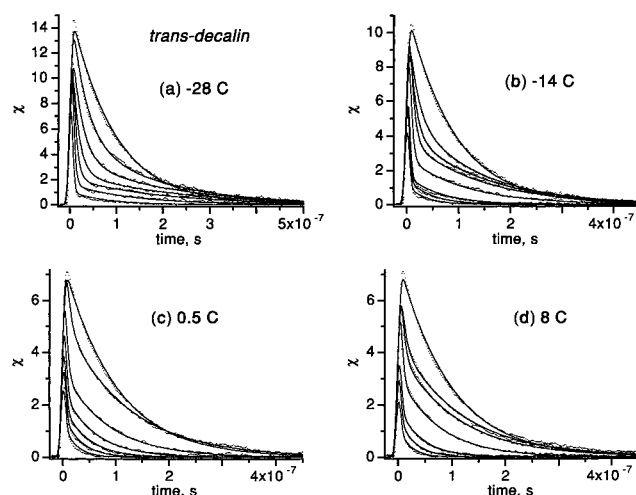

Figure 2. Decay kinetics χ for the scavenging of solvent holes in *trans*-decalin by benzene as a function of temperature (15 μM of photosensitizer (triphenylene); delay time of the 2.3 eV pulse is 1 μs; the fluence of the 2.33 eV light is 0.85 J/cm^2). Dots are experimental kinetics; solid lines are simulations using multitrace least-squares fitting with eq 10 using reaction Scheme 2 (equally good fits were obtained using Scheme 1); the kinetics were convoluted with the Gaussian time profile of the 2.33 eV laser. See Figures 6 and 7 and Tables 2 and 3 for kinetic parameters. Solvent temperatures and benzene concentrations were (a) -28 °C (0, 0.11, 0.23, 0.45, 1.01, 2.14, and 4.35 mM), (b) -14 °C (0, 0.45, 0.85, 1.7, 3.92, 6.17, and 8.42 mM), (c) 0.5 °C (0, 0.44, 1.69, 2.94, 4.19, 6.07, and 8.57 mM), and (d) 8 °C (0, 0.51, 0.9, 2, 4.28, 6.5, and 8.75 mM), respectively.

versus 7.86 eV measured for benzene.[14] Thus, reaction (1) appears to be thermoneutral. Other estimates suggest exothermicity: With the AM1 calculation, the standard heat of reaction (1) was estimated as -0.39 eV for the 9-decalyl radical and -0.25 eV for other decalyl radicals (the same calculation overestimated the exothermicity of reaction (2) by 0.3 eV). In any case, these estimates suggest that reactions (1) and (2) are weakly exothermic.

2.2. Dimerization of C$_6$H$_6$•+. In benzene-containing decalin solution, the benzene monomer cation generated in reaction (2) would react with another benzene molecule, forming a sandwich dimer cation[15−23]

$$C_6H_6^{\bullet+} + C_6H_6 \rightarrow (C_6H_6)_2^{\bullet+} \qquad (3)$$

with a diffusion-controlled rate (which is $\approx(5-7) \times 10^9$ M^{-1} s^{-1} in decalin at 25 °C).[24] When the spectroscopy results of Mehnert et al.[19] and a formula suggested by Brocklehurst[20] are used, the standard heat of reaction (3) may be estimated as -0.65 eV. Gas-phase estimates for the binding energy of the dimer range from 0.64 to 0.89 eV[21,22] with most estimates at the lower end of this range.[22] Assuming that the dimer cation is 0.65 eV more stable than the monomer, we estimate that the backward hole transfer from the dimer to the solvent is endothermic by 0.9 eV (Figure 1). Even less exothermic charge-transfer reactions of decalin holes (e.g., to toluene, for which $\Delta IP_{liq} \approx -0.6$ eV) are irreversible;[8−11] therefore, we expect that the dimer (unlike the monomer) does not generate the solvent hole by reverse reaction (2).[23] It is worth mentioning that the benzene monomer could also decay by the H atom transfer reaction (4)

