Low Concentration Anomalies in the Electronic Energy Transfer Behavior of Saturated Hydrocarbon Liquids

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The transfer of electronic energy to 2,5-diphenyloxazole (PPO) from the neat liquids cyclohexane, *n*-hexadecane, and 2,3-dimethylbutane, and from dilute solutions of *cis*-decalin in the nonfluorescent solvents 2,2,4-trimethylpentane (isooctane), 2,2,4,4,6,8,8-heptamethylnonane (HMN), and 2,2-dimethylbutane has been studied for excitation at 161 nm over a PPO concentration range from 10^{-2} to 10^{-5} M. The results confirm and generalize earlier measurements showing that in saturated hydrocarbon liquids there exists an anomalously efficient sensitization of PPO fluorescence that is mainly manifested at low PPO concentrations and derives from a state, T, other than the normal fluorescing state. The T state process is shown not to depend on the viscosity of the system or on the concentration of the donor liquid. A mechanism is suggested involving the generation of an ion-pair state and the migration of its charge separation to PPO.

I. Introduction

Electronic energy transfer has been recently reported[1] from *cis*-decalin to 2,5-diphenyloxazole (PPO) when their liquid mixtures were optically excited at 7.7 eV (161 nm). This energy lies above the first electronic absorption system of *cis*-decalin but below its liquid-phase ionization potential.

As the concentration of PPO in the *cis*-decalin was decreased from 1×10^{-2} M to 2×10^{-5} M, the quantum yield of the *cis*-decalin fluorescence ($\Phi^{161}{}_{D}$) was increased and the quantum yield of the PPO fluorescence ($\Phi^{161}{}_{A}$) was decreased but the decrease in the PPO yield was always found to be significantly less than could be accommodated for by the increase in the quantum yield of the *cis*-decalin fluorescence. The fractional disparity increased as the PPO concentration declined below 1×10^{-3} M and was interpreted to imply the existence of a dark state of *cis*-decalin (neither itself fluorescent nor acting as a precurser to the fluorescent state) but capable of sensitizing the PPO fluorescence much more efficiently than does the fluorescing state of the *cis*-decalin.

Although only *cis*-decalin and PPO were used in these experiments, earlier studies[2] had indicated that for solutions of PPO in other saturated hydrocarbon liquids, the dependence of the fluorescence intensities from the PPO and the saturated hydrocarbon behaved also as would be expected for a two-state transfer. On the other hand, when benzene was used as a donor solvent, instead of the saturated hydrocarbon, the concentration dependence of the sensitization of the PPO fluorescence showed no peculiar anomalies. Instead the behavior appeared to be entirely consistent with the presence of only a single transferring state, i.e., the S_1 state of the benzene.

In a continuing attempt to characterize the nature of the anomalous transfer mechanism, the present study reexamines the benzene + PPO system using the same procedures as were recently used for the *cis*-decalin + PPO system[1] and, additionally, examines the behavior of three other saturated hydrocarbon liquids, cyclohexane, *n*-hexadecane, and 2,3-dimethylbutane which are much less fluorescent than *cis*-decalin and for which, unlike *cis*-decalin, the excitation at 161 nm does not internally convert to the emitting state with ca. unit efficiency. Finally, we compare the effects of dilution of the *cis*-decalin with the nonfluorescent liquids 2,2,4-trimethylpentane (isooctane), 2,2,4,4,6,8,8-heptamethylnonane (HMN), and 2,2-dimethylbutane.

II. Experimental Section

The apparatus used and techniques employed are all as previously described.[1] Relative lamp intensities were monitored from 161 to 185 nm with the excitation invariant emission yield of neat *cis*-decalin (placed in the same sample cell as were the sample solutions) and from 185 to 315 nm with a freshly prepared sodium salicylate screen. The latter was checked by comparison with the PPO fluorescence from a 0.01 M solution in isooctane and showed that the ratio of this fluorescence intensity to that from the salicylate was independent of wavelength from 315 to 185 nm (where the isooctane begins to compete with the PPO for light absorption).

Corrections due to light directly absorbed by the PPO in *n*-hexadecane and cyclohexane at 161 nm were obtained from measurement of the PPO emission intensity in isooctane. Since this liquid is nonfluorescent,[3] the presumption is that its PPO emission intensitiy must derive predominantly from the direct absorption of the exciting light by the PPO. The intensity of the PPO emission in isooctane was ca. 5−6% of that in the fluorescent solvents at the highest concentration of 0.01 M and less than 1.5% at concentrations below 1×10^{-4} M. Any contibution to the PPO emission in the isooctane from energy transfer would therefore make these corrections upper bounds. Attempts were made to correct for the difference in absorption coefficients at 161 nm of the isooctane and the cyclohexane, *n*-hexadecane, and 2,3-dimethylbutane solvents by measurement of the fluorescence from solutions of these liquids in isooctane. However, a strong quenching of the fluorescence of these liquids by the isooctane prevented an accurate measurement of their relative absorptivities (albeit ratios of absorptivities of the order of unity seemed best to fit the data). In view of the relative unimportance of the PPO direct absorption correction, especially

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at the lower concentrations where our interest is mostly centered, we have used the uncorrected isooctane data. Measurement of the PPO fluorescence intensity at 161 nm in another nonfluorescent solvent, 2,2-dimethylbutane, was 40% less than that of isooctane and was used for corrections to the results with 2,3-dimethylbutane.

Corrections for the PPO absorption in the 10% (or lower) solutions of *cis*-decalin in the various nonfluorescent diluent solvents were made by using the intensity of the 161 nm excited fluorescence of PPO in these neat diluent solvents as background. Although the corrections here were much larger, they are considered more reliable since the solution used for background has essentially the same absorption characteristics with and without the *cis*-decalin.

cis-Decalin (Aldrich 99%), *n*-hexadecane (MCB 99+%), cyclohexane (Fisher Scientific 99.8%), 2,2,4-trimethylpentane (American Burdick and Jackson, high purity), 2,2,4,4,6,8,8-heptamethylnonane (Aldrich 98%), 2,3-dimethylbutane (Aldrich 98%) and 2,2-dimethylbutane (Aldrich 99%) were purified via percolation through Ag-activated alumina. Benzene (Aldrich, 99.8%) was purified by fractional recrystallization from the melt and PPO (Aldrich, scintillation grade) was used without further purification. Unless stated otherwise, all measurements were made on solutions at ca. 20 °C and deaerated via N_2 purging.

