scavenging H atoms before they can react with ethylene. However,

$$H+C_2H_4\rightarrow C_2H_5. \quad (16)$$

C_2H_5 radicals are probably produced in the primary process (4), and these would be quite independent of the quenching of $C_2H_4^*$ or the scavenging of hydrogen atoms by NO. Thus, it seems likely that at least part of the reduction in the production rates of C_3H_8 and n-C_4H_{10} can be attributed to simple scavenging of alkyl radicals by NO. There remains to be considered the possibility that CH_3CH reacts with nitrogen to form diazoethane. It has been observed[13] that CH_2 reacts with N_2 at low temperatures and, if CH_3CH is a well-behaved carbene, it would be expected to react with nitrogen. In the present experiments, no positive evidence for such a reaction has been obtained. If CH_3CHN_2 were formed, however, it might escape detection and decompose on the chromatographic column. Frey[14] has observed that diazoethane decomposes on a chromatographic column and the various butenes are formed. Only a very small amount of butene-1 was observed and can be accounted for by association of vinyl and ethyl radicals. It is concluded that diazoethane is not formed in our system. This observation is not inconsistent with the experiments of Moore and Pimentel[13] since the CH_3CH has an alternative not open to CH_2—rapid isomerization to the olefine.

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[13] G. B. Moore and G. C. Pimentel, J. Chem. Phys. **41**, 3504 (1964).

[14] H. M. Frey, J. Chem. Soc. **1962**, 2293.

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Triplet–Triplet Absorption in Sensitized Solvent Decomposition: An EPR Study* †

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The decay of the steady-state electron paramagnetic resonance (EPR) signal from naphthalene triplet-state molecules in ether and other glasses under continuous near-ultraviolet irradiation at 77°K has been examined in some detail. It has been shown that free radicals are produced by sensitized solvent decomposition at a rate proportional to the rate of the disappearance of the triplet-state EPR signal. Also, it has been demonstrated that the latter decay process has a first-order dependence upon naphthalene concentration and that it exhibits a dependence upon excitation intensity, which is consistent with a stepwise two-photon absorption mechanism.

The experimental results are discussed in terms of a model that involves the resonant transfer of energy from a highly excited triplet state of naphthalene to the solvent. Excitation of the excited triplet state takes place via the absorption of a photon by a naphthalene molecule in its lowest triplet state. The free radicals are produced by the decomposition of the sensitized solvent molecule. It is believed that the naphthalene molecule is not destroyed in this process but that the EPR signal decay arises from a radical–molecule interaction which effectively shortens the lifetime of the triplet state.

I. INTRODUCTION

THE various modes by which a system composed of a molecule embedded in a nonabsorbing matrix can absorb or lose electronic excitation energy are schematically illustrated in Fig. 1. There have been many experimental investigations of the processes labeled 1 through 5, both in the gas phase and in condensed systems. The participation of molecules in the first triplet state (T_1) has been postulated for many organic photoreactions.[1] Also, with the development of flash-lamp techniques, the triplet–triplet absorption processes (Process 6 in Fig. 1) have received some attention from a spectroscopic viewpoint over the last 10 years or so.[2] However, energy-transfer and photochemical reactions resulting from the absorption of radiation by molecules in excited triplet states (Processes 7 and 7′) have received very little attention despite their potential importance in condensed-phase reactions. For molecules with long-lived first triplet states, appreciable

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[1] For example, see the review of R. Livingston in *Radiation Biology*, edited by H. Hollender (McGraw-Hill Book Company, Inc., New York, 1955), Vol. 2, pp. 1–40.

[2] For example, see (a) R. G. W. Norish, Proc. Chem. Soc. **1958**, 247; and (b) G. Porter and M. Windsor, Proc. Roy. Soc. (London) **A245**, 203 (1958).

populations (greater than 20% depopulation of the ground state) in these states can be achieved relatively easily; therefore, the reactions involving triplet–triplet absorption steps are of considerable interest.

The recent development of the use of electron paramagnetic resonance (EPR) techniques for the observation of molecules in their triplet states[3–5] has made available a powerful tool to help elucidate the role that the triplet state plays in photolytic degradation mechanisms. Smaller[5] has already made some contribution in this direction.

In the study described here, EPR techniques are used to examine the sensitized solvent decomposition in systems composed of naphthalene ($\tau = 2.3$ sec) dissolved in low-temperature (77°K) ethanol, ether, or hydrocarbon glasses (none of which absorb above 2100 A). The experimental results show that the sensitized decomposition occurs during near-ultraviolet photolysis via resonant energy transfer to the solvent from a highly excited state of the aromatic solute. It is postulated that the active excited solute state lies in the triplet manifold of states and that it is excited by a triplet–triplet absorption process.

II. EXPERIMENTAL

A. Electron Paramagnetic Resonance Spectra

The paramagnetic resonance spectra were taken utilizing a Varian X-band EPR spectrometer equipped with 100-kc/sec modulation and an optical transmission cavity containing a quartz Dewar. A 4-mm-o.d. quartz tube containing the sample was placed in the Dewar and *in situ* photolysis was achieved by focusing the output of a high pressure, compact mercury arc onto the sample by the use of quartz lenses. In some cases, two lamps were used, one at each end of the transmission cavity. The EPR spectra were recorded in the form of the first derivative of the absorption curve on a Moseley X–Y recorder (Model 2D–S).

