absorption coefficient and from spin–orbit coupling, the experimental value of the lifetime seems to be reasonable.

The possibility exists that the emission rate process detected by the photomultiplier was not governed by the spontaneous transition probability of the $^3B_1$ state of SO_2 but was instead controlled by a diffusion process. Diffusion processes can be important in optical fluorescence experiments when only a small fraction of the volume of gas is illuminated. In the present experiments, however, the discharge and its resulting emission filled the entire body of either of the two cells. Along the line of vision of the detector, therefore, as many excited molecules would diffuse into view as were diffusing away from view. The population of excited molecules could not be depleted by this process unless the cell wall played a part in deactivation. On the basis of the experiments with the 12-l. bulb, one concludes that wall effects were not important. At all of the pressures which were used in this vessel, the diffusion displacement of an excited molecule was much less than the radius of the bulb. Under this condition the wall would not be expected to participate in quenching. The lifetimes which were measured with this vessel agree well with lifetimes measured in the small cell in the same pressure range. We conclude that diffusion and wall deactivation had no effect upon our experimental results.

Something should be said about the differences in the values of the lifetime obtained by the use of the two different excitation sources. Figure 1 and Table I show that the spark coil unit produced slightly larger values of the lifetime at a given pressure than the trigger transformer. It is believed that there are no fundamental differences in the function performed by the two units. Each provided a high-voltage pulse which decayed to essentially zero amplitude in a very short time relative to the lifetime which was to be measured. No predictable systematic errors could be found in the associated apparatus in the two cases. It is possible that a difference in the voltage output or in the damping characteristics of the two units may have produced an unknown chemical change in the gas which resulted in the small discrepancy in the observed lifetimes. It is very unlikely that physical differences in the makeup of the plasma which was created by the high-voltage spark would have any effect on the lifetime, because nearly all of the triplet emission originates in the lowest vibrational level of the $^3B_1$ state. The lifetime of the vibrationless level of the triplet state should not be affected by the initial energy distribution during excitation. It is felt that the discrepancy is not serious enough to cast doubt upon the validity of the results, but we cannot explain its origin.

In conclusion, we wish to point out that the uncertainty in these measurements is not of unusual magnitude for lifetime measurements in polyatomic systems. For example, a survey of ref 9–13 shows that deviations of 15 to 25% are not unusual for a set of measurements on a given diatomic or polyatomic system. Agreement of the lifetime of a given system obtained by different electron bombardment methods will be seen to be only within a factor of 2 or 3 in many cases. From this point of view, we feel confidence in our results.

Triplet-State Yield of Aromatic Nitro Compounds

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Abstract: Electronic energy-transfer experiments using *cis*-1,3-pentadiene (*cis*-piperylene) indicate that the triplet yields of nitrobenzene and 1-nitronaphthalene are 0.67 ± 0.10 and 0.63 ± 0.10, respectively. The results confirm the rapid deactivation of the nitrobenzene triplet as the prime cause of inefficient photochemistry, whereas with 1-nitronaphthalene a slow hydrogen-abstraction rate constant ($<10^2\ M^{-1}\ sec^{-1}$) accounts for the lack of photochemical activity in isopropyl alcohol. The rate constants for radiationless decay of the nitrobenzene and 1-nitronaphthalene triplet were estimated to be 10^9 and $<4 \times 10^5\ sec^{-1}$, respectively. The rate constant for triplet energy transfer from 1-nitronaphthalene to *cis*-piperylene was estimated to be $7 \times 10^7\ M^{-1}\ sec^{-1}$.

One of the imposing demands of photochemists today is the need to know the triplet-state yield of photoexcited molecules. Lamola and Hammond[1] have devised a triplet-counting method based on the *cis–trans* isomerization of piperylene (1,3-pentadiene). Other methods[2–4] recently reported depend on light emission phenomena and have also been found useful.

