

all the *S*-*n*-propyl thioesters which have been studied, indicating that the potential functions for internal rotation about τ_2 (CXCC) in thio and oxyesters are different.

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Supplementary Material Available: Tables III–VI containing the observed band frequencies, $J + 1$ values, and $B + C$ values for *S*-*n*-propyl cyanothioformate, tri-

fluorothioacetate, chlorothioformate, and fluorothioformate (5 pages). Ordering information is available on any current masthead page.

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Activated and Activationless Localization and Impurity Trapping of the Electron in C_2H_5OH and C_2H_5OD

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Dry electron localization by solvent and trapping by impurity acceptors have been examined for several molecules in C_2H_5OH and in C_2H_5OD from 150 to 300 K. The concentration of acceptor required to reduce the initial yield of electrons to 37% is $C_{37} = k_{loc}/k_e$ in terms of rate constants for localization and electron trapping. As the temperature decreases, C_{37} decreases and becomes constant below ~ 150 K. Each process involves two channels, one activated, the other activationless. Consequently, $k_{loc} = k_{loc,T} + k_{loc}^0$ and $k_e = k_{e,T} + k_e^0$. For impurity $k_{e,T}$ exhibits a negative isotope effect and k_e^0 corresponds to the gas phase resonance. The compound negative ion of the solvent molecule is considered to be stabilized by solvation in the condensed phase as the "solvated electron". Below ~ 150 K, activationless processes dominate and correspond to those in low-temperature amorphous solids. Both are dependent upon the zero-point kinetic energy of strongly scattered electrons of short wavelength in disordered materials. Yields of solvated electrons in ice below ~ 273 K appear to depend almost entirely on activated localization with $E_{act} = 0.16$ eV but electron attachment by the near-resonant process may occur for hot electrons with small yields since there is no zero-point kinetic energy, unlike aqueous glasses.

Introduction

Chase and Hunt³ observed that trapping dry electrons (e^-) by toluene in propanol became much more efficient as the temperature decreased. This interesting effect suggested a more detailed investigation of similar systems. The discovery that the trapping efficiency is approximately linear in the concentration of chemically bound oxygen for water and alcohols³ seems to be related to solvent isotope effects.⁴ These provide important supplementary means to study temperature dependence since dry-electron trapping by an impurity competes with localization by solvent. Ten molecules known to react slowly with solvated electrons (e_s^-) were selected to facilitate time resolution of fast and slow reactions. Measurements below room temperature are also advantageous while C_2H_5OH and C_2H_5OD are suitable solvents, providing a relatively long lifetime for e^- and more efficient trapping.³ An improved understanding of the temperature dependence is the objective of this work, which extends a preliminary examination.⁴

Experimental Section

Irradiations of ~ 1 krd were performed with 10-ns pulses of ~ 8 -MeV electrons. The efficiency of electron trapping was measured from the decreased absorbance of solvated electrons, relative to undoped solvent, measured at λ_{max} for each temperature. Other details have been described.⁵ Results are expressed in terms of C_{37} , the concentration of electron scavenger required to reduce the electron yield to 37% of that in the undoped solvent.

Results

Of the dry-electron scavengers examined previously,⁵ ten have been selected for further work in the range 150–300 K in C_2H_5OH and C_2H_5OD . Values of C_{37} decrease with decreasing temperature but tend to constants, C_{37}^0 , at < 150 K. This is shown for $(CH_3)_2SO$ in Figure 1. Its temperature dependence is typical, but C_{37} does not obey an Arrhenius dependence, while empirically $C_{37} - C_{37}^0$ does. This dependence is a useful guide for evaluating C_{37}^0 , but it is not the only one. With two exceptions, C_{37}^0 is only