III. Data Anaysis

Donor Fluorescence. The intensity of the donor fluorescence, I^{λ}_{D},when excited in the presence of the acceptor (i.e., PPO) at a concentration, *c*, and at wavelength λ can be expressed as

$$I^{\lambda}_{\mathrm{D}} = N^{\lambda}_{\mathrm{D}} f^{\lambda}_{\mathrm{D}} \Phi^{\lambda}_{\mathrm{D}} J^{\lambda} \tag{1}$$

where N^{λ}_{D} is an apparatus constant, f^{λ}_{D} is the fraction of light absorbed by the donor, $\Phi^{\lambda}_{\mathrm{D}}$ is the quantum yield of donor fluorescence per quantum absorbed by the donor and J^{λ} is the intensity of absorbed exciting light of wavelength λ. If we excite the same donor at the same λ but in the absence of the acceptor, a similar equation applies so that

$$\Phi^{\lambda}_{\mathrm{D}}/\Phi^{\lambda}_{\mathrm{D}_0} = (I^{\lambda}_{\mathrm{D}}/I^{\lambda}_{\mathrm{D}_0})(f^{\lambda}_{\mathrm{D}_0}/f^{\lambda}_{\mathrm{D}}) \tag{2}$$

where the subscript D_0 refers to the solution in the absence of acceptor. For PPO concentrations not exceeding 0.01 M, the ratio, $f^{161}_{\mathrm{D}_0}/f^{161}_{\mathrm{D}}$, is close to unity based on estimates of the appropriate extinction coefficient ratios.

Acceptor Fluorescence. For the emission intensity, I^{λ}_{A}, from the acceptor in the solution of concentration, *c*, we have, in analogy to eq 1

$$I^{\lambda}_{\mathrm{A}} = N^{\lambda}_{\mathrm{A}} f^{\lambda}_{\mathrm{D}} \Phi^{\lambda}_{\mathrm{A}} J^{\lambda} \tag{3}$$

where $\Phi^{\lambda}_{\mathrm{A}}$ is the quantum yield for acceptor fluorescence per photon absorbed by the donor. The experimental parameter I^{λ}_{A} is defined here to have been corrected for any direct light absorption by the acceptor. In the special case that λ and *c* are chosen to be at a wavelength λ_0 and at a concentration c_0 such that D has relatively no absorption (i.e., $f^{\lambda_0}_{\mathrm{D}} = 0$ and $f^{\lambda_0}_{\mathrm{A}_0} = 1$; $\lambda_0 = 225$ nm for saturated hydrocarbon donors and 300 or 314 nm for benzene at $c_0 = 0.01$ M), an equation similar to eq 3 applies so that

$$\Phi^{\lambda}_{\mathrm{A}}/\Phi^{\lambda_0}_{\mathrm{A}_0} = (I^{\lambda}_{\mathrm{A}}/I^{\lambda_0}_{\mathrm{A}_0})(J^{\lambda_0}/J^{\lambda})(N^{\lambda_0}_{\mathrm{A}_0}/N^{\lambda}_{\mathrm{A}})(1/f^{\lambda}_{\mathrm{D}}) \tag{4}$$

where $\Phi^{\lambda_0}_{\mathrm{A}_0}$ is the quantum yield of A fluorescence per quantum absorbed by A at the concentration c_0 and at the wavelength λ_0.

Since the emission spectrum of the PPO acceptor is independent of λ, the two instrumental factors $N^{\lambda_0}_{\mathrm{A}_0}$ and N^{λ}_{A} can only differ by virtue of different penetration depths of the exciting light. In our applications of eq 4, λ_0 and c_0 have been additionally chosen to make $N^{\lambda_0}_{\mathrm{A}_0}/N^{\lambda}_{\mathrm{A}} = 1$. On the other hand, by choosing c_0 to be not necessarily the same as *c*, the "intrinsic" quantum yields of the PPO (i.e., per S_1 state generated) for excitation at λ_0 and at λ will be slightly altered due to self-quenching effects. For PPO concentrations less than 0.001 M, this effect is quite small both in benzene and in the saturated hydrocarbons and was usually ignored. At the higher concentrations, a small correction was applied.

Internal Conversion Efficiencies. Equations 2 and 4 provide the basic links between the quantum yield ratios that we seek and the experimental observables. However two additional parameters are also required. Since we excite the donor to a state at λ which is significantly higher in energy than is its fluorescing state, hereafter referred to as D_1, it is important to know the efficiency with which the donor makes internal conversion to this D_1 state. We label this efficiency as $\beta^{\lambda}_{\mathrm{D}}$. Similarly, since the acceptor has its fluorescing state, A_1, energetically lower than the terminal states of the energy transfer process, the internal conversion efficiency of the acceptor $\beta^{\lambda}_{\mathrm{A}}$ is also required. In both cases these parameters are obtained from appropriate excitation spectra. For *cis*-decalin as donor, and for PPO as acceptor, $\beta^{\lambda}_{\mathrm{D}}$, $\beta^{\lambda}_{\mathrm{D}_0}$, and $\beta^{\lambda}_{\mathrm{A}}$ have been previously shown to be unity over the spectral ranges $\lambda = 120-185$ nm for *cis*-decalin[4] and $\lambda = 180-350$ nm for PPO.[1] For the *cis*-decalin this range includes excitations down to the absorption edge and is adequate for our purposes. For PPO, however, solvent absorption beginning at ca. 180 nm prevents the determination of $\beta^{\lambda}_{\mathrm{A}}$ to the shorter excitation wavelengths of 173 or 161 nm. However, since the donors that we have studied all fluoresce with a spectral distribution with maxima at ca. 210−230 nm, it is unlikely that such donors will have states at wavelengths less than 180 nm that live long enough to sensitize PPO (at least not at concentrations less than 0.01 M). This conjecture is somewhat strengthened by the fact that for all saturated hydrocarbon donors we have studied, the internal conversion efficiency of D is the same whether PPO is present or not (i.e., $\beta^{\lambda}_{\mathrm{D}}/\beta^{\lambda}_{\mathrm{D}_0} = 1$). The implication of this is that there exist no upper states of D that can internally convert to D_1 (either directly or via lower states) *and also* energy transfer to A.