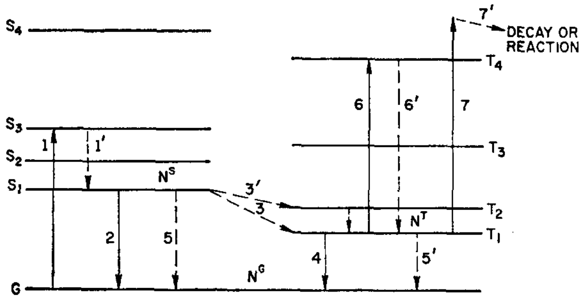

FIG. 1. Jablonski-type diagram of the excitation processes in a molecular system. The manifold of states S_1 to S_4 and T_1 to T_4 are the singlet and triplet states of the molecule, respectively. The solid arrows refer to processes involving the absorption or emission of a photon; the broken arrows denote radiationless-type transitions. Processes 3 and 3′ are the so-called intersystem crossing transitions in which the excitation is transferred from the singlet to the triplet manifold of states. The processes symbolized by 7 and 7′ are the absorptions resulting in energy transfer and decomposition. The symbols N^S, N^T, and N^G refer to the steady-state populations of excited singlet, first triplet, and ground states, respectively. Finally, the nondestructive intermolecular energy transfer modes involving lower excited states are not included for simplicity of presentation.

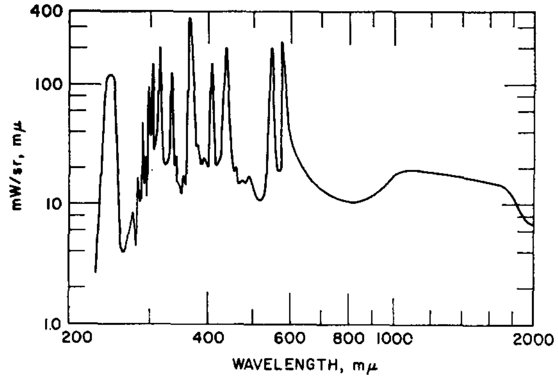

FIG. 2. The relative spectral power output of a typical PEK-500 high-pressure mercury arc taken from the company-supplied specification data.

Since the molecules are dissolved in rigid glasses, the $\Delta m = \pm 1$ transitions of the solute molecules in their triplet states are much too weak because of their anisotropic character[3] to be of much use as concentration monitors. Therefore, the intensity of the $\Delta m = \pm 2$ transitions[4] was used to follow the concentration of triplet-state molecules. It should be pointed out that the spectra from the triplet-state molecules and the photoproduced free radicals occur at widely different values of magnetic field. Although this spread results in no overlapping of the two spectra, it also means that the observations of the two spectra cannot be made simultaneously. The $\Delta m = \pm 2$ transitions occur at magnetic field values of approximately 1500 G, while the free-radical spectra occur at field values of 3300 G.

B. Lamps

The illumination sources were PEK-109 and PEK-500 high-pressure mercury arcs.[6] A major fraction of the ultraviolet radiation from the lamps occurs at wavelengths greater than 2800 Å. The intensity of emission from the lamps falls off drastically below 2800 Å and then picks up again below 2500 Å. The spectral intensities of the radiation output from the PEK-500 lamp are illustrated in Fig. 2. In most of the experiments, the unfiltered output of the lamps was utilized for photolysis. The nature of filtering when

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[3] C. A. Hutchinson Jr. and B. W. Mangum, J. Chem. Phys. **32**, 1261 (1960); **29**, 952 (1958).

[4] M. S. de Groot and J. H. van der Waals, Mol. Phys. **3**, 190 (1960); **4**, 189 (1961).

[5] B. Smaller, Advan. Biol. Med. Phys. **9**, 25 (1962); Nature **195**, 593 (1962).

[6] PEK Labs, Inc., Palo Alto, California.

employed is described at the appropriate place in the text. Effects of changes in relative intensity on the photolysis were examined using calibrated wire screens.

C. Solutes and Solvents

The solvents used were diethyl ether, ethanol, and methyl cyclohexane. Baker reagent-grade ether was used in most experiments without any special purification. However, several experiments were performed using ether that had been distilled over sodium. The ethanol used was U.S.I. absolute (reagent grade). The methyl cyclohexane used was Phillips research grade; before use, further purification was achieved by passing the methyl cyclohexane through a molecular still. The main effect of the solvent purification was to decrease the free-radical yield upon photolysis resulting from solvent impurities. However, the purification had no appreciable effect on the photolytic decay of the EPR signal from the solute molecules in their triplet states. Most of the experiments were run using the diethyl ether solvent, and unless otherwise indicated, ether was used as the solvent in the experiments described.

All of the quantitative experiments were made using naphthalene as the solute. The naphthalene used was scintillator-grade material, recrystalled twice from ethanol and then passed through a zone refiner.

D. Samples

Samples consisted of 0.05 to 0.3 cc of solution contained in 3-mm i.d. quartz tubes (4-mm o.d.). The quartz tubes were placed in the quartz Dewar containing liquid nitrogen for photolysis at 77°K; liquid argon was used for runs at 87°K. When the larger samples were used, only a fraction of the total volume of the solution was irradiated; however, with the smaller samples, the entire volume was in the irradiation zone. The concentrations of naphthalene used varied from zero to $0.1M$. The samples were not degassed; however, experiments on degassed systems showed that dissolved air had no observable effect on the photolysis process at 77° to 87°K.

