SINGLET ENERGY TRANSFER IN LIQUID ACETONE

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SUMMARY

Rate parameters of singlet energy transfer from acetone to various aromatic solutes have been determined by pulse radiolysis over a range of temperature. The values observed are an order of magnitude greater than expected for diffusion controlled processes. The implications to various energy transfer models are discussed.

INTRODUCTION

The transfer of energy between isolated aromatic molecules has been extensively studied and is now well-understood[1]. The analogous process of transfer from solvent donor species to suitable acceptor solutes has also received attention, especially in liquid benzene and alkyl benzenes, although there is still uncertainty about the mechanistic details[1]. Such solvent–solute transfer studies have not yet been extended to non-aromatic donor systems mainly due to experimental difficulties, including the inaccessibility of the solvent absorption band to photo-excitation. This can be overcome by using ionizing particle radiation, the energy of which is dissipated by coulombic interactions with bound electrons, thus ensuring that the major portion of the absorbed energy is imparted initially to the major component of the reacting system, *viz.* the solvent, causing excitation, initially to both ionized and bound states of the molecules. Ion-recombination and internal conversion processes very rapidly bring the primary species to the first excited level (singlet and triplet) whence the various uni- and bi-molecular reactions can occur exactly as if the solvent molecules had been photo-excited. This report is concerned with solvent–solute singlet energy transfer observed in liquid solutions of aromatic hydrocarbons in acetone.

EXPERIMENTAL

Materials

Acetone was fractionally distilled, dried with molecular sieve and stored in a nitrogen atmosphere. Anthracene (micro-analytical), 2,2′-dinaphthyl (scintillation grade), diphenyl oxazole (PPO) and 1,2-benzanthracene were used as supplied. De-aeration was achieved by prolonged bubbling with argon.

Procedure

The experiments were carried out using the pulse radiolysis facility at the Christie Hospital and Holt Radium Institute, Manchester, details of which have been published[2]. Briefly, an intense pulse (8 ns) of 10 MeV electrons was incident upon the liquid sample contained in a fused silica cell. In the mode used here, the scintillation luminescence was collected in an optical system and focused, *via* a monochromator onto a Hamamatsu R106 photomultiplier or an ITT F4014 biplanar vacuum photodiode connected to a cathode ray oscilloscope (CRO). The R106 was used with a Tektronix 556 oscilloscope and 1S1 plug-in giving an overall time resolution of about 2 ns. For the F4014 a 1S2 plug-in was used, giving a time resolution of approximately 120 ps. Photographs of the CRO traces provided information from which the time-dependence and wavelength-dependence of the emission could be obtained.

In these experiments a complete picture of fluorescence decay required about 1000 electron pulses at a repetition rate of 50 Hz. In all cases it was confirmed that build-up of radiolysis products was insufficient to alter the amount, or lifetime of the observed fluorescence.

RESULTS

Solutions of anthracene ($\sim 10^{-3}$ M) in liquid acetone when irradiated in the manner described emit light with a spectrum characteristic of anthracene fluorescence and a time-dependence (*e.g.* Fig. 1 inset) which coincides with that published[1] (5.4 ns) for this system excited directly. Similar behaviour was observed for solutes such as 1,2-benzanthracene, 2,2′-dinaphthyl and PPO but not for solutes such as benzene, naphthalene and biphenyl. The singlet levels of the last three solutes are higher than that of acetone, whereas the first group all have lower singlet levels than the solvent, indicating singlet energy exchange is occurring. It has been shown previously[3] that significant singlet yields are formed in acetone (0.35 molecules per 100 eV absorbed).