Although very little quantitative information is available concerning radiationless processes in aromatic nitro compounds, our recent investigation[5] of the hydrogen-abstraction process by the n,π* triplet of nitrobenzene in pure isopropyl alcohol raised questions concerning the cause of the low photochemical disappearance quantum yield (1.14×10^{-2}). The quantum yield for disappearance of nitrobenzene in isopropyl alcohol is much smaller than the value observed with benzophenone (disappearance yield ranges from 1 to 2).[6–8]

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In addition photochemical experiments with 1-nitronaphthalene at 366 mμ in isopropyl alcohol exhibited no photochemical activity.[9] The low photoreduction quantum yield for aromatic nitro compounds may be due to one or more of the following reasons: (1) inefficient population of the triplet, (2) rapid deactivation of the triplet, and (3) poor reaction of triplet with the solvent.

In view of the lack of information regarding the triplet yields of aromatic nitro compounds, we have investigated the photochemical energy transfer between nitrobenzene and 1-nitronaphthalene as sensitizers and *cis*-piperylene as the acceptor. 9-Nitroanthracene was not studied because of a rapid unimolecular photochemical process which results in anthraquinone and 10,10′-bianthrone.[10–12]

Experimental Section

Chemicals. Nitrobenzene and 1-nitronaphthalene used in this work were zone-refined samples from James Hinton (Valparaiso, Fla.). Spectrograde benzene was used in all experiments. *cis*-Piperylene (99%) was obtained from Chemical Samples Co., Columbus, Ohio, and used without further purification.

Apparatus and Procedures. The photochemical apparatus has been described elsewhere.[5] All experiments were performed at room temperature with 366-mμ light. Degassing by at least three freeze–pump–thaw cycles was used to remove dissolved oxygen.

The concentration of *trans*-piperylene produced during photolysis was determined with a Perkin-Elmer Model 154B chromatograph equipped with a flame ionization detector, and a 20 ft × 0.25 in. column of 15% β,β′-oxydiproprionitrile on 40–80 mesh Chromosorb.

The amount of reaction between nitrobenzene and *cis*-piperylene was determined by polarographic procedures described elsewhere.[5] The concentration of nitrobenzene was generally in the range of $2 \times 10^{-2}\,M$.

Method

In view of an addition reaction between sensitizer and acceptor, and the condition that only a small extent of isomerization was induced, the set of equations which were considered in the steady-state approximation are given in eq 1–8, where S and P represent sensitizer and piperylene, respectively. The equation for energy transfer to *trans*-piperylene was omitted because of the small concentration of *trans* formed during photolysis. Corrections for the reverse reaction, *i.e.*, *trans* → *cis*, were found to be negligible for the experimental conditions employed. Using this above simplified scheme, the quantum yield for *cis–trans* isomerization, $\Phi_{c\to t}$, is given by

$$\mathrm{S} \xrightarrow{h\nu} \mathrm{S}^{*1} \qquad (1)$$

$$\mathrm{S}^{*1} \overset{k_{ds}}{\rightsquigarrow} \mathrm{S} \qquad (2)$$

$$\mathrm{S}^{*1} \overset{k_{ic}}{\rightsquigarrow} \mathrm{S}^{*3} \qquad (3)$$

$$\mathrm{S}^{*3} \overset{k_{dt}}{\rightsquigarrow} \mathrm{S} \qquad (4)$$

$$\mathrm{S}^{*3} + cis\text{-P} \xrightarrow{k_{et}} \mathrm{S} + \mathrm{P}^{*3} \qquad (5)$$

$$\mathrm{S}^{*3} + cis\text{-P} \xrightarrow{k_r} \text{photoproducts} \qquad (6)$$

$$\mathrm{P}^{*3} \xrightarrow{k_7} cis\text{-P} \qquad (7)$$

$$\mathrm{P}^{*3} \xrightarrow{k_8} trans\text{-P} \qquad (8)$$

$$\Phi_{c\to t} = \phi_T \frac{k_8}{(k_7 + k_8)} \frac{k_{et}(cis\text{-P})}{[k_{dt} + k_{et}\,(cis\text{-P}) + k_r(cis\text{-P})]} \qquad (9)$$