E. Kinetic Runs

The decay of the EPR signal from the naphthalene triplet-state molecules and the rise of the EPR signal from the free radicals formed during photolysis were followed in two ways. First, the entire spectrum, or at least a sizable fraction of the spectrum, of each species was continually retraced; the peak-to-peak height of one line was used as a concentration index. Second, the alternative method was to stop the magnetic field scan at the maximum of a peak and then to follow the decrease or increase of the signal level as a function of time. Because of baseline and other instabilities in the system, the latter method was used only for systems in which the half-life of the decay was less than 600 sec. The former method was used for smaller decay rates.

III. RESULTS

A. Triplet-State EPR Signal

At low incident radiation levels (I), the intensity of the EPR signal (denoted by E^T) from the naphthalene molecules in their lowest lying triplet state (T_1) rises to a steady-state value in approximately 12±2 sec. However, as the magnitude of I is increased, E^T still rises to a maximum value in 12 sec but then decreases with continuing irradiation. The behavior of E^T as function of time after the maximum is reached is illustrated in Fig. 3. If the exciting light is extinguished at any time t during the photolysis, the remaining signal intensity decreases with an exponential decay and a time constant of approximately 2.3 sec. The latter decay is merely that due to the dark decay of the naphthalene triplet state to the ground state and is to be distinguished from that occurring *during* photolysis. Re-excitation of the sample without any warming yields a value of E^T that is essentially equal to the value at time t when the light was originally shut off. Small differences were observed for large photolytic decay rates, but they are easily attributed to the decay that occurs during the 12-sec rise of the triplet-state signal. After re-excitation, the photolytic decay process continues on the original decay curve when the dark period is accounted for on the time scale.

The effect of the initial napthalene concentration on the decay rate was somewhat complicated by the fact that at the higher concentrations the incident light was strongly absorbed by the solute. Therefore, the effect of concentration on the observed decay process depended upon the magnitude of the incident intensity. If at a particular value of I the ratio of the initial maximum values of the EPR signals for two naphthalene concentrations is equal to the ratio of the latter

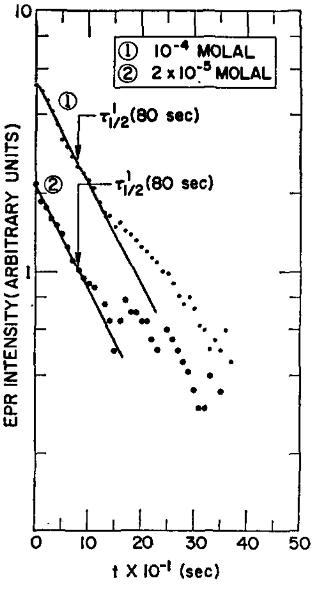

FIG. 3. Photolytic decay curves of the EPR signal from the naphthalene molecules in their triplet states. The intensity scale is arbitrary and the relative intensities between the two experiments have no meaning. The parameter $\tau_{\frac{1}{2}}$ is defined as the time necessary to go to one-half the initial intensity. Zero on the time scale is taken at the time when the EPR signal from the triplet-state molecules reaches its maximum value.

TABLE I. Effect of incident light intensity on E^T.

Run No.	Relative light intensity[c]	$\tau_{\frac{1}{2}}$(sec)[d], Ratio	Initial slope[e]	Ratio	Initial concentrationi[f] of total naphthalene (molal)	Ratio of $E^T{}_{\max}$
129-X[a]	2.1	68	2.5×10^{-1}		2×10^{-5}	
		2.8		3.0		~1.1±0.1
	1	190	8.6×10^{-2}			
129-A[a]	4.8	50	2.1×10^{-1}		1.2×10^{-4}	
	2.1	3.3		3.5		1.2
	2.3	165	6.0×10^{-2}			
		3.7		6.2		1.7
	1	610	9.7×10^{-3}			
129-B[a]	2.1	45	3.1×10^{-1}		1.2×10^{-4}	
		3.0		3.4		1.2
	1	136	9.0×10^{-2}			
129C[a]	4.8	46	3.2×10^{-1}		1.2×10^{-4}	
		10.5		16		1.9
	1	486	2.0×10^{-2}			
129-L[a,g]	2.1	134	6.7×10^{-1}		1×10^{-3}	
		3.4		6.8		1.7
	1	462	1.0×10^{-1}			
129-P[a]	1	80	7.4×10^{-2}		1.0×10^{-4}	
				4.4	2.0×10^{-5}	4.7
	1	80	1.7×10^{-2}			
122[b]	4.8	240	3.6×10^{-2}		1.0×10^{-4}	
	2.1	3.4		6.8		1.7
	2.3	820	5.3×10^{-3}	48		
				7.1		1.8
	1	...	7.5×10^{-4}			

[a] PEK-500 lamp used.

[b] PEK-109 lamp used, the uncertainty in this run is approximately a factor of 2 greater than in the other runs.

[c] Relative intensities are good only within each run.

[d] Time necessary for E^T to reach $E^T{}_{\max}/2$.

[e] Arbitrary units per second.

[f] Concentration is in moles per 1000 g of diethyl ether.

