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Excited Singlet-State Yields in Hydrocarbon Liquids Exposed to X-rays

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The yields of excited singlet states formed in some liquid hydrocarbons are reported for exposure to synchrotron X-rays of energies between 5 and 14 keV. The yields are derived from measurements of ultraviolet fluorescence emission of the hydrocarbons. Results reported are relative to the yield of excited singlets in liquid benzene. The yields decrease with decreasing X-ray energy, and at the lowest energies studied $G(^1S^*) = 1.5/100$ eV for *cis*- and *trans*-decalin. Results are compared to computer simulations.

Introduction

Absorption of X-rays in hydrocarbon liquids leads to emission of energetic photoelectrons that come primarily from the K-shell of carbon and have energies equal to that of the X-ray photon less the binding energy of the electron (284 eV). These photoelectrons produce secondary ionization along their tracks as they lose energy. Because the rate of energy loss or linear energy transfer (LET) varies with electron energy, the density of ionization along the track is energy dependent. Subsequent recombination of the ions (holes) and electrons in the track occurs, forming excited states of the hydrocarbon. The time required for recombination depends mainly on the distance of separation between holes and electrons and the mobilities of these species. For ion pairs produced by a 1 MeV electron, 50% are predicted to recombine in 40 ps in decalin.[1] For kilovolt electron tracks the recombination is even faster.[1] During such short time intervals, the unpaired spins remain correlated. If the electron returns to its ion of origin (as is the case for an isolated ion pair), the excited state formed will be a singlet with 100% probability.

For electron radiation, ionizations occur along the track of the electron and combination of electrons with holes from other ionization events can occur. Electrons in the kilovolt range lose energy rapidly; that is, the LET is high. Consequently ionizations are very dense and the fraction of excited states that is singlet is expected to approach 0.25, which is the fraction expected for completely random combination.[1,2] Electrons in the MeV range lose energy slowly, i.e., the LET is low. Initial ionizations occur far apart, but the lower energy secondary electron produces additional ionization in the vicinity. This group of two or more ionizations is called a spur. The fraction of excited states, expected to be singlet for a two-ion pair spur would statistically be 0.625. Theoretical predictions of the magnitude of this track or LET effect for electron irradiation indicate that the excited singlet state fraction should be approximately 0.61 for MeV electrons and 0.3 for electrons of low energy, around 4 keV.[1]

Pulse radiolysis studies of aromatic solutes in 2,2,4-trimethylpentane, cyclohexane, and *n*-hexane show that for MeV electrons the fraction of excited states that are triplets is 0.5 ± 0.1.[3] Use of a quantum oscillation technique to observe the fluorescence from solutes in *cis*- and *trans*-decalin indicated that the fraction of recombining ion pairs that is singlet is 0.52.[4] In a study of the magnetic field effect on the fluorescence from alkanes containing 2,5-diphenyloxazole, LaVerne et al.[5] showed that initially the singlet fraction is 0.7 for exposure to 0.5 and 2.2 MeV β particles and 0.27 for exposure to 2 MeV helium ions. For such helium ions the ionization density is very high because the LET is close to 100 eV/nm.

Another aspect of this track effect is that the free ion yield, the yield of electrons that escape the track, should decrease as the extent of track cross-recombination increases. It has been shown both by computer simulation[6] and by experimental measurements[7−9] that the free ion yield for hydrocarbons decreases as the X-ray energy decreases from 30 to 2 keV and that a minimum in yield occurs near 2 keV.

In this study we report the yields of excited singlet states for three hydrocarbons determined by measuring the intensity of the UV fluorescence as a function of excitation by X-rays of energy from 5 to 14 keV. In a related X-ray experiment, Brocklehurst[2] observed the effect of a magnetic field on the luminescence of solutions of *p*-terphenyl in squalane and found the singlet fraction increased from 0.4 to 0.5 as the X-ray energy increased from 6 to 15 keV.

Experimental Section

X-rays from 6 to 14 keV are obtained from a Si 311 crystal monochromator at beamline X7B at the National Synchrotron Light Source at Brookhaven National Laboratory. During each use the energy scale is calibrated with metal foils by observing the K-edges of V, Fe, Co, Cu, and Zn or the L-edge of Pt. The resolution of this monochromator is $\Delta E/E = 2 \times 10^{-4}$. Measurements of beam intensity with and without Al foils of known thickness indicate higher order radiation is negligible for this crystal in this energy range.