Figure 1(a) illustrates the dependence of the fluorescence intensity of anthracene (at 450 nm) on solute concentration. The increase below 10^{-2} M is due to energy transfer competing with the natural decay of the acetone singlet; the decrease above 10^{-2} M is caused by concentration-quenching forming anthracene excimer as observed in liquid benzene solutions[4].
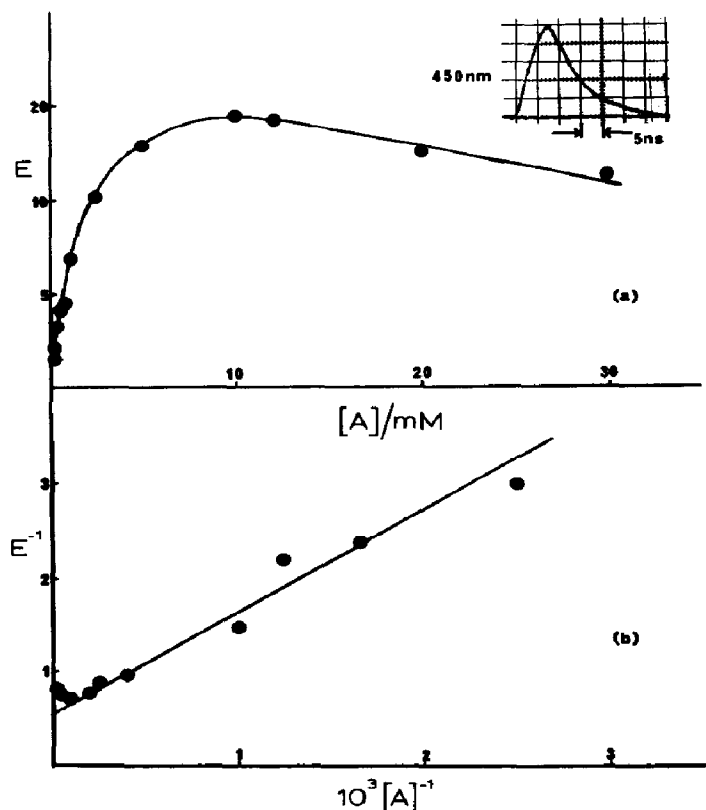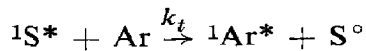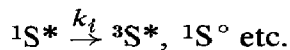
Fig. 1. (a) Anthracene fluorescence yield (E) at 450 nm from acetone solutions irradiated with a 5 ns pulse. Points refer to total area under decay curves as in inset. (b) Data of Fig. 1 (a) plotted according to expression (A) (see text).

In the sequence:

$$^1S^* \xrightarrow{k_i} {}^3S^*,\ {}^1S^\circ \text{ etc.}$$

$$^1S^* + Ar \xrightarrow{k_t} {}^1Ar^* + S^\circ$$

the emission intensity E at a concentration of aromatic $[Ar]$ is given by:

$$\frac{E_0}{E} = 1 + \gamma\ [Ar]^{-1} \tag{A}$$

where E_0 is the limiting value of E as $[Ar] \to \infty$ and $\gamma = k_i/k_t$.

Figure 1 (b) shows a plot of the data in Fig. 1(a) according to eqn. (A). At values of $[Ar]$ below the onset of concentration quenching the linear behaviour is consistent with the simple energy transfer scheme. Values of γ for different aromatics extracted from plots such as Fig. 1 are collected in Table 1.

Using the fluorescence lifetime of acetone determined by photon counting[5] of 1.7 ns allows k_t for each solute in Table 1 to be evaluated. The rate parameter

TABLE 1

Solute	γ (mole l^{-1})	k_t (l mole^{-1} s^{-1})
Anthracene	1.83×10^{-3}	3.2×10^{11}
1,2-benzanthracene	1.92×10^{-3}	3.06×10^{11}
PPO	6.78×10^{-4}	8.8×10^{11}
2,2'-dinaphthyl	1.28×10^{-3}	4.6×10^{11}

for diffusion controlled transfer between equally sized molecular species in acetone is $k_{diff} = 2.89 \times 10^{10}$ l mole^{-1} s^{-1} [6]; the experimental values in Table 1 are at least an order of magnitude in excess of this.