IV. Results

Donor Fluorescence. In all cases studied, the ratio of $I^{\lambda}_{\mathrm{D}_0}/I^{\lambda}_{\mathrm{D}}$ was linear on *c* for PPO concentrations less than 0.01 M. The implication from eq 1 (with $f^{\lambda}_{\mathrm{D}_0}/f^{\lambda}_{\mathrm{D}} = 1$) is that $\Phi^{\lambda}_{\mathrm{D}_0}/\Phi^{\lambda}_{\mathrm{D}}$ obeys the usual Stern−Volmer form

$$\Phi^{\lambda}_{\mathrm{D}_0}/\Phi^{\lambda}_{\mathrm{D}} = (1 + Q) \tag{5}$$

where $Q = \alpha_{\mathrm{D}} c$.

The Stern−Volmer constants, α_{D}, are presented in Table 1.[5] Also shown in this table are the internal conversion efficiencies, β_{D}, determined as the ratios of the donor emission intensity (in the absence of PPO) for excitation at 161 nm to that at a wavelength close to the long-wavelength edge of the hydrocarbon absorption system. The values we obtain for β_{D} agree well with those previously reported.[4,6]

TABLE 1: Quenching Constants of Donor Fluorescence by PPO (α_D) and Donor Internal Conversion Efficiencies to D_1 for Excitation at 161 nm (β_D)

donor	α_D (M^{-1})	β_D
cis-decalin[a]	53	1.0
cis-decalin in isooctane[b]	115	1.0
cis-decalin in HMN[b,c]	47	1.0
cis-decalin in 2,2DMB[d]	110	1.0
cyclohexane	62	0.7
n-hexadecane	83	0.7
2,3-dimethylbutane	98	0.4
benzene	975	0.5_5[e]
benzene (air)	335	0.5_5[e]

[a] From ref 1. [b] 10 vol % or lower. [c] 2,2,4,4,6,8,8-Heptamethylnonane. [d] 10 vol % in 2,2-dimethylbutane. [e] From ref 6 and corrected for surface quenching.

TABLE 2: Energy Transfer Parameter $\Psi = \Phi^{161}{}_A\Phi^{161}{}_{D_0}/\Phi^{161}{}_D\Phi^{225}{}_{A_0}$ and Its Ratio to $Q = \alpha_D c$ for the System *cis*-Decalin + PPO

	decalin (10% iso)[a]			decalin (10% HMN)[b]		
$c \times 10^3$ M	Ψ	Ψ/Q	Ψ(fit)[c]	Ψ	Ψ/Q	Ψ(fit)[c]
1.25×10^{-5}	0.0037	2.5	0.0036	0.00115	2.0	0.00113
2.50×10^{-5}	0.0073	2.5	0.0070	0.00227	1.9	0.00223
5.00×10^{-5}	0.014	2.4	0.013	0.00450	1.9	0.00434
1.00×10^{-4}	0.026	2.2	0.025	0.00876	1.9	0.00829
2.50×10^{-4}	0.053	1.8	0.052	0.0190	1.6	0.0187
5.00×10^{-4}	0.096	1.7	0.089	0.0350	1.5	0.0336
1.00×10^{-3}	0.156	1.4	0.155	0.0600	1.3	0.0602
2.50×10^{-3}	0.346	1.2	0.340	0.131	1.1	0.134
5.00×10^{-3}	0.661	1.1	0.642	0.247	1.1	0.254
7.50×10^{-3}	0.970	1.1	0.944	0.365	1.0	0.373
1.0×10^{-2}	1.27	1.1	1.24	0.489	1.0	0.492

[a] See ref 1 (values at 1.25, 2.5 25, 250, and 750 × 10^{-5} M are interpolated from measured values). [b] 2,2,4,4,6,8,8-heptamethylnonane. [c] Fit to eq 9 in the text.

TABLE 3: Energy Transfer Parameter $\Psi = \Phi^{161}{}_A\Phi^{161}{}_{D_0}/\Phi^{161}{}_D\Phi^{\lambda_0}{}_{A_0}$ and Its Ratio to Q = $\alpha_D c$ for the Systems Cyclohexane and Hexadecane + PPO

	cyclohexane (neat)			*n*-hexadecane (neat)		
c, M	Ψ	Ψ/Q	Ψ(fit)[a]	Ψ	Ψ/Q	Ψ(fit)[a]
1.25×10^{-5}	0.00178	2.3	0.00180	0.00133	1.3	0.00130
2.50×10^{-5}	0.00341	2.1	0.00338	0.00268	1.3	0.00256
5.00×10^{-5}	0.00604	1.9	0.00610	0.00511	1.2	0.00497
1.00×10^{-4}	0.0105	1.6	0.0105	0.00954	1.1	0.00945
2.50×10^{-4}	0.0204	1.2	0.0203	0.0203	0.97	0.0211
5.00×10^{-4}	0.0328	1.0	0.0336	0.0350	0.84	0.0384
1.00×10^{-3}	0.0576	0.93	0.0581	0.0624	0.75	0.0695
2.50×10^{-3}	0.125	0.81	0.129	0.150	0.72	0.158
5.00×10^{-3}	0.240	0.78	0.246	0.300	0.72	0.302
1.00×10^{-2}	0.474	0.77	0.480	0.613	0.74	0.590

[a] Fit to eq 9 in the text.