where ϕ_T is the true triplet yield of the sensitizer, and $k_8/(k_7 + k_8)$ is the fraction of piperylene triplets which produces the *trans* isomer. Using the ratio of k_7/k_8 for piperylene equal to 0.81 as measured by Lamola and Hammond,[1] an isomerization yield, Φ', corrected for the decay ratio of the piperylene triplet to *cis* and *trans* molecules is defined by the following expression.

$$\Phi' = \Phi_{c\to t}\frac{(k_7 + k_8)}{k_8} = \phi_T \frac{k_{et}(cis\text{-P})}{[k_{dt} + k_{et}(cis\text{-P}) + k_r(cis\text{-P})]} \qquad (10)$$

The inverse of the above expression leads to the working expression

$$\frac{1}{\Phi'} = \frac{1}{\phi_T}\left\{1 + \frac{k_r}{k_{et}} + \frac{k_{dt}}{k_{et}(cis\text{-P})}\right\} \qquad (11)$$

which predicts that a plot of $1/\Phi'$ *vs.* $1/(cis\text{-P})$ is linear with an intercept equal to $(1/\phi_T)\{1 + (k_r/k_{et})\}$ and a slope equal to $(1/\phi_T)(k_{dt}/k_{et})$. The only remaining quantity to be determined is k_r/k_{et}, the ratio of rates for photochemistry to energy transfer, which is obtained experimentally.

Results

The most significant result from the energy-transfer experiments was the observation that the *cis–trans* isomerization quantum yield of *cis*-piperylene increased with increasing concentration of *cis*-piperylene (0–2.4 *M*) when nitrobenzene was used as the donor. In contrast, the results for benzophenone energy transfer to *cis*-piperylene indicate that all the benzophenone triplets are quenched when the piperylene concentration is 0.05 *M*.[1] 1-Nitronaphthalene exhibited no significant dependence of the isomerization yield with *cis*-piperylene concentration. The results are presented in Figure 1, which illustrates the faster deactivation in nitrobenzene relative to 1-nitronaphthalene. This marked difference in behavior for the two compounds in the quenching experiments also parallels the phosphorescence results for these molecules at 77°K in an EPA glass. 1-Nitronaphthalene exhibits a well-defined phosphorescence spectrum with a quantum yield of 0.13 ± 0.02 while nitrobenzene under identical conditions exhibits a very weak phosphorescence with a quantum yield $\leq 10^{-3}$.[13] It follows from the above data that radiationless decay is extremely rapid in nitrobenzene and simple aromatic nitro compounds. It is also noteworthy that the faster deactivation in nitrobenzene relative to 1-nitronaphthalene is in accord with an n,π* and π,π* assignment for the lowest triplet state of the two molecules, respectively.

In the experiments with nitrobenzene it was found that nitrobenzene reacts with *cis*-piperylene, which made it

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difficult to determine the stationary state, $(cis)_s/(trans)_s$, in the presence of nitrobenzene. The extent of disappearance of nitrobenzene by photochemistry was determined from polarograms of solutions before and after the energy-transfer experiments. The addition of nitrobenzene to olefins, which probably accounts for the disappearance of nitrobenzene and piperylene, has been reported.[14-16]

Nitrobenzene. The ratio of rate constants for photochemical disappearance of nitrobenzene to energy transfer, k_r/k_{et}, was experimentally determined to be 0.18, *i.e.*, approximately four out of five excited sensitizer triplets result in energy transfer rather than photochemical addition.