[g] The ratio of initial EPR signal to the ratio of concentration of naphthalene was not constant over the entire concentration range of 10^{-4} to $10^{-3}m$.

concentrations, then the photolytic decay curves from the two systems are essentially superimposable on a semilog plot (see Fig. 3). Alternatively, if the ratio of EPR signals is not equal to the ratio of total naphthalene concentrations, then the normalized decay rates are not identical. For the latter case, it was found that the normalized photolytic decay rate of E^T decreased as the total naphthalene concentration increased at a constant value of I. These results indicate that at low solute concentrations, when the incident intensity is sufficiently intense to uniformly excite the entire volume of sample in the EPR cavity, then the initial photolytic decay rate is proportional to the first power of the initial naphthalene concentration. Therefore, the decay process is kinetically first order in its dependence on naphthalene concentration. For the lamp intensities used in this study, the first-order dependence was satisfied over a range of concentrations from approximately 2×10^{-5} to $5\times10^{-3}m$. The nonexponential behavior evident in Fig. 3 must arise from a source other than the order of the kinetic process.

The dependence of the rate of the photolytic decay of E^T on the magnitude of the incident intensity was found using the calibrated screens. The results are given in Table I. Use of the screens gives a constant fractional decrease in lamp intensity, independent of wavelength. Larger variations in the light intensity, while desirable in order to fix the exact intensity dependency, was impractical since the rate of decay would have been impractically small. The time ($\tau_{\frac{1}{2}}$) necessary for the magnitude of E^T to drop to one half of its maximum value has an $I^{-1.4}$ to $I^{-1.7}$ dependence on incident light intensity. The initial slope of the photolytic decay curve of E^T has an $I^{1.5}$ to $I^{2.5}$ dependence on the incident light intensity. Similar results are obtained when methyl cyclohexane or ethanol is used as the solvent. Also, as can be seen from an examination of Table I, the maximum values of E^T are not directly proportional to I; the intensity dependence of E^T is less than unity in all cases.

The last result shows that there was an appreciable depopulation of the ground-state concentration of naph-

TABLE II. Transmission[a] of No. 6540 filter[b] as a function of wavelength. $\tau_{\frac{1}{2}}(0)/\tau_{\frac{1}{2}}(\text{No. }6540)=0.48\pm10\%$.

λ (Å)	I/I_0
2300	<0.1
2400	0.35
2500	0.59
2600	0.71
2700	0.77
2800	0.85
2900	0.88
3000	0.90

[a] Supplied by the Englehard-Hanovia Corporation. The filter is made from Vycor No. 7910.

[b] The transmission of this filter was determined on a Cary 15 ultraviolet spectrometer.

thalene molecules. From the variation of the maximum value of E^T with I and the use of the steady-state solution for the excited triplet-state population (*vide infra*), it is possible to estimate the fraction of molecules present in the excited triplet state. The triplet-state population varied from approximately 90% in Run 129-X, to 20 to 30% in Runs 122 and 129-L.[7]

The rate of photolytic decay of E^T depended strongly upon the age of the lamp used. When a new lamp was used, the decay rate was faster by more than a factor of 3 than that found in using a lamp run about 50 h. Efficiency of the lamps decreased very rapidly as far as the decay reaction was concerned; however, the maximum value of E^T was a much less sensitive function of lamp age since it was constant within 20% over more than 50 h of lamp operation. The last observation indicates that the wavelengths responsible for the decay reaction are different than those responsible for the majority of the magnitude of E^T.

Naphthalene molecules in their ground state do not absorb appreciably above 3000 Å. However, these wavelengths are also inactive as far as the photolytic decay process is concerned. This statement is based on the results of a series of experiments in which a second lamp was also employed (at the opposite end of the optical transmission cavity) after the photolytic decay of E^T had started; however, the second lamp had a Pyrex filter in front of it. The photolytic decay proceeded with no observable perturbation due to the radiation from the second lamp, which, because of the Pyrex filter, was all above 3000 A. When only one lamp was used with a Hanovia No. 6540 filter (Vycor No. 7910), whose transmission characteristics are given in Table II, the value of $\tau_{\frac{1}{2}}$ increased by approximately a factor of 2 over that found when no filter was used. The corresponding magnitude of the maximum value of E^T decreased by approximately 10% when the latter filter was used.

Anticipating the analysis which is given in Sec. IV, it can be demonstrated that the stepwise two-photon absorption mechanism predicts that the relative intensities of the radiation responsible for the EPR decay process [denoted by I_2 in Eq. (4)] with and without the No. 6540 filter can be written as the relative value of the product $(\tau_{\frac{1}{2}}E^T_{\text{max}})^{-1}$. Using the experimentally determined values of $\tau_{\frac{1}{2}}$ and E^T_{max}, it was found that the intensity of I_2 decreased by approximately 35% to 45% when the filter was used. Examination of Table II shows that, according to the model, the responsible wavelengths lie approximately at 2500 to 2600 Å. This conclusion is in agreement with the age behavior of the lamps in respect to photolytic efficiency as discussed above, since the intensity of the shorter wavelength radiation is a more sensitive function of age than are the intensities of the longer wavelengths. Also, it should be pointed out that the most effective triplet state populating wavelengths under the experimental conditions employed were between 2700 and 3000 Å (as was determined using appropriate filters). Therefore, since I_2 is at 2500 to 2600 Å, the model predicts that the initial values of E^T would not be as sensitive a function of lamp age as would be $\tau_{\frac{1}{2}}$, in agreement with experiment.