Acceptor Fluorescence. The ratios $\Phi^{161}{}_A/\Phi^{225}{}_{A_0}$ were determined via eq 4 (with $N^{225}{}_{A_0}/N^{161}{}_A = 1$). The lamp spectrum was usually such that the ratio J^{225}/J^{161} was in the range of 0.075−0.090. For the pure liquids, $f^{161}{}_D$ was unity and for the 10 vol % mixtures, $f^{161}{}_D$ (determined from the ratios of the fluorescence intensities of the *cis*-decalin in the solution to that in the neat liquid) was 0.13 in isooctane, 0.10 in 2,2,4,4,6,8,8-heptamethylnonane (HMN), and 0.19 in 2,2-dimethylbutane. Our results for some representaive liquids are displayed in Tables 2 and 3 in the form of the ratio

$$\Psi = \Phi^{161}{}_A\Phi^{161}{}_{D_0}/\Phi^{161}{}_D\Phi^{225}{}_{A_0} \qquad (6)$$

Also presented is the ratio of this to Q (i.e., $\alpha_D c$) using the value of α_D obtained from Table 1. To extract from the tables the values of $\Phi^{161}{}_A/\Phi^{225}{}_{A_0}$, it is only required to divide Ψ by $(1 + Q)$.

For comparison purposes, some previous results for *cis*-decalin in isooctane are also provided.

V. Discussion

General Considerations. With $\beta^\lambda{}_A = 1$, it follows from the definitions of $\Phi^\lambda{}_A$ and $\Phi^{\lambda_0}{}_{A_0}$ that their ratio, $\Phi^\lambda{}_A/\Phi^{\lambda_0}{}_{A_0}$, must simply be the probability that the absorption of a quantum of λ light by D has generated a fluorescing state of A. Dividing this ratio by $\beta^\lambda{}_D$ gives us the same probability but per D_1 state generated.

On the other hand, since $\beta^\lambda{}_D/\beta^\lambda{}_{D_0} = 1$, it follows from the definitions of $\Phi^\lambda{}_D$ and $\Phi^\lambda{}_{D_0}$ that $1 - \Phi^\lambda{}_D/\Phi^\lambda{}_{D_0}$ must be the probability that D_1 was quenched by A and, accordingly, that all or some fraction, ϵ, of the quenched states will have generated excited A. Since the probability that *some* state of D has generated an excited A (i.e., $\Phi^\lambda{}_A/\beta^\lambda{}_D\Phi^{\lambda_0}{}_{A_0}$) cannot be inferior to the probability that *one* state, D_1, has excited A (i.e., $\epsilon\,(1 - \Phi^\lambda{}_D/\Phi^\lambda{}_{D_0})$), it follows that the sum

$$\Phi^\lambda{}_A/(\beta^\lambda{}_D\Phi^{\lambda_0}{}_{A_0}) + \epsilon\Phi^\lambda{}_D/\Phi^\lambda{}_{D_0}$$

cannot be less than ϵ. Substituting into this the parameters Ψ^λ and Q from eqs 5 and 6 gives the following inequality:

$$\Psi^\lambda/Q \geq \epsilon\beta^\lambda{}_D \qquad (7)$$

In the case that D_1 is the exclusive donor transferring state, eq 7 becomes an equality and, therefore, Ψ^λ/Q becomes less than or equal to unity. Accordingly, if Ψ^λ/Q *exceeds* unity, we can conclude, quite generally, that there must exist a mechanism for exciting A other than transfer via the D_1 state. Of course, such a mechanism may exist also in the case that Ψ^λ/Q does not exceed unity.

For all of the saturated hydrocarbons thus far examined, the ratio Ψ^{161}/Q always significantly exceeds unity over all or at least part of the PPO concentration range from 1.0×10^{-2} to 1.25×10^{-5} M. Tables 2 and 3 show this for some representative cases. Additionally, Ψ^{161}/Q always increases as c decreases, (implying that the contribution to the PPO sensitization that comes from the second transferring channel falls off more slowly as the PPO concentration decreases than does the contribution from the D_1 state). Finally, we call attention to the fact that for saturated hydrocarbons, the ratio of Ψ^{161}/Q at high c is usually within 10% of the independently measured value of $\beta^{161}{}_D$ (as is listed in Table 1), implying (as was already implicitly assumed in our previous analysis of the *cis*-decalin systems)[1] that the quenching of the donor fluorescence by PPO always results in an excited PPO (i.e. $\epsilon = 1$). To go beyond these rather general statements requires now the construction of some mechanism.

Two-State Transfer. The conjecture that two independent states of the saturated hydrocarbon sensitize the fluorescence of PPO has been previously shown to predict well the concentration dependence of Ψ^{161} for the *cis*-decalin systems.[1,2] In this case, the probability that some state of D has generated an excited state of A ($\Phi^{161}{}_A/\Phi^{225}{}_{A_0}$) was expressed as a sum of transfer yields, one from the D_1 state and one from some other state, T. Both transfer yields were found to be well described by simple Stern−Volmer forms, i.e.

$$\Phi^{161}{}_A/\Phi^{225}{}_{A_0} = \beta^{161}{}_D Q/(1 + Q) + \chi\Theta/(1 + \Theta) \qquad (8)$$

where $\Theta = \alpha_T c$ and α_T is the Stern–Volmer constant for the T state and χ is the yield of the T state per photon absorbed at 161 nm. In the present study where $\beta^{161}{}_D$ is sometimes less than unity, the first term on the RHS of eq 8 is multiplied by $\beta^{161}{}_D$ to bring both terms to the same quantum yield basis.