To confirm these unexpectedly high rate constants in an independent manner an experiment was designed to directly observe the rate of formation of anthracene singlet. The principle was to observe the emission characteristics during the interval (770 ps) between the fine structure pulses which make up the envelope of the 8 ns electron pulse (Fig. 2a). At appropriate values of [Ar] the formation time of the anthracene singlet state should be such that a measurable grow-in during the fine structure interval occurs. As Fig. 2(b) shows, the amount of emission at 2×10^{-3} M anthracene does increase but the present instrumental sensitivity was insufficient
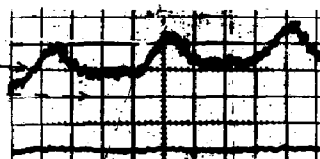
(a)

Visible Cerenkov emission

from fine structure pulses
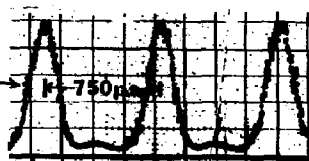
(b)

Cerenkov

Anthracene Emission (410 nm)

(c)

Total Anthracene Emission

produced by 5 ns pulse with

associated Cerenkov peaks

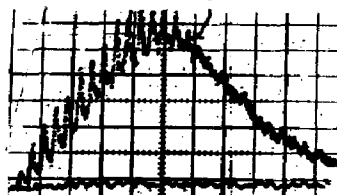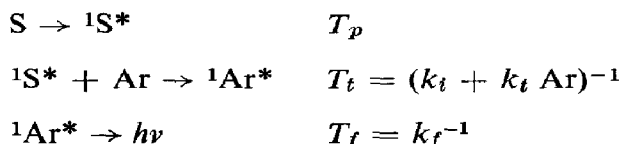Fig. 2. (a) Emission from ethanol at 450 nm, 5 ns pulse, 200 ps/div. (b) 2×10^{-3} M anthracene in acetone, 5 ns pulse, 200 ps/div. (c) As (b), 2 ns/div.

to measure rate data between the sub-pulses. It was possible, however, to analyze the overall emission curve (*e.g.* Fig. 2c) in terms of delay times by assuming the sequence:

$$S \rightarrow {}^{1}S^* \qquad\qquad T_p$$

$$^{1}S^* + Ar \rightarrow {}^{1}Ar^* \qquad T_t = (k_t + k_t\, Ar)^{-1}$$

$$^{1}Ar^* \rightarrow h\nu \qquad\qquad T_f = k_f^{-1}$$

According to the method outlined in the Appendix the total delay time T_L is $T_p + T_t + T_f$ and direct measurement of T_L and T_p by integration of the approximate sections of overall CRO traces such as Fig. 2(c) together with estimation of T_f from the exponential tail, allowed T_t to be evaluated. For several anthracene concentrations, values of k_t fell close to 10^{12} 1 mole^{-1}s^{-1} which, considering the inherent sensitivity problems in the analysis, indicated that k_t values arrived at from kinetic considerations were essentially correct.

Further observations were made as follows: (i) the γ-coefficient was measured at various temperatures in the range 196–297 K, for anthracene solute and found to be invariant. Since k_t is also unaffected by temperature[7], we conclude that k_t is invariant; (ii) γ (and hence k_t) was unchanged on dilution of acetone in benzene in the range 100%–1% acetone. (In dilute solution, singlet acetone is populated by energy transfer from the major component, benzene. At the concentrations used, this process is completed during the exciting electron pulse.)

DISCUSSION

In benzene and several alkyl derivatives, singlet energy is transferred from solvent to solute with rate parameters a factor of approximately 2 higher than diffusion control requires. In the cases examined here an order of magnitude is involved, which parallels the observations of Chien and Connor[8] on the quenching of diethyl ketone singlets by paramagnetic metal chelates.

Migration of solvent excitation in aromatic liquids has been examined theoretically and different models proposed[1]. Voltz[9] considers that solvent-solvent multipole–multipole interactions contribute a migration coefficient Λ_D which supplements the solvent molecule diffusion coefficient D_D:

$$Z_D = D_D + \Lambda_D \qquad\qquad\qquad\qquad\qquad\qquad \text{(B)}$$

Birks and Conte[10], on the other hand, see excitation migration resulting from the alternate making and breaking of excimer linkages between neighbouring solvent species which, according to later work[11], may be viewed as simple molecular diffusion but with an enhanced interaction radius of the donor.