For experiments, the X-ray beam passes through a N_2-filled ionization chamber to measure the beam intensity prior to entering the sample cell. The cell is made of UV grade quartz but has a 25.4 μm Mylar entrance window on the front for the X-ray beam to enter. UV fluorescence emerging from the back of the cell is collected by a spherical mirror and focused on the window of a photomultiplier tube. Two tubes are used: an EMI 9813QA and a Hamamatsu 2496. The fluorescence beam is intercepted by an interference filter which passes a fraction of the fluorescence and cuts out stray light. For the decalins, a filter passing 228 nm is used, and for benzene one at 295 nm is used; for both the fwhm is 10 nm. The PM tube is operated in the single photon counting mode. The pulse resulting from a fluorescence photon is amplified by an EG&G 5185 preamplifier and discriminated using a constant fraction discriminator (Ortec 584). The discriminator output is converted to an analogue voltage by an Ortec 449 ratemeter. This voltage is read by the beamline counting system. Lifetimes of excited singlets are measured as described previously.[10]

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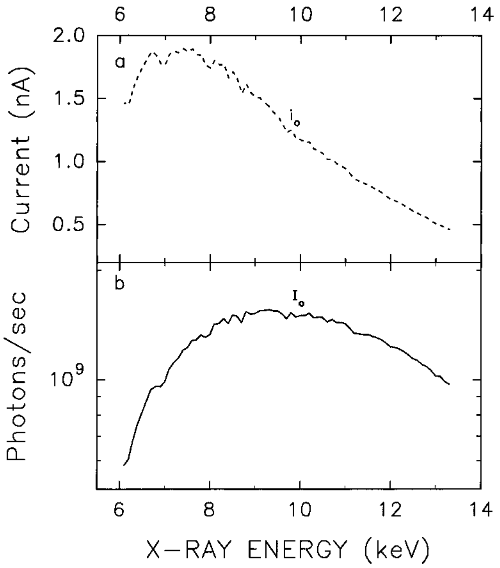

Figure 1. Upper frame: the current from the ion chamber as a function of X-ray energy for a typical run. Lower frame: derived intensity of X-rays emerging from the chamber.

For measurements of fluorescence as a function of X-ray energy, the monochromator is moved in 25 eV steps and the fluorescence recorded for 10 s at each energy. The ion chamber signal is monitored simultaneously using a Kiethley 427 current amplifier. Figure 1a shows a typical plot of the ion chamber current (i_0) versus X-ray energy. Both signals are fed to voltage-to-frequency converters, the outputs of which are read by a computer. Subsequently, signals may be recovered, normalized and plotted separately.

Dosimetry. The yield of excited singlets is measured relative to the dose of X-rays absorbed by the sample. Dosimetry requires measurement of (a) the X-ray intensity, (b) calculation of the fraction (F_w) of X-rays transmitted through intervening windows and (c) the fraction (F_a) absorbed by the hydrocarbon sample. The intensity of X-rays (I_0; see example in Figure 1b) is obtained from the current recorded in the ionization chamber, i_0, using

$$I_0 = i_0 W(N_2) R/(E_x e) \tag{1}$$

where $W(N_2) = 35.8$ eV/ion pair,[11] R is the ratio of the number of X-ray photons transmitted by the ionization chamber to the number absorbed, E_x is the X-ray energy, and e is the charge on the electron. The ratio R is given by

$$R = \exp[-\sigma_N(E)\rho_N l]/(1 - \exp[-\sigma_N(E)\rho_N l]) \tag{2}$$

where $\sigma_N(E)$ is the nitrogen absorption cross section, l the length of the collecting electrode in the ion chamber, and ρ_N is the density of nitrogen (in g/cm^3).

The fraction of the beam transmitted (F_w) by the windows and gas gaps between the ionization chamber and the liquid sample is calculated from known cross sections, $\sigma_i(E)$, and densities of atoms, ρ_i:

$$F_w = \prod_{i=1}^{n} \exp[-\sigma_i(E)\rho_i t] \tag{3}$$

where t is the thickness of the filter or gap. In this study F_w is generally greater than 0.9.