$$C_6H_6^{\bullet+} + C_{10}H_{18} \rightarrow C_{10}H_{17}^{\bullet} + C_6H_7^+ \qquad (4)$$
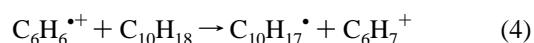
which has the same enthalpy as reaction (1) because of close gas-phase IP's of decalins and benzene.
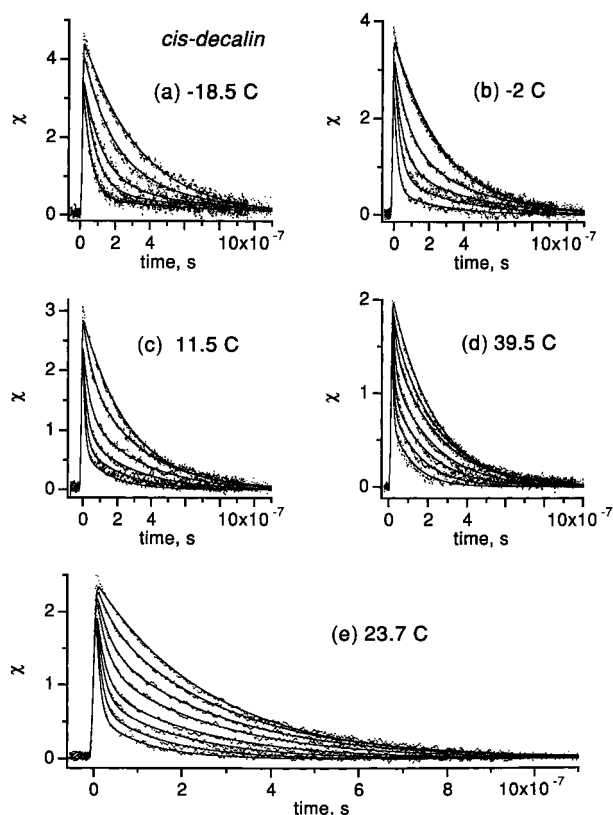
Figure 3. Same as Figure 2 for benzene in *cis*-decalin (35 μM of triphenylene was added for 2.33 eV photosensitization; $t_d = 1.4$ μs). The data were fit using reaction Scheme 1 (equally good fits were obtained using Scheme 2). See Figures 6 and 7 and Tables 2 and 3 for kinetic parameters. Solvent temperatures and benzene concentrations were (a) -18.5 °C (0, 0.11, 0.28, 0.56, and 0.95 mM), (b) -2 °C (0, 0.17, 0.4, 0.84, and 1.39 mM), (c) 11.5 °C (0, 0.17, 0.39, 0.78, 1.34, and 2.16 mM), (d) 39.5 °C (0, 0.11, 0.34, 0.73, 1.12, 1.66, and 2.48 mM) and (e) 23.7 °C (0, 0.11, 0.28, 0.51, 0.78, 1.17, 1.72, and 2.53 mM), respectively.

2.3. Scavenging Kinetics. As shown below, the addition of 0.1−10 mM of benzene results in biexponential decay kinetics of the decalin holes. For a given concentration of the solute, lowering the temperature of the reaction mixture reduces the weight of the slower component and slows down its decay (Figures 2 and 3). This behavior is indicative of a dynamic equilibrium and may be accounted for either by a reversible charge transfer (Scheme 1) or by the formation of a metastable complex (Scheme 2). Reversible charge transfer had been observed in reactions of cyclohexane holes with 1,1- and 1,3-dimethylcyclopentanes and 2,3-dimethylpentane.[25] The heats of these reactions were between -0.20 and -0.25 eV which is comparable to those for reaction (2) (Table 1). The formation of metastable complexes was observed in reactions of decalin holes with aliphatic alcohols.[12] Henceforth, both of these possibilities must be considered.

In reaction Scheme 1, reversible charge-transfer reaction (2) (with equilibrium constant $K_2 = k_2/k_{-2}$) competes with proton-transfer reaction (1). The equilibrium is shifted to the right side because reaction (3) continually removes the monomer cation. In reaction Scheme 2, the solvent hole forms a complex with benzene in reaction (5); the equilibrium constant of this complexation $K_5 = k_5/k_{-5}$. The complex decays either by proton transfer, reaction (6), or charge transfer to a second benzene molecule, reaction (7) (we expect that $k_3 \approx k_7$). Note that these two reaction schemes become kinetically equivalent if $k_1 = 0$ and $k_6 = k_4$. In the following, we assume that $k_4 = 0$.
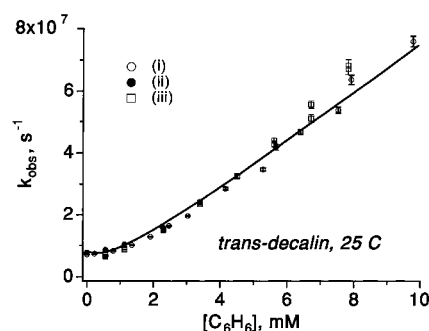