Examination of the present results according to these models leads to the following conclusions.

(1) Singlet energy transfer from acetone to aromatic solute occurs at a rate greatly in excess of that which can be understood in terms of simple molecular diffusion.

(2) The sensitising entity is unlikely to be a group of acetone molecules diffusing through the medium and involving excimer interactions (solvent excitation radius model[11]) since: (a) excimer formation in acetone is unknown; (b) the lack of temperature variation is not consistent with molecular diffusion; (c) molecular aggregation in dilute solutions will be diminished.

(3) The data are altogether more consistent with the concept of migration being due to resonance interactions[9] between acetone molecules, which should not be affected by temperature, and be effective over relatively large distances. The enhanced diffusion coefficient Z_D will be invariant with temperature when $\Lambda_D \gg D_D$. For anthracene in acetone Λ_D can be calculated using the time-independent part of the Smoluchowski equation[1]:

$$k_t = \frac{4\pi N}{1000} R(D_A + Z_D) = 3.2 \times 10^{11} \text{ l mole}^{-1} \text{ s}^{-1}$$

where R, the donor (D)–acceptor (A) interaction distance is taken as being the sum of the molecular radii ($r_D + r_A$). Taking $r_D = 0.28$ nm and $r_A = 0.35$ nm and D_A (from Stoke's law) $= 3.7 \times 10^{-5}$ cm^2 s^{-1}, we obtain:

$$Z_D = 63.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$
and since $D_D = 2.38 \times 10^{-5}$ cm^2 s^{-1} (Stoke's law)
$$\Lambda_D = 61.1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

Thus temperature variations in D_D will not be noticeable in Z_D. The resonance interaction energy which determines the magnitude of Λ_D will decrease with intersolvent distance as is evidenced by the fact that at very low acetone concentrations ($10^{-4}M$) in hexane[12] the transfer becomes diffusion controlled.

One criticism of this application of solvent excitation migration is that the large energy gap (12,000 cm^{-1}) between the Franck–Condon maxima in the absorption and fluorescence spectra of pure acetone suggests different geometries of the ground and first excited singlet state[13]. It may be, however, that resonance interaction occurs between planar ground states and planar excited states (corresponding to a vertical transition) during the time in which relaxation to the fluorescent (pyramidal) state is occurring.

APPENDIX

In very fast pulse radiolysis the stimulating electron pulse cannot be regarded as an ideal pulse of finite dose and zero time width; account must be taken of the structure of the pulse and also of the response-time limitations of the recording
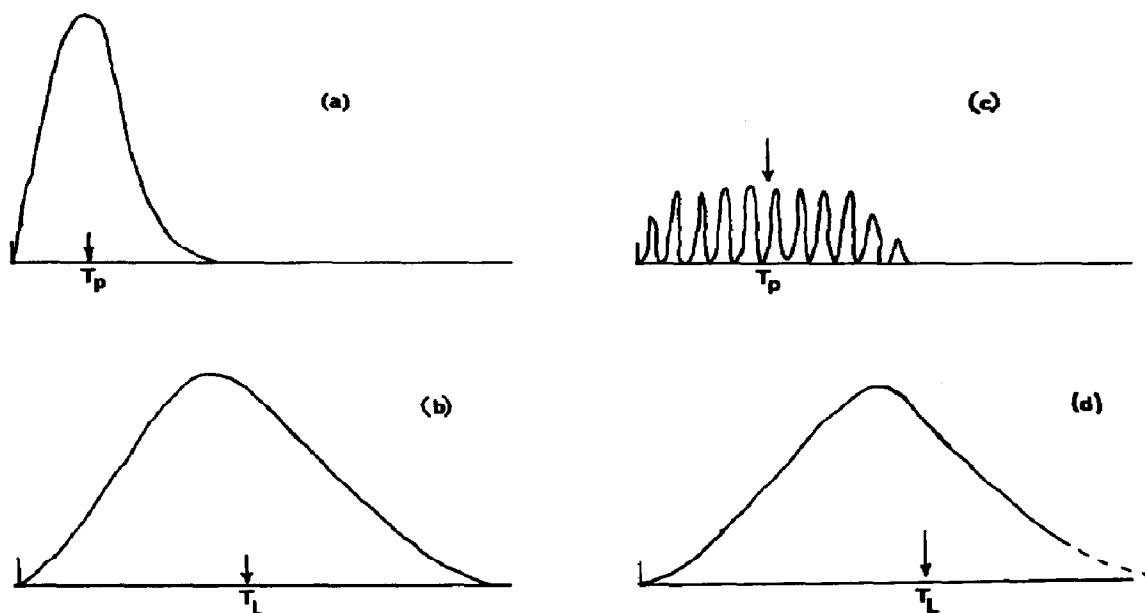
Fig. 3 (a) and (b). An input and an output pulse. (c) A train of input pulses. (d) The output pulse. T_p and T_L show the positions of the mean delay times.