The fraction of beam absorbed (F_a) by a sample of depth d is given by

$$F_a = 1 - \exp(-\mu_{HC} d) \tag{4}$$

where $\mu_{HC} = \sigma_C(E)\rho_C + \sigma_H(E)\rho_H$. F_a ranges from 0.5 at 14 keV to 1.0 at 5 keV. Cross sections are obtained from Thomas[12] or McMaster.[13]

The relative yield of fluorescence photons $G(\mathrm{ph})_{rel}$ is given by

$$G(\mathrm{ph})_{rel} = (\text{PM counts} - \text{dark counts})/(10^{-A} I_0 E_x F_w F_a) \tag{5}$$

where A is the self-absorbance of the sample. The factor 10^{-A} corrects for the loss of fluorescence photons by reabsorption in the sample since the fluorescence is collected from the rear surface of the cell. The average depth of penetration of the X-rays varies from near 5 mm at 14 keV to about 1 mm at 4.5 keV. This average depth $\langle d \rangle$ is defined by

$$\langle d \rangle = \int_0^d x \exp(-\mu_{HC} x)\, dx \Big/ \int_0^d \exp(-\mu_{HC} x)\, dx \tag{6}$$

Finally, the yield of excited singlet states per 100 eV is given by

$$G(^1S^*) = [\tau_{uv}/\tau_x(E)] G(\mathrm{ph})_{rel}/(\Phi_f F_f F_c F_{PM}) \tag{7}$$

where τ_{uv} is the lifetime for isolated excited states; $\tau_x(E)$ is the lifetime observed for X-rays, which can be energy dependent;[10] Φ_f is the quantum yield of fluorescence; F_f is that fraction of the fluorescence passing the interference filter, which is obtained by integrating the transmission of the filter over the fluorescence spectrum; F_c is the fraction of all fluorescence photons collected by the mirror which impinge on the PM tube; and F_{PM} is the efficiency of the photomultiplier tube. The product of the $F_c F_{PM}$ was determined by measuring the relative fluorescence yield from benzene at 8.1 keV energy and assuming the calculated value for $G(^1S^*)$ for benzene (vide infra).

Fluorescence spectra were obtained by inserting a monochromator (Instruments SA Model H10) between the sample chamber and PM tube. In this case, data acquisition and the monochromator were controlled by a PS/2 Model 60, utilizing a GPIB interface and digital ports of a Stanford Research Systems SR245 interface.

Results and Discussion

Spectra. The fluorescence spectra of *cis*- and *trans*-decalin were observed for excitation with 10 keV X-rays. The spectra were obtained by normalizing the photomultiplier signal to the X-ray intensity, as monitored by the ion chamber current, without corrections for photomultiplier tube efficiency or self-absorption. The maxima in the spectra obtained were very close to the maxima reported for UV excitation, at 231 and 217 nm, respectively.[14]

Lifetimes. Figure 2 shows typical fluorescence decays for *trans*-decalin and benzene along with computed fits. The fluorescence lifetimes derived from such decays are shown in Figure 3 with results reported earlier.[10] For benzene as well as toluene the fluorescence decays showed two components. The lifetimes shown are for the long-lived component (vide infra). The previous results showed a monotonic decrease in lifetime with decreasing X-ray energy for *cis*-decalin and dodecane. For *trans*-decalin there is a slight decrease in lifetime as the X-ray energy decreases, but the average value for X-rays is very comparable to that observed for UV excitation, 2.82 ns.[15] In an earlier study,[10] the change in lifetime with X-ray energy was attributed to quenching of excited states by free radicals also