Figure 4. Concentration dependence of pseudo-first-order rate constant for the scavenging of *trans*-decalin$^{\bullet+}$ by benzene at 25 °C (i, ii) with and (iii) without 10 μM triphenylene. Points (ii) were obtained by exponential fitting of the tails of the χ kinetics. To obtain points (i) and (iii), least-squares fitting by exponential kinetics convoluted with the pulse shape of the 2.33 eV laser was used. The solid line is the least-squares fit using eq 11 (see the text).

In reaction Scheme 2, the decay kinetics of the solvent hole (H$^+$) and the complex (C$^+$) are given by

$$d[H^+]/dt = -(r_1 + r_3)[H^+] + r_2[C^+] \tag{8}$$

$$d[C^+]/dt = r_1[C_{10}H_{18}^{\bullet+}] - (r_2 + r_4)[C^+] \tag{9}$$

where $r_1 = k_5[C_6H_6]$, $r_2 = k_{-5}$, $r_3 = k_0$, and $r_4 = k_6 + k_7$-[C$_6$H$_6$]. Here, k_0 is the rate constant for scavenging of the solvent hole by impurity or added photosensitizer. Solving eqs 8 and 9, one obtains

$$[H^+]_t = [H^+]_0\{\beta \exp(-\lambda_1 t) + (1 - \beta) \exp(-\lambda_2 t)\} \tag{10}$$

where $\beta = (r_2 + r_4 - \lambda_1)/\Delta$, $\lambda_{2,1} = (r \pm \Delta)/2$, $\Delta^2 = r^2 - 4(r_2r_3 + r_3r_4 + r_4r_1)$, and $r = \sum_i r_i$. In reaction Scheme 1, the decay kinetics of the solvent holes are given by similar expressions in which $r_1 = k_2[C_6H_6]$, $r_2 = k_{-2}' = k_{-2}[C_{10}H_{18}]$, $r_3 = k_0 + k_1[C_6H_6]$, and $r_4 = k_3[C_6H_6]$ (the molarity of the solvent is given in Table 1). These two schemes become kinetically equivalent for $k_2 = k_5$ and $k_{-2}' = k_{-5}$: one can always find rate constants k_0, k_3, k_6, and k_7 that yield a set of identical kinetics for a given range of benzene concentrations. Therefore, reaction Schemes 1 and 2 cannot be distinguished by kinetic analyses alone.

When the settling of equilibria (2) or (5) is rapid, the scavenging kinetics may appear monoexponential: only the slower exponential component is observed on the time scale of the experiment. For $\lambda_2 \gg \lambda_1$, the observed exponential constant $k_{obs} \approx \lambda_1$ is given by

Scheme 1

$$k_{obs} \approx \{k_0 + k_1[C_6H_6] + k_3 K_2'[C_6H_6]^2\}/(1 + K_2'[C_6H_6])$$

Scheme 2

$$k_{obs} \approx \{k_0 + (k_6 + k_7[C_6H_6])K_5[C_6H_6]\}/(1 + K_5[C_6H_6]) \tag{11}$$

where $K_2' = K_2[C_{10}H_{18}]^{-1}$. Equation 11 becomes equivalent for $K_2' = K_5$, $k_3 = k_7$, and $k_1 = k_6K_5$. These equations predict nonlinear dependence of k_{obs} on [C$_6$H$_6$], even when the decay kinetics of solvent holes are exponential. Such scavenging kinetics were observed for benzene in room temperature *trans*-decalin (Figure 4).