Both Q and $\beta^{161}{}_D$ are independently measured from the fluorescence of the donor. Thus eq 8, which connects the fluorescence quantum yields of A with the concentration of A, is simply a two-parameter equation in χ and α_T and can be graphically displayed in several simple ways to verify its validity. For example, multiplication of eq 8 by $(1 + Q)$ gives

$$\Psi^{161} = \beta^{161}{}_D Q + \chi\Theta(1 + Q)/(1 + \Theta) \qquad (9)$$

and this can be rearranged to

$$(1 + Q)/(\Psi^{161} - \beta^{161}{}_D Q) = 1/\chi(1 + (\alpha_T c)^{-1}) \qquad (10)$$

which predicts that the experimental data, when arranged in the form of the LHS of eq 10, should be linear on $1/c$. Such linearity has been demonstrated for the *cis*-decalin systems previously studied[1] and the parameters χ and α_T extracted therefrom. Alternatively, when the fluorescence intensity is weak (as is the case for cyclohexane, *n*-hexadecane, and 2,3-dimethylbutane and, accordingly, the accuracy of Ψ^{161} and $\beta^{161}{}_D Q$ are too low to make reliable their difference), we have found another technique to be preferable. Defining $\Gamma = c\Phi^{225}{}_{A_0}/\Phi^{161}{}_A$, a simple rearrangement of eq 10 shows that in the case that $\alpha_T \gg \alpha_D$, Γ should approach at high c

$$\Gamma \rightarrow (1 + \alpha_D c)/\alpha_D(\chi + \beta^{161}{}_D) \qquad (11)$$

and, accordingly, be linear on c with a slope to intercept ratio of α_D. In the opposite limit of low c, eq 9 predicts that

$$\Gamma \rightarrow (1 + \gamma c)/(\alpha_D \beta^{161}{}_D + \chi\alpha_T) \qquad (12)$$

where

$$\gamma = (\alpha_T - \alpha_D)/(1 + \alpha_D \beta^{161}{}_D/\chi\alpha_T)$$

which again predicts a linearity of Γ on c but with an intercept from which we can reliably extract the product $\chi\alpha_T$ and a slope to intercept ratio, γ, from which α_T can be obtained. At intermediate concentrations Γ is expected to be concave downward on c. Finally, to assist in the intrepretation of the tables, we note here that for concentrations of PPO less than ca. 0.001 M, the fraction of PPO light that derives from the T state can be estimated from $(1 - Q\beta_D/\Psi^{161})$.

Saturated Hydrocarbon Donors. Figures 1–3 in which are plotted Γ vs c illustrate well the behavior predicted by eqs 11 and 12 for all of the saturated hydrocarbon systems presented in Tables 2 and 3. Although not shown, the same behavior has been observed for the neat liquid 2,3-dimethylbutane and for 5% dilution of *cis*-decalin in HMN and a 10% dilution of *cis*-decalin in 2,2-dimethylbutane. In all cases, the prediction of eq 11 that the slope-to-intercept ratio in the high c limit be equal to α_D agrees within 8% with the values of α_D independently obtained and displayed in Table 1. With regard to eq 12, its predicted linearity appears also to be verified. Table 4 provides the parameter $\chi\alpha_T$ extracted from the intercept of the least-squares linear regressions of the low concentration data for all of the systems studied.

The parameter α_T can also be extracted from the low concentration data, but somewhat less reliably than the product $\chi\alpha_T$. Additionally, the value of α_T so obtained does not usually provide the best fit for the higher concentration data. The values of α_T displayed in Table 4 were therefore obtained by seeking a value that best fit eq 9 to the experimental values of Ψ in Tables 2 and 3 over the entire concentration range. The quality of this fit is shown also in these tables. Unfortunately, in the case that $\alpha_T \gg \alpha_D$, eq 9 is not particularly sensitve to α_T and the values displayed in Table 4 must be considered to have an

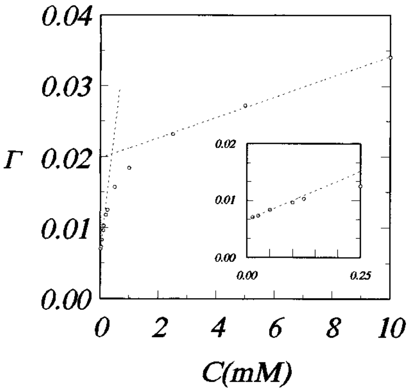

Figure 1. Parameter $\Gamma = c\Phi^{161}{}_A/\Phi^{225}{}_{A_0}$ as a function of PPO concentration, c (millimolar) for the donor solvent, neat cyclohexane. The dashed lines show the predicted linear behavior in the limits of high and low c. The insert shows Γ vs c (millimolar) expanded at the lower concentrations.

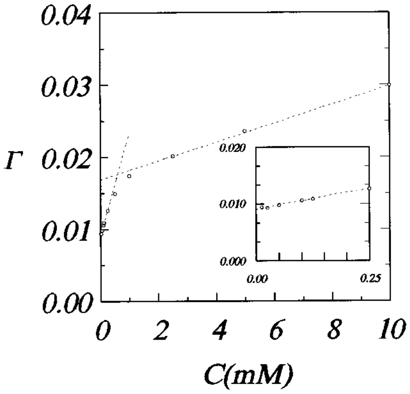

Figure 2. Parameter $\Gamma = c\Phi^{161}{}_A/\Phi^{225}{}_{A_0}$ as a function of PPO concentration, c (millimolar) for the donor solvent, neat *n*-hexadecane. The dashed lines show the predicted linear behavior in the limits of high and low c. The insert shows Γ vs c (millimolar) expanded at the lower concentrations.

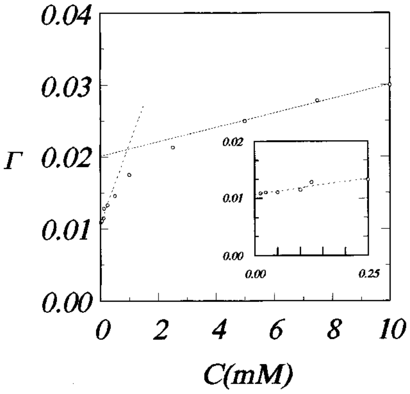

Figure 3. Parameter $\Gamma = c\Phi^{161}{}_A/\Phi^{225}{}_{A_0}$ as a function of PPO concentration, c (millimolar) for the donor solvent, 10 vol % *cis*-decalin + 90 vol % HMN. The dashed lines show the predicted linear behavior in the limits of high and low c. The insert shows Γ vs c (millimolar) expanded at the lower concentrations.