TABLE I: Electron Attachment by Impurities in C₂H₅OH and C₂H₅OD^a

Electron acceptor	C ₃₇ ⁰		C ₃₇ ^b		(C - C ⁰)/C ⁰		Ratio	k _e ^{-c}
	H	D	H	D	H	D		
C ₆ H ₅ Cl	0.13	0.16	0.28	0.19	1.2	0.2	6	4.6 × 10 ⁸
C ₆ H ₅ F	0.25	0.21	0.39	0.29	0.52	0.6	1.3	9.3 × 10 ⁷
C ₆ H ₅ CH ₃	0.26	0.28	2.09	1.07	7.0	2.8	2.5	8.5 × 10 ⁶
C ₄ H ₄ S*	0.31	0.33	0.77	1.05	1.5	2.2	0.8	4.0 × 10 ⁷
C ₆ H ₅ NH ₂ *	0.35	0.38	1.70	1.68	4.0	3.5	1.1	3.6 × 10 ⁷
C ₆ H ₅ OCH ₃ *	0.35	0.40	0.96	1.40	1.7	2.5	0.7	1.1 × 10 ⁷
(CH ₃) ₂ SO	0.40	0.56	2.14	0.73	4.3	0.3	12	1.2 × 10 ⁸
C ₆ H ₆ *	0.40	0.29	1.37	0.99	2.4	2.5	1.0	7.9 × 10 ⁶
C ₆ D ₆ *	0.40	0.36	1.87	2.23 ^d	3.7	5.2 ^d	0.7	6.8 × 10 ⁶
CH ₃ CO ₂ C ₂ H ₅	0.56	0.44	1.24	0.61	1.0	0.6	1.7	8.6 × 10 ⁷

^a Systems marked by an asterisk obey eq 5. ^b Measured at 273 K. ^c Rate constants in M⁻¹ s⁻¹ at 298 K in C₂H₅OH. ^d From a smoothed curve of C₃₇ vs. T the value at 273 K would be 1.80 and (C₃₇ - C₃₇⁰)/C₃₇⁰ would be 4.0.

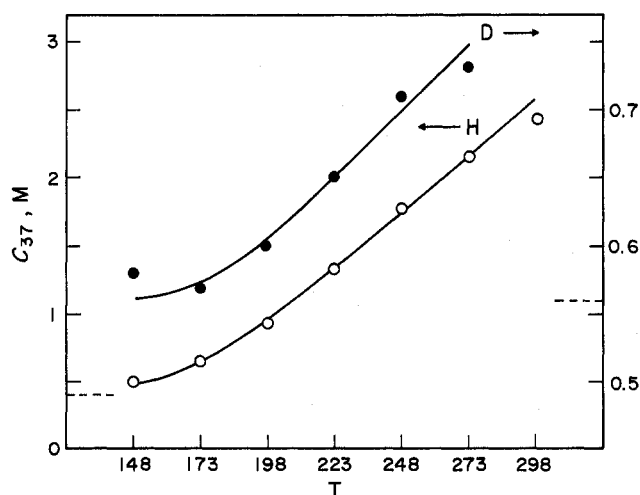


Figure 1. Values of C₃₇ for (CH₃)₂SO in C₂H₅OH and C₂H₅OD. Broken lines locate estimated values of the activationless C₃₇⁰.

~6% less than C₃₇ at 150 K. (Electron localization by the matrix and trapping by impurities is still efficient at much lower temperature.) Values of C₃₇⁰ are summarized in Table I. As an indication of the temperature dependence, values of C₃₇ at 273 K are included. For later consideration, values of (C₃₇ - C₃₇⁰)/C₃₇⁰ are also included together with k_e⁻. An example of log (C₃₇ - C₃₇⁰) vs. T⁻¹ appears in Figure 2 for C₆H₆ and in Figure 3 for C₆H₅NH₂.

Discussion

For a first-order reaction of e⁻ with an acceptor over its lifetime τ, relative to localization by solvent, eq 1 and 2

$$k_e - C_{37}\tau = 1 \quad (1)$$

$$C_{37} = k_{loc}/k_e \quad (2)$$

apply for k_e⁻ (M⁻¹ s⁻¹), C₃₇ (M), τ (s), and k_{loc} (s⁻¹) □ τ⁻¹ [solvent]. Consequently, C₃₇ measures a competition of solvent and solute for e⁻. If k_{loc} and k_e⁻ were simple rate constants, C₃₇ should obey an Arrhenius dependence. It does not for any system. We postulate that in the range >150 K the components of C₃₇ are resolved by eq 3 where

$$k_{loc} = k_{loc,T} + k_{loc}^0 \quad (3a)$$

$$k_e = k_{e,T} + k_e^0 \quad (3b)$$

k_T's are activated and k⁰'s are activationless.⁶ By hypothesis, k⁰'s contribute to k_{loc} and k_e⁻ at all temperatures. A special case of interest is eq 4 for k_{e,T} << k_e⁻⁰. Letting