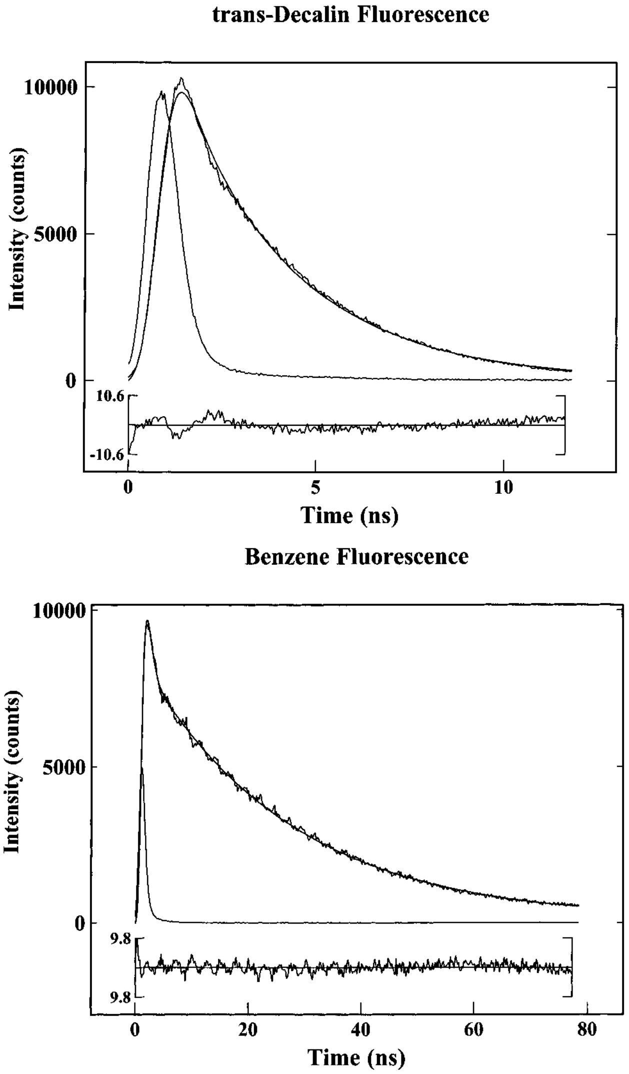

Figure 2. Fluorescence decays for *trans*-decalin (top) and benzene (bottom) at 6 keV. Smooth lines are computed fits. Lifetimes obtained by deconvolution.[10]

present in the track. This requires that the transient concentration of free radicals, on the scale of nanoseconds, be on the order of 10 mM for *cis*-decalin and dodecane. This value appears to be reasonable, as a recent diffusion-kinetic model of the chemistry of spur processes in cyclohexane indicates the concentration of cyclohexyl radicals present in the spur is between 10 and 75 mM on this time scale.[16] *trans*-Decalin is expected to have a track structure similar to *cis*-decalin because the range of low-energy electrons is comparable in both.[17] Thus, if the radical yields are also similar, the same effect is to be expected.

For benzene and toluene a very slight decrease in lifetime with decreasing X-ray energy is observed. In an absolute sense, however, for benzene the change is slight and the lifetimes for X-ray excitation are close to the value reported for UV excitation, 27 ns,[18] and the value found for electron irradiation, 26 ns.[19] The yields, and thus the concentration of radicals, are expected to be less in the aromatic hydrocarbons.[20] Consequently quenching of excited states by radicals will also be less. LaVerne reports that the lifetime of the benzene singlet is less for heavy-particle radiation at high LET.[21] The LET of the heavy particles was between 10 and 1000 eV/nm. A small decrease in lifetime was found for protons at LET values above 10 eV/nm. The highest LET in the present study is 5 eV/nm for the lowest energy electrons, 5 keV.