TABLE 4: T State Energy Transfer Constant to PPO, α_T, and Its Product with the T State Formation Efficiency, χ

donor	$\chi\alpha_T$ (M^{-1})	α_T (M^{-1})
cis-decalin	130	3000
cis-decalin in isooctane[a,b]	180	4000
cis-decalin in HMN[b,c]	45	2500
cis-decalin in 2,2DMB[d]	110	3500
cyclohexane	108	8500
n-hexadecane	56	3000
2,3-dimethylbutane	37	2500

[a] From ref 1. [b] 10 vol % or lower. [c] 2,2,4,4,6,8,8-Heptamethylnonane. [d] 10 vol % in 2,2-dimethylbutane.

TABLE 5: Energy Transfer Parameter $\Psi = \Phi^{\lambda}{}_{A}\Phi^{\lambda}{}_{D_0}/\Phi^{\lambda}{}_{D}\Phi^{\lambda_0}{}_{A_0}$ and Its Ratio to $Q = \alpha_D c$ for the Systems Nitrogenated and Aerated Benzene + PPO at Excitation Wavelengths of $\lambda = 161$ or 254 nm

	benzene[a] (N_2)		benzene[a] (air)		benzene[b] (air)	
c, M	Ψ^{161}	Ψ^{161}/Q	Ψ^{161}	Ψ^{161}/Q	Ψ^{254}	Ψ^{254}/Q
1.25×10^{-5}	0.00676	0.55_4	0.00248	0.59	0.00423	1.01_0
2.50×10^{-5}	0.00134	0.54_8	0.00479	0.57	0.00810	0.98
5.00×10^{-5}	0.00268	0.55_1	0.00952	0.57	0.0161_4	0.96
1.00×10^{-4}	0.0523	0.53_6	0.0192	0.57	0.0328	0.99
2.50×10^{-4}	0.130	0.53_2	0.0467	0.56	0.0776	0.93
5.00×10^{-4}	0.265	0.54_5	0.0943	0.56	0.159	0.95
1.00×10^{-3}	0.512	0.52_5	0.181	0.54	0.328	0.98
2.50×10^{-3}	1.33	0.54_4	0.466	0.56	0.866	1.03
5.00×10^{-3}	2.72	0.55_8	0.954	0.57	1.94	1.16
1.00×10^{-2}	5.55_5	0.57_0	2.02	0.60	4.61	1.38

[a] $\lambda_0 = 300$ nm. [b] $\lambda_0 = 314$ nm.

uncertainty of ca. 30%. The product $\chi\alpha_T$ has a much higher reliability of ca. 5−10%.

Although eq 9 appears to work rather well, it does not provide a perfect fit to the data. The equation always slightly overpredicts at high concentrations and underpredicts at low concentrations. Nevertheless, via the parameters, $\chi\alpha_T$ and α_T, it serves as a useful quantifier of the efficiency of the T state process and it is in this capacity that we utilize it in the following discussion.

Benzene Donor. The results for benzene are displayed in Table 5. The slight differences in the absolute value of Ψ^{161}/Q ratio for the aerated and nitrogenated solutions of ca. 5% are not considered significant and are attributed to small errors in calibration factors. The dependence of Ψ^{161} on *c* is, on the other hand, independent of calibration factors and accordingly was examined rather carefully for signs of concavity at low PPO concentrations. Since α_D is so large for benzene, even if $\chi\alpha_T$ and α_T were of the same order of magnitude for benzene as for saturated hydrocarbons, only a very small increase in the ratio Ψ^{161}/Q and/or in the ratio $\Psi^{161}(N_2)/\Psi^{161}(\text{air})$ with decreasing concentration would be predicted. The entries shown in Table 5 for the nitrogenated solutions were constructed, for each concentration, from four independent experimental determinations of $I^{161}{}_A/I^{161}{}_D$ over a period of about a month using different cells and methods of solution preparation with an average standard deviation of $I^{161}{}_A/I^{161}{}_D$ at a single concentration of 1.7 ± 0.8%.

All experiments at 161 nm showed a small decline in Ψ^{161}/Q as *c* decreases from 1×10^{-2} to 1×10^{-3} M due to some reabsorption of the benzene fluorescence by PPO.[7] However, below 1.0×10^{-3} M, the ratios for the nitrogenated solutions remained essentially constant within the 1.7% uncertainties. There is perhaps a tendency for the ratio to increase slightly, but, unfortunately, this tendency is so small that it is difficult to eliminate with any certainty artifactual origins. The air-equilibrated solutions excited at 161 nm show more of a tendency for increase in Ψ^{161}/Q as *c* declines, whereas those for excitation at 254 nm show less of a tendency for change, but both of these experiments were somewhat less reliable than the nitrogenated ones. Certainly, the Ψ/Q ratios always remain very close to the value of $\beta^{\lambda}{}_D$ that are predicted from independent measurements (i.e., $\beta^{161} = 0.55$, $\beta^{254} = 1.00$), and the ratio of $\Psi^{161}(N_2)/\Psi^{161}(\text{air})$ exhibits no sign of a tendency to either increase or decrease with change in c.