$$C_{37} = (k_{loc,T} + k_{loc}^0)/k_e^0 \quad (4)$$

$$C_{37}^0 = k_{loc}^0/k_e^0 \text{ we have}$$

$$(C_{37} - C_{37}^0)/C_{37}^0 = k_{loc,T}/k_{loc}^0 \quad (5)$$

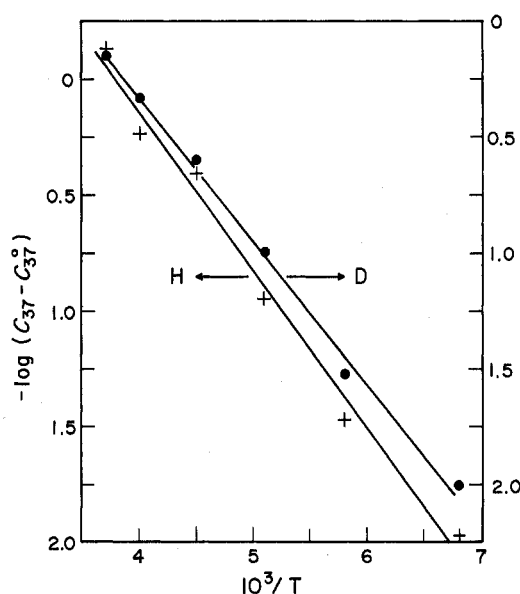


Figure 2. The dependence log (C₃₇ - C₃₇⁰) vs. T⁻¹ according to eq 5 for C₆H₆.

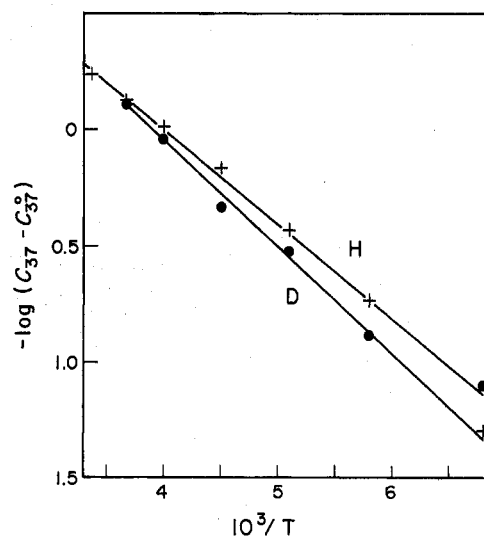


Figure 3. Similar to Figure 2, for C₆H₅NH₂.

For systems which obey eq 5, the value of the left-hand side depends only on the solvent at each temperature. There must also be a common isotope effect for various impurities in one solvent. If the Arrhenius dependence is obeyed, there is a single value of E_{act} in one solvent. In Table I, acceptors marked with an asterisk meet these criteria approximately. Errors in C₃₇ and C₃₇⁰ are esti-

mated at $\sim 15\%$, those for C_{37}^0 being reinforced in $(C_{37} - C_{37}^0)/C_{37}^0$. Values of E_{act} for the systems marked are 2.2 kcal in C_2H_5OH and 2.7 kcal in C_2H_5OD with average deviations 0.3 and 0.4 kcal, respectively. The expected zero-point energy difference is 0.7 kcal for C–O–H and C–O–D bending, which is considered to be the mode involved in activated localization,^{4,7} but quantitative experimental support is barely indicated due to errors.

Below ~ 150 K neither electron localization by solvent nor trapping by impurity in measurable yields is activated. Both processes are well known for many systems in the range ≤ 77 K with relatively good yields and no evidence for activation. Benzyl acetate in ethanol at 77 and 300 K is an example with C_{37} about 0.06 and 0.09 M, respectively.⁸ For the range >150 K activated localization is expected to have an isotope effect. Although this cannot be unambiguously distinguished from solute effects, most systems exhibit the expected change. For all systems the improved efficiency of acceptors at lower temperatures is relative to localization by ethanol, which becomes less effective. The ratio $k_{\text{loc},T}/k_{\text{loc}}^0$ can be estimated by the average value of $(C_{37} - C_{37}^0)/C_{37}^0$ for the marked systems as 2.7 for data at 150 and 273 K in C_2H_5OH .

The activationless mechanism of electron localization by ethanol is attributed to a low-energy electron resonance which is embedded in the "band" of extended states of the disordered system. The electron is considered to be near the bottom of this band at V_0 , with local fluctuations, just prior to localization. In terms of the bulk electron affinity χ (where $\chi \equiv -V_0$) the resonance maximum is at $(0.5 + \chi)$ eV in ethanol at 77 K.⁹ By analogy with resonances for gases, the cross section is expected to tail smoothly toward lower energy. The threshold lies at >0 eV and the energy is supplied mainly by the zero-point kinetic energy of e^- .⁴ The same applies to many of the solutes in Table I.