If the irradiated sample is kept at 77°K, there is no recovery of the EPR signal from the triplet-state molecules upon reirradiation, even though the sample is kept in the dark for an hour or more. However, when a small sample (all of which was in the radiation zone) of a $1\times10^{-4}m$ solution of naphthalene in methyl cyclohexane was irradiated to a 40% decrease in E^T, essentially all the original signal was recovered upon warming and refreezing. This procedure results in an approximate 5% decrease in initial values of E^T. When the procedure was repeated again, another 5% was lost. Continued repetition of this procedure lead to appreciable reduction in signal intensity. Similar results were obtained when ether or ethanol was used as the solvent. These results showing the recovery of the EPR signal indicate that the naphthalene molecules are not destroyed *during* the photolysis. The slight over all decrease found upon warming and refreezing for one cycle may be due to some reaction between the solvent radicals and naphthalene during the warming cycle.

The loss of the EPR intensity from the molecules in their first triplet state during photolysis can be attributed to a shortening of the triplet-state lifetime, probably by an interaction with the solvent radicals. Evidence in support of this supposition that the naphthalene molecules are not themselves destroyed by the photolysis but rather the lifetime of the T_1 state is shortened was obtained by examining during the photolysis the optical emission in the 520±30-mμ wavelength region (part of the normal naphthalene ($T_1\rightarrow G$) phosphorescence region). These observations were made using a 1P21 phototube on one end of the op-

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[7] The large depopulation for Run 129-x can be easily seen by examining the values of $E_{\text{max}}{}^T$ given in Table I. In Table I, it is shown that $E_{\text{max}}{}^T$ is essentially a constant over a factor of 2 in incident excitation intensity.

tical transmission cavity as well as suitable filters to isolate the phototube from the exciting wavelengths. The initial emission (before any decay had taken place) had a phosphorescence lifetime of 2.3 sec, which is the value to be expected for naphthalene. However, as the photolysis proceeded, the emission intensity increased sharply. A 70% decrease in the magnitude of E^T during photolysis corresponded to a factor of 30 increase in photoemission. The time constant for the decay of the *added* emission after light extinction was less than 10 msec (the limit of the response of the detection system used). The disappearance of all emission which occurred with the use of Pyrex filters showed that the added emission came from species that absorb only below 3000 Å, and use of the No. 6540 filter showed that the latter species also absorb in the 2600-to-3000-Å range, as do the original naphthalene molecules. Therefore, it is not inconsistent to assume that the added emission arises from naphthalene molecules in their lowest triplet state which are perturbed in such a manner that the radiative phosphorescence decay constant (as well as the corresponding radiationless decay constant) is substantially increased. The perturbing mechanism is probably an interaction with a neighboring photoproduced radical (*vide infra*). The ratio of the added emission (short-lifetime portion) to the change in the magnitude of E^T (i.e., $E^T{}_{\max}-E^T$) was found to be constant within experimental error over a 70% decrease in E^T. Finally, melting and refreezing of the sample led to the removal of the *added* emission upon re-excitation.

Experiments run at 87°K (in liquid argon) showed that there was no temperature effect over the 10°K range between 77° and 87°K. The phosphorescence lifetime of the triplet state was also constant over this temperature range.

B. Free-Radical Production

As the $\Delta M=\pm 2$ spectrum from the naphthalene molecules in the triplet state decreased in intensity during photolysis, an EPR spectrum at $g=2.0$ (the free-radical region) was observed to grow in intensity. The radical spectrum obtained with diethyl ether is shown in Fig. 4. This latter spectrum compares quite favorably with those obtained from γ-irradiated ethane, ethylene, and ethyl chloride[8] and for photolyzed ethyl iodide,[9] all of which were assigned to the ethyl radical. Any slight differences between the spectrum in Fig. 4 and the published spectra can be easily accounted for in terms of instrumental factors such as magnetic field sweeps, time constants, and/or differences in microwave power, temperature, and matrix, all of which affect linewidths. Therefore, the spectrum in Fig. 4 can be safely taken to be due to the ethyl radical. The latter spectrum is also the most prominent feature of the spectra obtained using ethanol glasses. When methyl cyclohexane is used as the solvent, a spectrum that can be attributed to the methyl cyclohexyl radical[10] is obtained. The temperature dependence of the radical production, the time behavior of the radical spectra under continuous prolonged irradiation and after the excitation is extinguished, as well as the fate of the OH and CH_3CH_2O residues, are quite interesting topics, and they will be discussed elsewhere in some detail.[11]

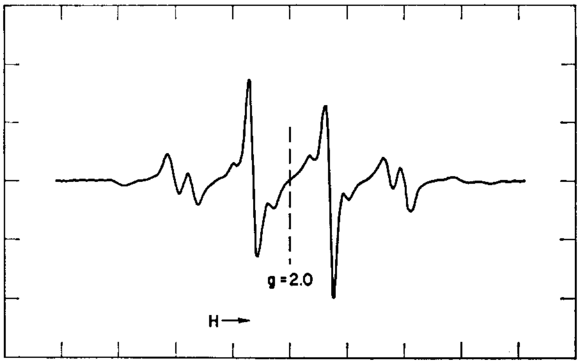

FIG. 4. The EPR spectrum of the radical obtained upon photolysis of ether solutions at 77°K. (For further spectra of the radical as a function of temperature and time see Ref. 11.)

The free-radical spectra could be produced without any naphthalene solute present. However, the intensity of the radical signal produced for any particular period of irradiation was considerably larger when the naphthalene solute was present (experiments run in ether solutions with naphthalene concentrations of $10^{-4}m$ had a factor of 5 larger rate of radical production than found for the solvent alone). The rate of radical formation for a freshly prepared naphthalene-free diethyl ether sample (refluxed over sodium followed by distillation) was approximately a factor of 4 to 5 smaller than the rate of radical production found in an ether sample which had been allowed to stand in an oxidizing atmosphere for several hours. With naphthalene-free methyl cyclohexane, passage of the solvent through a molecular seive column before use reduced the rate of radical formation by a factor greater than 500 over that found in the unpurified solvent. These results strongly indicate that the radical formation in the solute-free samples was caused by an interaction of the solvent with an ultraviolet absorbing impurity; the identities of the impurities were not determined.