To further study the possibility of a second transferring channel in benzene we have examined the ratio of Ψ^{161}/Q for aerated benzene solutions containing 0.040 M CCl_4 and also for solutions oxygenated at 1 atm. At 0.040 M CCl_4, the fluorescence quantum yield of aerated neat benzene was found to be reduced by a factor of 4.3_3 and the parameter, α_D to be similarly reduced from 335 to 78 M^{-1}. This value of α_D is now comparable to that for cyclohexane, *n*-hexadecane, and 2,3-dimethylbutane (see Table 1) and, therefore, were a second energy transfer channel available in the benzene solutions, we would have expected to see a similar curvature in Ψ^{161}/Q. But still we have observed no significant increase (i.e., if any, less than 3%) in Ψ^{161}/Q for PPO concentrations from ca. 1×10^{-4} to 2×10^{-5} M. In the case of oxygen saturation, the value of α_D was reduced by a factor of ca. 2.6_7 (i.e. to 125 M^{-1}) and again no increase in Ψ^{161}/Q was observed (i.e., if any, less than 4%) over a PPO concentration range from ca. 1.0×10^{-4} to 1×10^{-5}. Of course it remains possible that CCl_4 (and O_2) quench the two benzene channels to exactly the same extent, or, alternatively completely eliminate the second channel, but we consider this to be unlikely. Indeed for *cis*-decalin it has been reported that significant curvature remains in Ψ^{161}/Q even for heavily quenched O_2-saturated solutions.

In summary, then, our data tend to favor the conventionally accepted conjecture that benzene to PPO energy transfer involves only the D_1 state of benzene,[8] but further work is required to confirm this.

Some Comments on the Nature of the Second Channel. The possibility that the T state transfer process is essentially nondiffusive was first suggested by measurements of the energy transfer process from *cis*-decalin to PPO at −35 °C.[1] At this temperature the viscosity increased by a factor of ca. 20, the parameter α_D of the diffusion-controlled D_1 transfer process was appropriately reduced, but $\chi\alpha_T$ remained unaltered. On the other hand, experiments seeking evidence for some form of energy migration through the *cis*-decalin (as might be expected for a nondiffusive energy transfer process) were without success. The dilution of *cis*-decalin to 10% with isooctane increased *both* α_D and $\chi\alpha_T$ (albeit the increase in $\chi\alpha_T$ was much less than for α_D). Since isooctane is significantly less viscous than *cis*-decalin, it could be argued that perhaps the T state process also had a small diffusive component that masked the expected dilution effect on the energy migration process. However, measurements in 3% solutions (which should have had about the same viscosity as the 10% solution) showed essentially no further decline in $\chi\alpha_T$ from its value in the 10% solution.

In this investigation we have confirmed and extended the previous isooctane experiments. From 10% to 1% dilution, $\chi\alpha_T$ remains ca. 40% *higher* than in neat *cis*-decalin, independent of the *cis*-decalin concentration. With HMN as diluent, we also find that dilutions from 10% to 5% leave $\chi\alpha_T$ unchanged, albeit in this case the value is ca. 4 times *lower* than in *cis*-decalin. Since HMN has a viscosity comparable to that of *cis*-decalin (and indeed, as expected, α_D is unaffected by the dilution), this reduction of $\chi\alpha_T$ again points to factors other than viscosity that control its magnitude. Accordingly, the *increase* in $\chi\alpha_T$ when *cis*-decalin is diluted with isooctane cannot be simply interpreted as an effect of viscosity (even though its change now is in the right direction) and the previous argument[1] that perhaps the viscosity change was masking the effect of the dilution to reduce the migration effect must be dismissed. The conclusion then is that there can be no significant contribution to T state transfer either from diffusion or from processes involving energy migration through the *cis*-decalin The invariance of $\chi\alpha_T$ to additional dilution further strengthens this view.

So why then does $\chi\alpha_T$ increase in isooctane, remain about the same in 2,2-dimethylbutane, and decline in HMN? Clearly the diluent solvent cannot be playing a passive role. It does not serve as a background medium through which the *cis*-decalin T state diffuses nor does it serve as an insulating medium that simply thwarts the percolation of energy through the donor solvent. Rather, we suggest, the diluent is utilized much more directly by providing some type of intermediate state in the D to A transfer process. Since the excited neutral states of the diluent solvents that we employ are very unstable (as is evidenced by their very low fluorescence quantum yields of less than 10^{-6}),[3] it is suggested that the intermediate states are characterized by some form of charge separation. Indeed, as is developed below, we suggest that the entire T state process, even in the neat liquids, involves charge-separated states.

As pointed out earlier, the extraction of χ and α_T from the product $\chi\alpha_T$ carries with it a relatively large uncertainty. Nevertheless, using the values of α_T in Table 4, we find that the values of χ seem generally to be low for donor systems with low β_D. Since χ enters eq 8 as a quantum yield for formation of the T state per photon absorbed, the implication is that the T state, whatever its nature, lies energetically close to the D_1 state (as has been previously surmised from other measurements),[1] and is generated from the initial excitation at 161 nm via a similar internal conversion.

In saturated hydrocarbons, the energy difference between the liquid phase ionization threshold and the D_1 absorption threshold is only 1.5 eV[4] whereas in liquid benzene this difference is ca. 3.2 eV.[9] A consequence of the smaller gap is that ion-pair states (involving charge localization on neighboring molecules, D^+D^-) should exist in saturated hydrocarbons at energies much closer to the D_1 onset and recent studies[4] of the recombination fluorescence in saturated hydrocarbons confirm their presence within a few tenths of an electrovolt of D_1.

Our conjecture then is to identify T with a low-lying ion-pair state, D^+D^-. Since our excitation energies are well below the liquid phase ionization threshold, D^+D^- must be accessed via internal conversion from the neutral states.[10] Also, since arguments have already been advanced that suggest T cannot have D_1 as its precursor, the internal transitions that lead to D_1 from the initially excited state (e.g., at 161 nm) must branch off at some energy close to D_1 to enter the manifold of D^+D^- ion-pair states. In dilute solutions of D in a diluent Y, this conversion (the efficiency of which we now identify with χ in eq 9) must terminate on a final state of the form D^+Y^-. This would explain why χ in Table 4 is different for *cis*-decalin in different solvents. Were χ simply to represent an efficiency for production of a state completely localized on *cis*-decalin (e.g., a triplet state) it would be difficult to explain this solvent variability.

The T state does not decay to D_1. Accordingly, there is left only the relatively low probability transitions to the lowest triplet or to the ground state of D as possible exit channels competing with its energy transfer to PPO. On the other hand, any ion-pair states formed in benzene would likely, by virtue of their higher energy above D_1, have significantly shorter lifetimes due to their possible decay to several lower singlet neutral excited states.