It is generally accepted that delocalized electrons have short scattering free paths λ_s in liquid hydrocarbons.¹⁰ This is supported by constant electron mobilities up to rather high fields, in apparent contradiction with the assumed De Broglie wavelength¹¹ (which is undefined for liquids). In strongly dipolar media such as ethanol it can be assumed that electrons are even more strongly scattered and that λ_s approximates the intermolecular distance. The wavelength cannot exceed λ_s . This establishes a large zero-point kinetic energy, with large dispersion, which is available for a transition to a nonscattering state, e.g., an anion. Electron attachment by molecules with negative electron affinity, A (e.g. benzene, $A = -1.15$ eV), or high thresholds for dissociative attachment (e.g., CH_3F , 1.2 eV) has been attributed to hot electrons.¹² Such processes must occur at large acceptor concentrations, but they cannot account for small values of C_{37}^0 , e.g., 0.13 M for chlorobenzene ($A = -0.8$ eV). Such acceptors serve as useful probes to provide evidence for the phenomenon. In crystalline media, attachment should not occur for such impurities.

It has been shown that in ethanol and methanol $e_s^- + h\nu \rightarrow H^{\cdot}$.^{8,13} Consequently, we conclude with Bush and Funabashi⁷ that the visible absorbing species can be described as ROH^{\cdot} , the solvent radical ion (this is an authorized translation of "small polaron"⁷), and that the infrared absorbing species is interstitial in a hydrocarbon environment. For the present purpose, activationless localization involves formation (in the limit) from ground state C_2H_5OH of a compound negative ion which relaxes to $C_2H_5OH^-$, which will be represented by e_s^- since "solvated electron" can scarcely be improved upon. By hypothesis, supported by the isotope effect, only prior

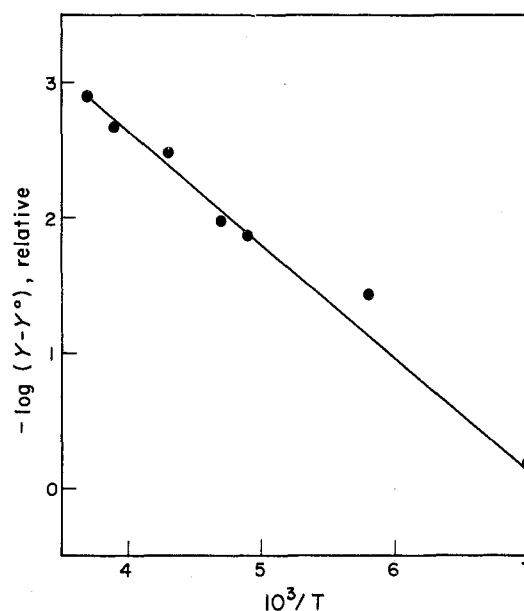


Figure 4. Yields of e_s^- , Y , in arbitrary units, of undoped ice vs. T , with Y^0 the activationless yield, from data in Table II of ref 14.

excitation of C–O–H bending contributes to the activated mechanism. This was proposed for an ordered system, where it is required, and extended to the disordered system.⁷

The preceding considerations are expected to apply to other systems and one interesting possibility is the dependence on temperature of the yield of e_s^- in undoped ice following pulsed irradiation, from the data of Taub and Eiben.¹⁴ In terms of the absorbance at the spectral peak, their dose-normalized yields have been fitted to the dependence $\log(Y - Y^0)$ vs. T^{-1} where $Y = [e_s^-] M \times 10^7 / (\text{dose})$ in Figure 4. The arbitrary unit of dose is that delivered per 10^{-6} s of pulse duration. The value of Y^0 has been taken arbitrarily as the measured value of Y at the lowest temperature, 113 K. It is 15% less than the yield at 143 K but it is only $\sim 1\%$ of the yield at 268 K. The justification of the Arrhenius dependence rests on very simple considerations. The probability of activated localization, proportional to $(Y - Y^0)$, is given by $k_{\text{loc}}[H_2O]\tau$, where the lifetime τ relates to recombination and is averaged for all events. The lifetime is not expected to be temperature dependent. Consequently, $Y - Y^0 = \text{constant} \times k_{\text{loc},T}$. The corresponding plot in Figure 4 gives $E_{\text{act}} = 0.16$ eV. For H–O–H bending, $\hbar\omega = 0.20$ eV.