3. Experimental Section

In this study, the solvent holes were generated by "hole injection", that is, by laser-induced oxidation of the solvent by

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a solute radical cation, for example, triphenylene•+:

$$\text{triphenylene}^{\bullet+} + h\nu \rightarrow \text{triphenylene}^{\bullet+*} \quad (12)$$

$$\text{triphenylene}^{\bullet+*} + C_{10}H_{18} \rightarrow \text{triphenylene} + C_{10}H_{18}^{\bullet+} \quad (13)$$
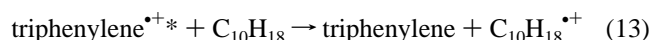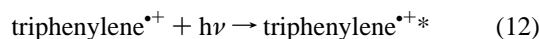
As shown in the Supporting Information, excitation of the benzene dimer cation with 1.165- and 2.33 eV photons also causes the solvent oxidation. The details of the technique are given in part 1 of this series[12] and other publications from our laboratory.[10,11,25−27] Very briefly, a 20 ns fwhm 5 eV laser pulse was used to ionize 5−50 μM of triphenylene (whose absorption at 248 nm is 460 times stronger than that of benzene), and the photoelectrons were scavenged within 1 ns by 0.01 M of CO_2. Several microseconds after the ionization event, a second laser pulse of 2.33 eV light was triggered. At this delay time (t_d), the geminate ion recombination was over and the solvent holes "injected" by 5 eV photolysis of triphenylene•+ (during the pulse) are completely scavenged by solutes and impurity.

The decay kinetics of dc conductivity with (σ_{on}) and without (σ_{off}) the 2.33 eV pulse were acquired, and normalized kinetics $\chi(t) = (\sigma_{on} - \sigma_{off})/\sigma_{off}$ were regarded as the decay kinetics of solvent holes (this approach is justified in ref 12). About 5−8 of such decay curves for several concentrations of benzene were fit simultaneously using eq 10, as shown in Figures 2 and 3. To take into account the decay of the holes during the pulse, the simulated kinetics were convoluted with the time profile of the 2.33 eV laser pulse ($\approx$6 ns fwhm). Optimum kinetic parameters were obtained from these least-squares fits.

The photoconductivity apparatus and kinetic analyses were as in the previous work.[12] Some experiments were done using 1064-nm pulses (3 ns fwhm) from a Quantel Nd:YAG laser. The molar concentrations of benzene are given at 25 °C, even if the measurements were performed at different temperatures.

4. Results and Discussion

4.1. Room-Temperature *trans*-Decalin. In room-temperature *trans*-decalin containing 10 μM of triphenylene, the scavenging kinetics of solvent holes generated by 2.33 eV hole injection was exponential. The concentration dependence of k_{obs} was nonlinear (Figure 4, traces (i) and (ii)). At low concentrations of benzene, the slope is close to 5×10^9 M^{-1} s^{-1}; at higher concentrations the slope is approaching 10^{10} M^{-1} s^{-1}. Very similar dependencies (save for slightly different offset, k_0) were observed in solutions containing no triphenylene (Figure 4, trace (iii)). These dependencies may be fit using eq 11, though there is no unique choice of parameters K_2, k_1, and k_3 (or K_5', k_6, and $k_7 \approx k_3$). Using the estimate for $K_5' \approx 850$ M^{-1} obtained by extrapolation of the van't Hoff plot shown in Figure 5b, we estimate $k_6 \approx 8 \times 10^6$ s^{-1} ($k_1 \approx 6.8 \times 10^9$ M^{-1} s^{-1}) and k_3 (or k_7) $\approx 8.1 \times 10^9$ M^{-1} s^{-1}.

4.2. Temperature Dependencies. Scavenging kinetics for the solvent holes were obtained in the temperature range that was limited by the melting points of the solvents and the onset of monoexponential decay (8 °C for *trans*-decalin and 40 °C for *cis*-decalin). Kinetics shown in Figures 2 and 3 were analyzed as described above. The Arrhenius plots for rate constants of reactions (1)−(6) are shown in Figures 6 and 7; the activation energies are given in Tables 2 and 3. van't Hoff plots for the equilibrium constants K_2 and K_5 are shown in Figure 5. Standard enthalpies and entropies of reactions (2) and (5) were determined from the least-squares fit of these plots (Tables 2 and 3).
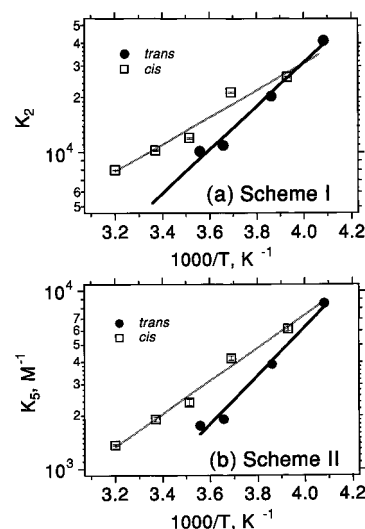