From previous measurements, it appears that in the absence of PPO, the T state cannot live longer than ca. 10 ns.[1] The transfer to PPO of its energy (which is essentially that of D_1) could either occur via a Forster-type process (with the ion-pair nonradiatively decaying to D + D) or via injection of the ion pair hole into PPO followed by its radiative recombination with the electron. Assuming an encounter radius of 10 Å for this transfer and the upper bound lifetime of 10 ns requires, therefore, an effective diffusion constant for the percolation of the ion pair of not less than ca. 4×10^{-4} cm^2/s in order to accommodate an α_T of 3000 M^{-1}.

Since there is not much disparity either in ionization thresholds or in electron affinities between various saturated hydrocarbons, the ion pair states D^+D^-, D^+Y^-, Y^+D^- and Y^+Y^- where D and Y represent different hydrocarbons might be expected to lie sufficiently close in energy to allow T state transfer even in the diluted systems. How the various diluent solvents differ in the efficiency of this migration would be controlled by many factors including their conduction band energies, V_0, (which determines, in part, the spatial diffuseness of the electron in the solvent),[10] and geometry differences between the cation and the neutral (which determines how resonant will be the hole transfer). It is interesting to note that the values of $\chi\alpha_T$ that we have obtained for the diluents isooctane, HMN, and 2,2-dimethylbutane, show some correlation with V_0.[10]

Finally, we address the question of why, if the diluent solvents isooctane, HMN, and 2,2-dimethylbutane can act as intermediaries in the T state transport, is there then so little PPO fluorescence when their solutions with PPO are excited at 161 nm? The answer we believe is that their excited neutral states are so unstable (as was alluded to above) that internal conversions to the ion-pair states compete poorly with their decomposition.[11] Thus, we believe that the ion-pair states of these liquids can only be generated via electron and hole transfer from ion pairs of other liquids with more stable neutral excited states, or, alternatively by optical excitations which lie above the ionization threshold.[12]

VI. Conclusions

The absorption of light by a variety of neat liquid saturated hydrocarbons, D, at energies of 7.7 eV (ca. 0.5−0.6 eV below their liquid ionization thresholds) generates, by a succession of internal conversions, two types of relatively stable states, the fluorescing state, D_1, and an ion-pair state D^+D^- that lies energetically close to D_1. The generation quantum yield of D_1 ranges from $\beta_D = 1.0$ in *cis*-decalin to 0.4 in 2,3-dimethylbutane whereas the generation quantum yield of D^+D^- is much lower ranging from $\chi = 0.04$ in *cis*-decalin to 0.01 in cyclohexane.

In the presence of PPO, the D_1 state sensitizes the PPO fluorescence via the usual diffusion-controlled process with Stern−Volmer constants ranging from ca. 40 to 100 M^{-1} depending on the lifetime of D_1 and the viscosity of the liquid. The ion-pair states also sensitize the fluorescence of PPO, but via a process which is independent of the viscosity of the liquid. At PPO concentrations less than 10^{-4} M, the sensitization of the PPO fluorescence by the ion pair has an intrinsic energy transfer efficiency (i.e., per ion pair formed) which is ca. 50−100 times larger than that due to the intrinsic D_1 sensitization efficiency (i.e., per D_1 state formed). This compensates for the unfavorable ratio of χ/β_D and leads to fluorescence yields of PPO at low concentrations that are anomolously large as compared to what is expected from D_1 sensitization. At PPO concentrations $\geq 10^{-3}$ M, both D_1 and D^+D^- sensitization mechanisms approach unit intrinsic efficiency and the large disparity then between β_D and χ causes the ion-pair process to become obscured. Under these conditions, the sensitization appears to behave as a normal D_1 diffusion-controlled process.

Upon dilution of D to 10 vol % or lower with another saturated hydrocarbon, Y, that has no stable neutral excited state (e.g., isooctane, 2,2,4,4,6,8,8-heptamethylnonane, or 2,2-dimethylbutane), the efficiency of the energy transfer process due to D_1 changes in a manner entirely consistent with differences in the viscosity of the D and Y liquids. The efficiency of the ion-pair process is also altered, but not, however, by virtue of viscosity changes. The Y solvent, it is suggested, provides intermediate states such as D^+Y^-, Y^+D^- and Y^+Y^- and it is their relative stability to Coulomb collapse and their relative abilities to transfer their charge separation that now raises or lowers the efficiency of the ion-pair process in the mixed system.

For excitations of liquid benzene from 161 to 254 nm, a careful search has so far revealed no evidence for sensitization other than that via D_1.

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References and Notes

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(5) The value of $\alpha_D = 975$ M^{-1} for benzene is somewhat lower than a previously reported value of 1100 M^{-1} excited at 147 nm (2). The origin of this discrepancy is unknown.

(6) Saik, V. O.; Lipsky, S. *J. Phys. Chem.* **1995**, *99*, 10471 and references therein.

(7) This conjecture is supported by results at $\lambda = 254$ nm where reabsorption is expected to be larger (since the penetration depth is significantly less), and the ratio Ψ^{161}/Q for $c > 1.0 \times 10^{-3}$ M now becomes strongly concentration dependent (see Table 5).

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(11) Indeed, it was to eventually utilize this argument, that we have earlier suggested that the ion-pair state is generated via an internal conversion rather than via a direct optical transition. However, other arguments against optical transitions to charge-separated states in these systems have been presented elsewhere.[4]

(12) Even at 161 nm, which is ca. 0.7 eV below the ionization threshold there may be some evidence for a very low yield of PPO fluorescence in these liquids from some energy transfer mechaninsm. Thus we have found that whereas the intrinisic fluorescence quantum yields of PPO are the same in all of these nonfluorescent solvents, the PPO fluorescence yields that are excited at 161 nm exhibit solvent variabilities that seem inconsistent with changes in the optical absorptivities of either the solvent or of PPO. A more complete analysis of this will be presented elsewhere.