apparatus. Information on the electron pulse structure can be obtained from the emitted Cerenkov light. This light and the light from the chemical system under investigation are passed through the same optical and electronic recording system. Since Cerenkov light is emitted instantaneously, any time differences between these signals must be due to the chemical system. For convenience we shall call the Cerenkov light the input signal and that from the chemical system the output and we shall assume that the system is linear, *i.e.* if several inputs were combined then the total output is the sum of the individual outputs. In Fig. 3, (a) represents an input signal *i.e.* the Cerenkov light from a simple electron pulse and (b) the emission output, which is assumed to decay eventually to zero. Then the mean delay times of these pulses is defined by T_L and T_p where:

$$T_L = \int_0^\infty t\, y\ (t)\ \mathrm{d}t / \int_0^\infty y(t)\ \mathrm{d}t$$

and $y\ (t)$ is the deflection at time t and is referred to some zero time, which may or may not be the beginning of the pulse. If the input and output pulses are distorted by the inherent shape of the electron pulse or by the electronics then the time difference $T_L - T_p$ remains unchanged and can be related to the chemical reaction rates. For a simple exponential build-up of the fluorescence species, followed by an exponential decay then

$$T_L - T_p = T_t + T_f$$

where T_t and T_f are the build-up and decay exponential time constants.

In Fig. 2(c) the input pulse is superimposed on the output pulse. These two can be separated because of the spiky structure of the input pulse and this is shown in Fig. 3(c) and (d). The shape of the micro-input pulses which have a half width of about 200 ps, is determined largely by the electronics (the actual electron pulse is of the order of 70 ps wide). The mean delay time T_p of the whole train is calculated by assuming each pulse to have the same shape and an area proportional to its height and a delay equal to the position of its maximum.

The delay time T_L of the emission output is calculated by numerical integration. If $Y_0, \ldots Y_i, \ldots Y_n$ are the outputs at equal time intervals ΔT, then the zero moment (area) and the first moment are calculated, using the trapezoidal rule, by the sums:

$$\sum_1^n (Y_i + Y_{i-1}) \Delta T/2 \quad \text{and} \quad \sum_1^n [(i-1/3) Y_i + (i-2/3) Y_{i-1}] \Delta T^2/2$$

The traces have only been measured as far as the end of the solid line in Fig. 3 (d) and so the contributions from the dashed tail must be estimated. This could be done because the part of the measured curve after the end of the pulse was found to be exponential and its decay time T_f was estimated by a conventional semilog plot. Assuming the tail continued as a single exponential then its contribution can be calculated.

Typical values for $T_L - T_p$ were 5.5 ns and for $T_f = 5$ ns giving $T_t = 0.5$ ns. The length of the input train of pulses was about 10 ns and so the use of delay times enables build-up times to be detected which are very short compared with the input pulse train. The input and output pulse pass simultaneously through the same optical and electronic systems and are then superimposed on the same oscilloscope recording, thus ensuring the correct time relationship.

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