Figure 5. The van't Hoff plots for the equilibrium constants of (a) reaction (2), Scheme 1 and (b) reaction (5), Scheme 2. Filled circles are for benzene in *trans*-decalin and open squares for benzene in *cis*-decalin.
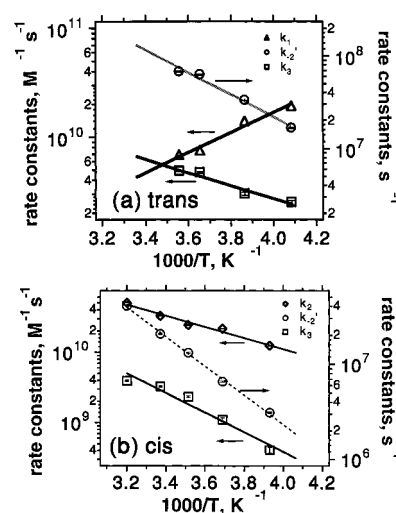

Figure 6. Arrhenius plots for rate constants of reactions (1)−(3) (see the legends) for benzene in (a) *trans*- and (b) *cis*-decalins (reaction Scheme 1). In *trans*-decalin, the temperature dependence for k_2 was weak, and we let $k_2 = 1.1 \times 10^{11}$ M^{-1} s^{-1} over the entire temperature range. Note the negative activation energy for k_1. In *cis*-decalin, the temperature dependence for k_1 was weak and we let $k_1 = 3.1 \times 10^9$ M^{-1} s^{-1} over the entire temperature range.

At any temperature, equally good fits of the kinetics were obtained using reaction Schemes 1 and 2. In both of these schemes, the optimum rate constants k_2 (k_5) in *trans*-decalin were within 10% of each other, and to reduce the variation in other parameters, we fixed this constant at 1.1×10^{11} M^{-1} s^{-1} (similar to the rate constant for complexation of *trans*-decalin with alcohols, $(1-1.2) \times 10^{11}$ M^{-1} s^{-1}).[12] Both electron- and proton-transfer reactions of solvent holes in *trans*-decalin (Table 1 and refs 12 and 27) exhibit near-zero activation energy, so this approach was justified.

In Scheme 1 (Table 2 and Figure 6), the activation energy for reaction (3) is close to that for the migration of molecular cations (see $E_a(\mu_i)$ in Table 1), while the activation energy for proton-transfer reaction (1) is either negative (*trans*-decalin, Figure 6a) or near-zero (*cis*-decalin, Figure 6b). For *cis*-decalin, the heat of electron transfer (2) is $\approx$9 kJ/mol less exothermic than that for *trans*-decalin (Table 2); the heat of electron transfer (2) for *trans*-decalin is close to ΔIP_{liq} estimated in Table 1. For
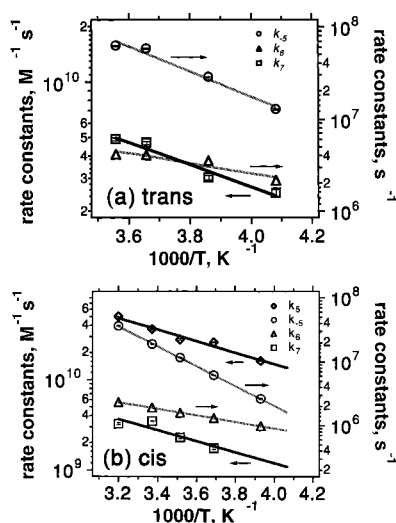
Figure 7. Arrhenius plots for rate constants of reactions (5)−(7) (see the legends) for benzene in (a) *trans*- and (b) *cis*-decalins (reaction Scheme 2). In *trans*-decalin, the temperature dependence for k_2 was weak, and we let $k_2 = 1.1 \times 10^{11}$ M^{-1} s^{-1} over the entire temperature range.