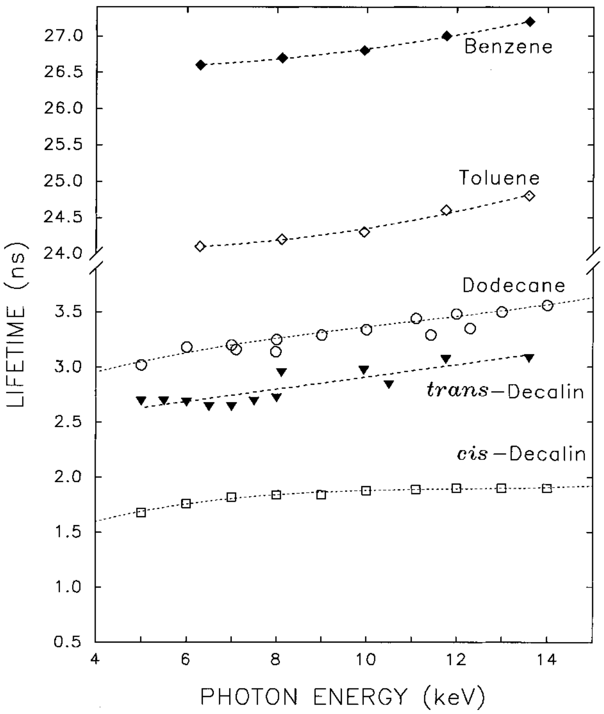

Figure 3. Fluorescence lifetimes for indicated hydrocarbons as a function of X-ray energy. Dodecane and *cis*-decalin data from ref 10.

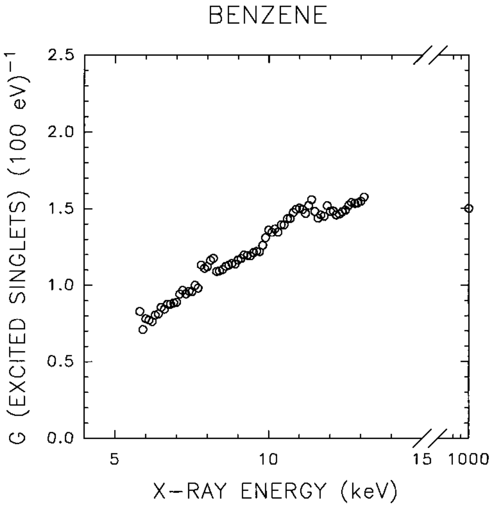

Figure 4. Normalized yield of excited singlets for benzene versus X-ray energy. The point at 1 MeV is an average value from ref 19.

The lifetime of the short-lived component in benzene and toluene is ≈0.6 ns. This decay time, although shorter than the time response of the apparatus, was obtained by deconvolution (see ref 10). This component is also seen in high LET radiolysis where its lifetime is somewhat longer.[18] No such component is seen in the alkanes.

Yields. The yields of *cis*- and *trans*-decalin excited states were determined relative to the yield of excited singlet states of benzene for excitation with 8.1 keV X-rays. The yield of singlet excited states of benzene was reported to be 1.6 per 100 eV by Scarstad et al.[22] for excitation with ^{14}C β particles, which have an average energy of 45 keV. Measurements by different techniques for a variety of high-energy excitation sources led to values in the range 1.4−1.6 per 100 eV.[23] Since we find the yield of singlet excited states to be dependent on X-ray energy (see Figure 4), we normalized the relative yield to a value of 1.5 in the 11−14 keV range. This procedure led to $G(^1S^*) = 1.15$ at 8.1 keV for benzene. This value was used with eq 7 to

TABLE 1: Singlet Yields for 8.1 keV Excitation

liquid	filter (nm)	F_f	Φ_f	$G(^1S^*)^a$
benzene	295	0.0255	0.032^b	1.15
trans-decalin	228	0.0247	0.023^b	2.02
cis-decalin	228	0.0297	0.021^c	1.66

[a] Yields per 100 eV experimental uncertainity ±10%. [b] Reference 23. [b] Reference 14.

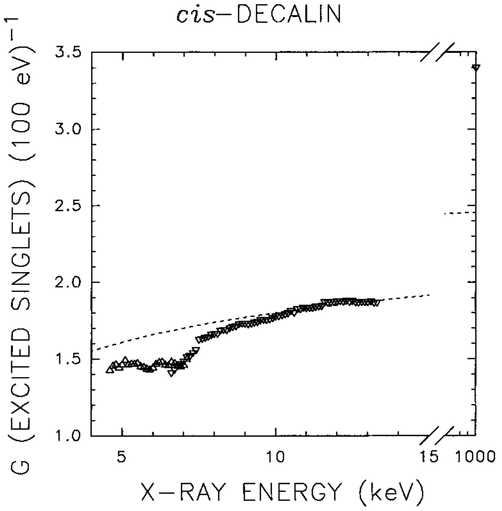

Figure 5. Yield of excited singlets versus X-ray energy for *cis*-decalin. Open triangles are experimental; point at 1 MeV from ref 19. Dotted line is computer simulation from ref 1.