The radicals are produced at the same normalized rate as the rate of decay of the magnitude of E^T and the production of the fast-decaying photoemission.

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[8] B. Smaller and M. S. Matheson, J. Chem. Phys. **28**, 1169 (1958).

[9] E. L. Cochran, F. J. Adrian, and V. A. Bowers, J. Chem. Phys. **34**, 1161 (1961).

[10] J. M. Flournoy and H. S. Judeikis, Paper X, Sixth International Symposium on Free Radicals, University of Cambridge, July 1963.

[11] S. Siegel and H. Judeikis, "Radical Matrix Interactions in Low-Temperature Glasses: Photo-Reversibility" (to be published).

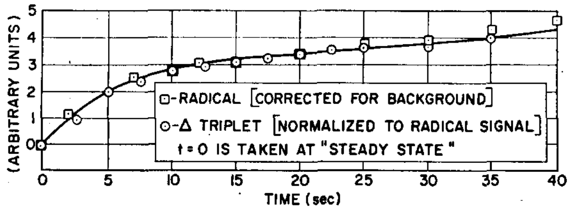

FIG. 5. Comparison of the decay of the EPR signal from the naphthalene molecules in triplet states and the rise of the EPR signal from the photoproduced free radicals. The □ points are the radical EPR signal intensities; the ⊙ points are the differences in the magnitudes of the naphthalene triplet-state EPR signals at time equal to zero and at time *t* which are normalized to the radical signal intensity scale. Zero on the time scale is taken at the time when the triplet state EPR signal reaches its maximum value. Also, the radical intensity is corrected for background due to (1) the radical concentration produced during the initial rise of the triplet-state EPR signal, and (2) the radical concentration produced upon irradiation of the solvent without the solute. One of the two large central peaks in Fig. 4 was used as a concentration index of the radical concentration.

There is a direct correlation between the loss of the signal from the naphthalene triplet-state population and the rise of the free-radical signal. This correlation is illustrated in Fig. 5, where the normalized values of the intensity of the free-radical signal and the magnitude of the difference $E^T(0)-E^T(t)$ (where zero refers to the time at which E^T reaches its maximum value) are given as a function of time. The zero of time is taken at the time at which E^T reaches its maximum value since any decay of the latter quantity taking place during the rise period of E^T would be masked. The radical signal intensity at the arbitrary zero point was substracted out of all the radical signal intensities used in Fig. 5. Also, corrections were made for the small contributions to the radical signal intensity by the unidentified impurities in the solvent. The similarity of the growth of the corrected radical signal and the decay of E^T is very striking. However, the magnitude of the initial slope of the radical formation curve was found to be a less sensitive function of the intensity of the incident radiation than was found for (dE^T/dt). For experimental conditions where the initial values of (dE^T/dt) and $\tau_{\frac{1}{2}}$ varied approximately as $I^{2.5}$ and $I^{-1.7}$, respectively, the initial values of dR/dt varied as $I^{1.7}$. [Again, anticipating the analysis in Sec. IV, the latter light-intensity dependence is that which would be predicted by Eqs. (2)–(4)].

IV. DISCUSSION

The sensitization of the solvent decomposition and the decay of the magnitude of E^T have been shown to be first order in the over-all naphthalene concentration and to possess a greater-than-linear dependence upon the incident radiation intensity. An obvious explanation of the experimental observations is that the reaction mechanism includes the absorption of two photons, not necessarily simultaneously. The probable reaction sequence proposed is: (1) a naphthalene molecule in its ground state absorbs a photon which excites a level in the singlet manifold, (2) the excitation is ultimately transferred to the triplet manifold, and a molecule in a metastable state results, (3) the latter molecule either returns to the ground state in a radiative or radiationless process, or the molecule in the metastable lowest triplet state absorbs another photon to produce a highly excited triplet state, and (4) the highly excited triplet state transfers its energy to the solvent which results in solvent decomposition but leaves the naphthalene molecule essentially unaffected.

A schematic of the proposed reaction sequence is given in Fig. 6. The decrease in the intensity of the EPR signal arising from the triplet-state molecules is postulated to occur because of an interaction between the unpaired electron on the radical and the neighboring excited naphthalene molecule, which results in a decreased lifetime for the phosphorescent state (i.e., lowest triplet state.) Experimentally, it was found that the lifetime of the perturbed naphthalene molecules was decreased by a factor greater than 100 over the normal phosphorescent lifetime of the naphthalene triplet state in these solvents. Therefore, the production of one radical results in the effective removal of one naphthalene molecule as a possible contributor to the magnitude of E^T. The reaction mechanism states that

$$R=N(0)-N(t), \qquad (1)$$

where R is the radical concentration and $N(0)$ and $N(t)$ are the over-all effective naphthalene concentrations, that is, the sum of the concentrations of ground $[N^G(t)]$ and triplet state $[N^T(t)]$ molecules *not* next to a radical, at times 0 and t, respectively. Also, it is assumed that, at all times, the fraction of the effective naphthalene concentration in the triplet state can be given by the steady-state equation

$$\frac{N^T(t)}{N^T(t)+N^G(t)}=\frac{N^T(t)}{N(t)}=\frac{KI_1}{1+KI_1}, \qquad (2)$$

where K is a collection of rate constants for processes of the type shown in Fig. 1, and I_1 is the intensity of