TABLE 2: Summary of Activation Energies and Equilibrium Parameters for Reversible Charge Transfer between Decalin Holes and Benzene (Reaction Scheme 1)

parameter	*trans*-decalin	*cis*-decalin
temperature range, °C	−28 to +8	−19 to 40
K_2 [a]	5 230	10 200
$-\Delta G°$, kJ/mol[a]	21.2 ± 4.8	22.9 ± 3.7
$-\Delta H°$, kJ/mol[a]	23.2 ± 2.3	14.4 ± 1.8
$\Delta S°$, J mol^{-1} K^{-1} [a]	−6.7 ± 8.6	28.6 ± 6.3
$E_a(k_2)$, kJ/mol[b]	≈0	15 ± 1.3
$E_a(k_{-2})$, kJ/mol[b]	23.2 ± 2.3	29.5 ± 0.8
$E_a(k_1)$, kJ/mol[b]	−17.7 ± 2	≈0
$E_a(k_3)$, kJ/mol[b]	11.5 ± 1.8	22.5 ± 6.5

[a] Equilibrium constant and standard thermodynamic potentials for reaction (5) at 25 °C. [b] Activation energy.

TABLE 3: Summary of Activation Energies and Equilibrium Parameters for Complexation of Decalin Holes by Benzene (Reaction Scheme 2)

parameter	*trans*-decalin	*cis*-decalin
temperature range, °C	−28 to +8	−19 to +40
K_5, M^{-1} [a]	880	1860
$-\Delta G°$, kJ/mol[a]	16.7 ± 5.4	18.7 ± 2.5
$-\Delta H°$, kJ/mol[a]	26 ± 2.5	17.7 ± 1.2
$\Delta S°$, J mol^{-1} K^{-1} [a]	−31.6 ± 9.6	3 ± 4.4
$E_a(k_5)$, kJ/mol[b]	≈0	12.2 ± 1.2
$E_a(k_{-5})$, kJ/mol[b]	26 ± 2.5	30 ± 0.3
$E_a(k_6)$, kJ/mol[b]	10.5 ± 2.6	9.8 ± 0.1
$E_a(k_7)$, kJ/mol[b]	11.5 ± 1.7	17.8 ± 3

[a] Equilibrium constant and standard thermodynamic potentials for reaction (2) at 25 °C. [b] Activation energy.

cis-decalin, forward reaction (2) is activated (Figure 6b and Table 2). Assuming that the activation energy for diffusion-controlled electron-transfer reactions of solvent holes in *cis*-decalin is 6.7 ± 0.4 kJ/mol (Table 1), the barrier for the electron transfer is 8 ± 2 kJ/mol. The entropy of reaction (2) is negative for *trans*-decalin and positive for *cis*-decalin; the difference between these entropies is ≈35 J mol^{-1} K^{-1}. In Scheme 2 (Table 3 and Figure 7), the activation energies for reaction (6) are ≈10 kJ/mol, for both *trans*- and *cis*-decalin, while reaction (7) is diffusion-controlled ($k_7 \approx k_3$). For *cis*-decalin, the heat of

reaction (5) is 6 kJ/mol less exothermic than that for *trans*-decalin, and the reaction is activated. The entropy of reaction (5) is negative in *trans*-decalin and near zero in *cis*-decalin; the difference between the entropies is again ≈35 J mol^{-1} K^{-1}.

4.3. The Complexation. Because both Figures 1 and 2 account for the data well, we chose between these two reaction schemes solely on the basis of peculiar activation energies for reaction (1) in Scheme 1 (Table 2). To account for the decay kinetics of solvent holes, proton transfer (1) should have either negative activation energy (*trans*-decalin) or near-zero activation energy (*cis*-decalin). Because in *cis*-decalin the migration of the solvent hole is activated, in both decalin solvents the enthalpy of formation for the collision complex is positive. To explain this, one needs to postulate reversible decay of the complex which is equivalent to accepting Scheme 2. Furthermore, proton-transfer reactions of decalin holes are known to proceed via complex formation for alcohols[12] and high-IP olefins,[8] and its is likely that benzene is no exception to this rule. A difference of 35 J mol^{-1} K^{-1} in the entropies of complexation for *cis*- and *trans*-decalin holes is the same as that observed in reaction of decalin holes with aliphatic alcohols.[12] Near-zero or positive entropies of complexation were also observed in such reactions. In ref 12, we argued that this thermodynamics is indicative of solvent structuring around the solvent hole, that is, its polaronic nature.[27]