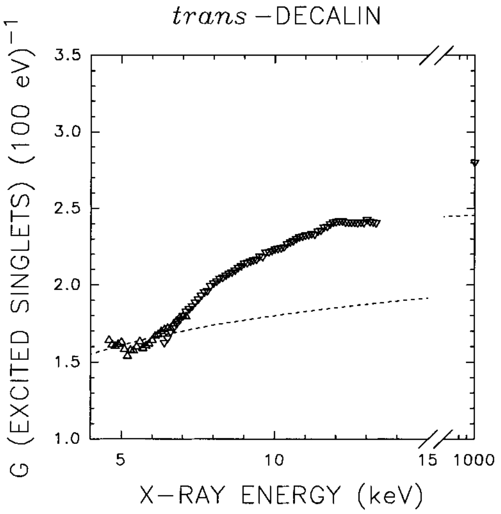

Figure 6. Yield of excited singlets versus X-ray energy for *trans*-decalin. Open triangles are experimental; point at 1 MeV from ref 20. Dotted line is computer simulation from ref 1.

calculate the singlet yields for *trans*- and *cis*-decalin given in Table 1. A consideration of the uncertainties in the quantities going into eq 7 indicates the experimental error on these values is ±10%. The rationale for normalizing at the high energy is that higher energy electrons will have the lowest LET and therefore will be more like the higher energy excitation sources used by others. The absolute values reported here are subject to the validity of this assumption.[24]

The dependences of excited singlet yields on X-ray energy observed for *cis*- and *trans*-decalin are shown in Figures 5 and 6. The spectra were obtained in overlapping scans. For the scans from 6.4 to 13.3 keV, the yields were normalized at 8.1 keV to the yields given in Table 1. For the scans from 4.6 to 7.2 keV, the yields were normalized at 7.0 keV to the yields found for this energy in the higher energy scans. The data shown are the averages of two runs for each set of conditions. For *cis*-decalin the data were corrected for the observed change in fluorescence lifetime with X-ray energy (see eq 7). For *trans*-decalin no lifetime correction was made since if there is a change in lifetime, it is small in this case. The points plotted at 1 MeV energy are singlet state yields deduced from fluorescence yields.[23,25]

In both decalins the yield of singlet excited states decreases as the X-ray energy decreases from 14 to 5 keV. For *trans*-decalin the yield at 14 keV is 2.4/100 eV, which is not significantly different from the value at 1 MeV, indicating the yield changes little in the higher energy range. For *cis*-decalin the yield at 14 keV is 1.9/100 eV, much less than the 1 MeV value of 3.4/100 eV, suggesting that the yield changes considerably over this energy range in this case. However, our results for *cis*-decalin are in good agreement with the computer simulation (see below).

Theory. Computer simulations have been performed to determine the probability of singlet formation as a function of electron energy.[1] A track of ionizations was assumed in which the positive charges are initially equidistant and on a straight line, with negative charges in a Gaussian distribution: $P(r) = (4r^2/\pi^{1/2}b^3)\exp(-r^2/b^2)\,\mathrm{d}r$, around each positive charge. The charges then diffuse and drift in their mutual field until recombination or escape occurs. It was assumed that geminate recombination leads to a singlet excited state 100% of the time and that cross-combination leads to singlets only one-quarter of the time. The calculation was done for an average thermalization length $b = 4.4$ nm, which is close to the value of $b_{GP} = 5.0$ nm reported for the decalins, based on measurements of zero-field free ion yields.[17] The computed lines (dotted) as shown in Figures 6 and 7 are based on a total yield of ion pairs of 4.0/100 eV. The calculation predicts a decrease in singlet yields with decreasing X-ray energy in the range studied. The dependence of the singlet yield on energy in the 5−14 keV region for both *cis*- and *trans*-decalin is greater than predicted; however, the yield of singlets at the lowest energy studied is close to 1.5 per 100 eV.

In summary, we observe decreases in the singlet yields as the X-ray energy decreases. The dependence of the yields on energy are greater than expected, but the yields observed at the lowest energies are in accord with theoretical calculations. This agrees with the concept that combination of uncorrelated ions in the denser tracks leads to the formation of more triplet excited states and consequently reduces the yield of singlet excited states.

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