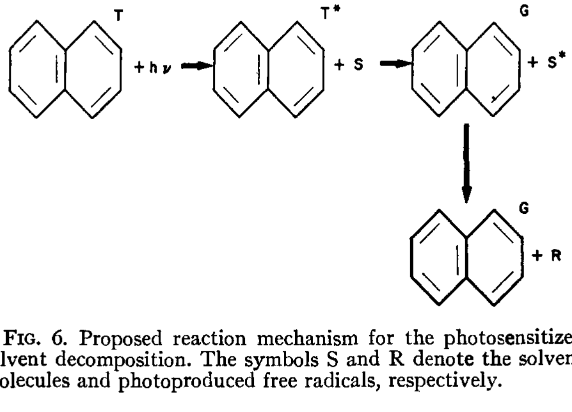

FIG. 6. Proposed reaction mechanism for the photosensitized solvent decomposition. The symbols S and R denote the solvent molecules and photoproduced free radicals, respectively.

the radiation absorbed by the ground-state naphthalene molecules. The latter assumption is equivalent to stating that the rate of attaining the steady-state is fast compared with the rate of the photolytic reaction, which is an adequate approximation for the results reported here.

Since the reaction proceeds by an absorption of a photon by a molecule in a triplet state, then *during* photolysis

$$dR/dt \equiv -dN(t)/dt = k_R I_2 N^T(t)\,S, \qquad (3)$$

where k_R is the combined rate constant for absorption and energy transfer per unit radiation intensity, I_2 is the intensity of the radiation which is absorbed by the triplet-state naphthalene molecules, R is the radical concentration, and S is the solvent concentration (which can be considered a constant).

By substituting Eq. (2) into Eq. (3), it can be easily demonstrated that for E^T

$$\tau_{\frac{1}{2}} \propto [I_1 I_2/(1+KI_1)]^{-1}; \qquad (4)$$

and since $N^T(t)$ is proportional to $E^T(t)$,

$$[dE^T(t)/dt]_{t=0} \propto I_1^2 I_2/(1+KI_1)^2. \qquad (5)$$

Equations (4) and (5) are independent of whether or not k_R is a constant over all sites in the glass. A comparison between the predicted dependence on incident radiation intensity and that found experimentally (see Table I) is shown in Table III. The experimental trends with increasing fractional population of the triplet state are in the correct predicted direction.[12]

The degree of depopulation and the magnitude of KI are indicated[13] by the departure from a direct proportionality between the intensity of the excitation radiation and the magnitude of $E^T{}_{\max}$. Also, combining Eqs. (2) and (5), it can be seen that the ratio

$$\frac{[dE^T(t)/dt]_{t=0}}{(E^T{}_{\max})^2(I_2)} \propto \frac{k_R S}{N(0)} \qquad (6)$$

is independent of light intensity and the fractional depopulation of the ground state. Therefore, dividing the ratios of the initial slopes given in Table I by the product of the relative light intensities and the square of the relative magnitudes of $E^T{}_{\max}$, should yield the value unity. The results of such a calculation which are tabulated in Table IV show that the latter condition is indeed satisfied by the experimental data. It is felt that the latter result, together with the observed agreement shown in Table III, as well as the other areas of agreement discussed previously, serves as strong support for the proposed two-photon mechanism.

TABLE III. Dependence on incident light intensity.

Experimental	Theory		
		$KI \gg 1$	$KI \ll 1$
$\tau_{\frac{1}{2}} \propto I^{-1.4}$ to $I^{-1.7}$	$\tau_{\frac{1}{2}}$	I^{-1}	I^{-2}
$(dN^T/dt)^{t=0} \propto I^{1.5}$ to $I^{2.5}$	$(dN^T/dt)^{t=0}$	I	I^3

TABLE IV. Relative values (R_{rel}) of the ratio $[(dE/dt)_{t=0}/(E_{\max}{}^T)^2 I]$ as a function of relative excitation intensity.

Run No.	I_{rel}[a]	R_{rel}
129-X	2.1	1.1
129-A	4.8	1.1
129-B	2.1	1.1
129-C	4.8	0.9
122	4.8	1.0

[a] While the light intensity during any one run varied only over a factor of 5, the fact that the 129 runs and run 122 were made with different lamps resulted in an over-all variation of about a factor of 13 in KI.

Since the solvents themselves do not absorb at wavelengths above approximately 2100 Å, the nature of the energy-transfer process becomes an interesting question. The triplet–triplet absorption spectrum of naphthalene in solution[2b] and the associated energies are given in Table V. Since the effective photolytic wavelengths were below 2600 Å, the triplet-state naphthalene molecules, which absorb at the three lower-energy absorption bands, do not transfer the energy to the solvent. It is only excitation within the high-energy absorption band that produces solvent sensitization. The total energy present in the naphthalene molecule after the absorption of the second photon takes place corresponds to a single photon in the absorption band of the solvent molecules. Therefore, it is postulated that the energy transfer mechanism is a resonance-type interaction, similar to sensitized luminescence or phorphorescence.[14–17] The latter analogy is better, since exchange

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[12] Since small increases in photoemission could be more easily detected than small decreases in the magnitudes of E^T, the initial slope of the increase in photocurrent (after the first 12 sec) was determined under conditions where $KI \ll 1$. The results showed that the increase in photocurrent (ΔP.C.) was proportional to I^3, within experimental error, over a factor of 2 in light intensity. Since, according to the assumed model $\Delta\text{P.C.} = IdR/dt$, then Eqs. (2) and (3) predict an I^3 dependence when $KI \ll 1$ for the initial rate of increase of the photocurrent. For larger values of I, it was found that ΔP.C. was proportional to $I^{2.2}$–$I^{2.5}$.