What could be the possible structure of the complex? We simulated the gas-phase {*trans*-decalin benzene}$^{\bullet+}$ complex using the AM1 semiempirical method and obtained a structure with a binding energy of 0.26 eV. This is comparable to ΔIP_{liq}, which may explain the stability of the complex. The benzene molecule was 80° tilted relative to the *trans*-decalin plane. In this complex, >95% of the positive charge and spin density is on benzene; that is, the "complex" in solution could be a solvated monomer cation of benzene. According to the same calculation, the van der Waals complex of benzonium cation and 9-decalyl radical is only 8 meV more stable than this complex. These AM1 calculations, should be viewed with caution: though we obtained good estimates for the adiabatic IP of benzene (9.22 versus 9.24 eV),[13] the IP for *trans*-decalin was overestimated (9.5 versus 9.25 eV),[13] which may bias the simulation toward increased localization of positive charge on benzene.

Note that if most of the positive charge in the solvation complex were on benzene, then first-order decay of this complex, reaction (6), would be an H atom transfer reaction (4).

4.4. Comparison with the Fluorescence Results. As discussed in the Introduction, Lipsky and co-workers[6,7] estimated that on the time scale of electron−hole recombination (<1 ns), benzene scavenges *trans*- and *cis*-decalin holes with a rate constant of 7.7×10^{10} M^{-1} s^{-1} at 25 °C. The natural lifetimes $\tau = (k_{-5} + k_6)^{-1}$ of the complexes formed in reaction (5) are ≈ 7 and ≈50 ns, respectively. Therefore, on the subnanosecond time scale, the scavenging constant should be given by the values of k_5 determined in the present work, that is, $k_5 \approx 1.1 \times 10^{11}$ M^{-1} s^{-1} for *trans*-decalin$^{\bullet+}$ and 3.6×10^{10} M^{-1} s^{-1} for *cis*-decalin$^{\bullet+}$ (at 25 °C). The latter estimate for *cis*-decalin is ≈2.2 times lower than the value of 7.7×10^{10} given in ref 6. We believe that our estimate is more accurate because even the fastest electron-transfer reactions of *cis*-decalin holes exhibit rate constants below 5.5×10^{10} M^{-1} s^{-1}.[11] The values determined here for k_5 are much closer to the value of 7.7×10^{10} M^{-1} s^{-1} of Lipsky and co-workers[6,7] than previous values in the literature for reaction with benzene[8−10] which actually

were for the decay of the complex by reaction with benzene. Therefore, the postulate by Lipsky and co-workers[6,7] of excited decalin cations seems unnecessary.

5. Conclusion

Solvent holes in liquid *cis*- and *trans*-decalin form long-lived complexes with benzene. These complexes are most likely solvation complexes of monomer radical cations of benzene, though partial charge transfer to the solvent is also possible. At 25 °C, the natural lifetime of the complex is 7 ns for *trans*- and 50 ns for *cis*-decalin. Thermodynamic potentials for the complexation are given in Table 3. *Cis*-decalin is shown to form more stable complexes because of near-zero entropy of the complex formation. The complex decays by proton (or H atom) transfer with activation energy $\approx$ 10 kJ/mol (that yields benzonium cation) or in a reactive encounter with a second benzene molecule (that yields benzene dimer cation) (see Scheme 2 and Table 3). The latter reaction is diffusion-controlled. Laser excitation of the benzene dimer cation with a single 1.165- or 2.33 eV photon causes valence band electron transfer and injection of a free solvent hole (with quantum yields $\approx 1.5 \times 10^{-2}$ and 0.3, respectively; see the Supporting Information for more detail).

Supporting Information Available: The photophysics of hole injection in decalin/benzene mixtures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Reaction (3) is reversible. Typical equilibrium constants for dimerization of polycyclic aromatic radical cations are $100-1000$ M^{-1} (see, for example, Kira, A.; Arai, S.; Imamura, M. *J. Chem. Phys.* **1971**, *54*, 4890). Benzene dimer cation has the highest binding energy among these aromatic dimer cations (refs 20 and 22). Assuming that the entropy of dimerization is close to that of excimer formation, Brocklehurst estimated the equilibrium constant at 25 °C to be 2.2×10^6 M^{-1} (ref 20). Consequently, in the concentration range explored in this study ($[C_6H_6] <$ 10 mM) the dissociation of the dimer cation is negligible: assuming that reaction 3 is diffusion-controlled at 25 °C, the lifetime of the dimer is $\approx$30 μs which is 10 times longer than the duration of typical decay kinetics shown in Figures 2 and 3.

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