The relatively very small value of Y^0 in ice, activationless by hypothesis, is in marked contrast to glassy ethanol. Since the well-annealed ice is ordered there is no short-range scattering with its associated zero-point kinetic energy to provide a mechanism for localization of e^- as H_2O^- by resonance attachment at V_0 . There remains the possibility of impact by hot electrons. The efficiency would probably be small. The tenfold increase in yield from ice to water near 273 K is attributed to the order-disorder transition. In aqueous glasses, localization is probably activationless but efficient as a consequence of large zero-point energy. No measurable yields of solvent-trapped electrons were found for seven undoped crystalline alkanes at 4 and 77 K.^{15,16}

The marked difference in localization efficiency of ordered and disordered media relates simply to the respective $V_{0,\text{ord}}$ and $V_{0,\text{dis}}$. If a self-trapping level is located in this interval it can produce e_s^- only in the disordered system. The same consideration applies to impurity trapping for $A < 0$ but there is no experimental evidence.

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Heavy Atom Effects on the Phosphorescent Triplet States of Several Aromatic Molecules

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Phosphorescence microwave double resonance techniques were used to observe the effects of inter- and intramolecular heavy atom perturbation on naphthalenes and quinolines. In order to observe intramolecular heavy atom perturbation in naphthalene, the 1 position was chlorinated whereas on quinoline, the chlorine was substituted on the 2, 4, and 8 positions. The effects of external perturbation were studied using 1,2,4,5-tetrachlorobenzene (TCB) as a host single crystal, while substituted single crystals of durene were grown to represent the least interactive matrix. The changes in the zero field splitting of these guest-host systems were interpreted in terms of the second-order spin-orbit contribution to the zero field splitting parameters. Relative radiative rate and total decay rate constants from the phosphorescent triplet state were interpreted in terms of out-of-plane vibronic coupling to the radiative process in these aromatic molecules.

Introduction

Heavy atom effects have been a subject of interest to researchers in triplet state spectroscopy for many years.¹⁻³ Interpretation has been limited to spectral properties such as vibrational analysis of the phosphorescence spectra and lifetime data at 77 K. With the use of the phosphorescence microwave double resonance (PMDR) method, a powerful and sensitive tool in the study of molecular perturbations, several workers have gained a better understanding of intra- and intermolecular heavy atom effect in several azanaphthalenes.^{4,5}

In this paper we shall present a systematic study on the effect of chlorine substitution in aromatic molecules, viz., naphthalene and quinoline, and the effects of externally chlorinated solvents on the lowest phosphorescent triplet state of these molecules. The changes in the zero field splittings and the phosphorescence relaxation parameters due to intra- and intermolecular heavy atom perturbation are interpreted in terms of the changes in the parameters relative to the parent molecules, naphthalene and quinoline.

Experimental Section

The guest molecules studied were naphthalene, 1-chloronaphthalene, quinoline, isoquinoline, 2-chloroquinoline, 4-chloroquinoline, 8-chloroquinoline, and quinoxaline. These molecules were purchased commer-

cially, and purified by multiple vacuum distillation or sublimation at reduced pressures. The hosts were durene and tetrachlorobenzene (TCB) which were purified by extensive zone refining under an inert atmosphere for an equivalent of over 300 passes after recrystallization from ethanol. The single crystals of the host were grown with guest concentrations of less than 0.05% mole/mole in the standard Bridgmann furnace. Single crystals were cut and shaped to fit a slow wave helix which was then immersed in the liquid helium cryostat. Further details of the PMDR apparatus were described in previous work.^{6,7}

The microwave zero field transition was observed by the microwave induced delayed phosphorescence (MIDP) technique as described by van der Waals et al.^{8,9} The microwave sweep was calibrated with an EIP microwave frequency counter and reproducibility of the detected transition was determined to be approximately ± 5 MHz. In several cases, two of the zero field transitions could be observed by the MIDP methods, but the third transition was observed by continuous pumping of a different transition with another microwave generator while the third resonance was swept (vide infra).

For phosphorescence decay measurements a vibronic band of the phosphorescence (usually the 0, 0 band) was isolated with a spectrometer slit width of ≤ 100 cm⁻¹. The filtered Hg excitation source was extinguished in about 2 ms by an electronically controlled shutter.