[13] The magnitude of KI can be estimated by the expression $KI = (\omega - 1)/(1-\rho)$ where ω is the ratio of the relative magnitude of $E^T{}_{\max}$ to the relative light intensity, and ρ is the relative magnitude of $E^T{}_{\max}$. In this manner, using the data in Table I, it can be shown that KI varies from a maximum of approximately 9.5 in Run 129-X to a minimum of 0.25 in some of the other runs (i.e., Run 122). (There is some uncertainty in the latter values since the ratio of differences between numbers of comparable magnitude are involved, and therefore experimental uncertainties are greatly magnified; however, the numbers given are certainly adequate for trend indications.)

[14] T. Forster, *Comparative Effects of Radiation* (John Wiley & Sons, Inc., New York, 1960).

[15] V. Ermolaev and A. Terenin, Izv. Akad. Nauk SSSR, Ser. Fiz. **26** (1), 21–32 (1962).

[16] S. Siegel and R. Eisenthal, J. Chem. Phys. **38**, 2785 (1963).

[17] S. Siegel and H. Judeikis, J. Chem. Phys. **41**, 648 (1964).

TABLE V. Band maxima of the absorption of triplet-state naphthalene molecules.[a]

$\lambda_{\max}$ (Å)	$\nu_{\max}$ (cm^{-1})	W_T^* (eV)[b]	W_T^* (kcal)[b]
4150	24 100	5.6	129
3915	25 550	5.8	134
3720	26 880	5.9	137
~2600	38 500	7.5	172

[a] The values for $\lambda_{\max}$ are taken from Ref. (2b).

[b] W_T^* is the total energy above the ground state possessed by the molecule directly after the absorption; i.e., 21 300 cm^{-1}+$\nu_{\max}$ cm^{-1}.

interaction is probably the mechanism of energy transfer in the sensitized-solvent decomposition reactions. The possibility of photoionization of the naphthalene molecules is discounted because there was no evidence of solvated electrons and positive (or negative) naphthalene ions.

The resonance energy-transfer mechanism discussed above supplies an explanation of the nonexponential decay curves for E^T observed during photolysis. Since the rate of energy transfer by exchange interactions depends upon the overlap of the wavefunctions of the relevant energy states of the solvent and solute molecules, then the value of the rate constant k_R in Eq. (3) depends upon the density of the glass and the geometrical arrangement of the naphthalene molecule in its cage. Glasses of the type used in this study have regions of varying densities; also, there is probably a random distribution of the arrangement of naphthalene molecules in their cages. Therefore, one would expect to have a variation in the magnitude of k_R; consequently, a nonexponential decay curve as experimentally observed would be predicted. In any case, the experimental results are not in contradiction to the proposed mechanism.

Finally, if the temperature of the glass is raised to a temperature where the triplet-state population is quenched because of O_2 diffusion (~100°K), then there are no radicals formed upon continued photolysis.[11] Also, the use of perdeuterated naphthalene as the solute resulted in an appreciably faster[11] rate of radical production. These last observations serve as more confirmatory evidence for the validity of the proposed mechanism since: (1) No radicals were formed when the triplet-state molecules were not present in appreciable concentration, and (2) the increase rate found by the deuteration of naphthalene most likely arose from the increased triplet-state population due to the longer lifetime of the deuterated molecules.[18] Deuteration does not appreciably affect the ground-to-singlet absorption probability.

V. CONCLUSION

The main features of the sensitized-solvent decomposition reaction are understood in a qualitative manner. Similar bahavior to that found for naphthalene was exhibited for solutions containing biphenyl as the solute. The sensitized decomposition of methanol solutions containing indole[5] can be attributed, as suggested by Smaller, to a two-photon absorption process (although there was no excitation dependence reported).[19] The present authors believe that the results reported here are characteristic of many solid-state photolysis reactions in which metastable states are easily available, such as photo- or radio-induced biological damage reactions. Extensions of the present study will be made in the near future to sensitized decomposition reactions in polymers or crystals at higher temperatures.

Finally, it should be pointed out that, despite the general understanding of the role of the triplet state as an intermediate energy storage stage and the two-photon nature of the sensitization reaction mechanism, there remain some unanswered questions. Two of these questions are: (1) What is the exact nature of the excited solute to solvent energy transfer process, and (2) what is the exact nature of the radical-solute interaction which results in the decreased phorphorescence lifetime of the solute? While answers to these questions can be (and are in this paper) speculated upon, the information necessary to give definitive answers is not available at the present time. Work is continuing in this laboratory to obtain the latter information.

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[18] C. A. Hutchinson Jr. and B. W. Mangum, J. Chem. Phys. **32**, 1261 (1960).

[19] Subsequent to the submission of this paper to the editor, we have found that there are some reports in the Russian literature on the two-photon nature of the sensitized decompositions of ethanol using aromatic amines as solutes [K. S. Bagesaryan, V. I. Muramtsev, and Z. A. Sinitsina, Dokl. Akad. Nauk SSSR **152**, 349, 374 (1963)].