The data obtained for the energy transfer of nitrobenzene to *cis*-piperylene are plotted in Figure 1, which indicate that even at high concentrations of *cis*-piperylene, not all the nitrobenzene triplets are quenched. The intercept leads to a triplet yield of 0.67 ± 0.10 for nitrobenzene, which is large, despite the small quantum yield for disappearance (1.14×10^{-2}) in pure isopropyl alcohol. The results indicate the same triplet yield for the two molecules studied, which arises from an intersystem crossing from an n,π^* singlet to an n,π^* triplet. In 1-nitronaphthalene, however, the lowest triplet is probably π,π^*. The possibility of singlet quenching of nitrobenzene by *cis*-piperylene seems to be unimportant on the basis of the linear behavior of the data presented in Figure 1. It is noteworthy that if singlet quenching were involved, the value of the ordinate, Φ'^{-1}, in Figure 1 would increase. The results do not indicate a trend in this direction. Hammond, *et al.*,[17] have remarked on the caution of interpreting triplet quenching data in concentrated solutions of piperylene where singlet quenching may become important.

From the slope of the line in Figure 1 the ratio k_{dt}/k_{et} is determined to be 0.71 M^{-1}, which implies that when $(cis\text{-P}) = 1.4\ M$ the radiationless decay for the triplet is equal to the rate for the energy transfer to *cis*-piperylene. Since the energy transfer from nitrobenzene to *cis*-piperylene is predicted to be diffusion controlled,[18] the results necessitate an unusually fast triplet deactivation for nitrobenzene ($\sim 10^{-9}$ sec). The reported triplet state energies for *cis*-piperylene, *trans*-piperylene, and nitrobenzene are 56.9, 58.8,[1] and 60 kcal,[19] respectively. We have observed that the small phosphorescence yield of nitrobenzene in degassed methylcyclohexane and EPA glasses at 77°K is an unstructured spectrum, which makes it difficult to establish accurately the 0–0 band.[20] With respect to the relationship of the triplet-state energy and the rate constant for energy transfer, it has been reported that the range of rate constants for electronic energy transfer was 10^7–$10^9\ M^{-1}\ \text{sec}^{-1}$ for a series of donor and acceptor pairs.[18] It is to be noted that the mean lifetime for the benzophenone triplet has been determined to be 1.9×10^{-6} sec in benzene at 20°.[21]

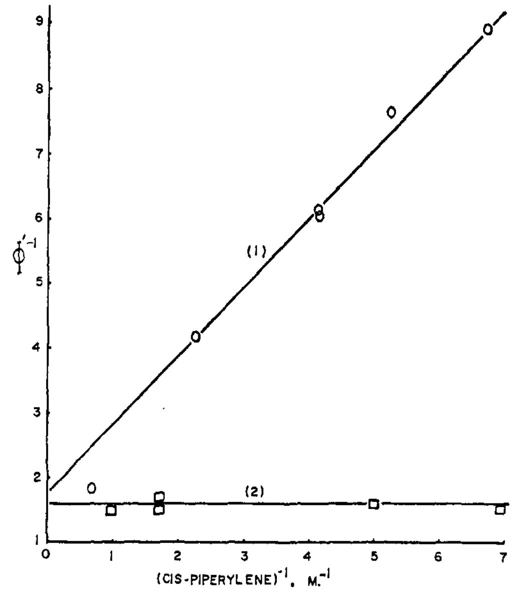

Figure 1. Reciprocal of *cis–trans* isomerization quantum yield for *cis*-piperylene obtained from electronic energy-transfer experiments in benzene using 366-mμ excitation. Donors: (1) nitrobenzene ($\sim 2 \times 10^{-2}\ M$), (2) 1-nitronaphthalene ($\sim 3 \times 10^{-3}\ M$).

1-Nitronaphthalene. In contrast to the results for nitrobenzene, the data for 1-nitronaphthalene exhibited no measurable dependence on the concentration of *cis*-piperylene. It appears that for this molecule the energy transfer is much more rapid than deactivation of the triplet even in dilute solutions. The triplet yield of 1-nitronaphthalene was determined to be 0.63 ± 0.10.

Another marked difference with the behavior of 1-nitronaphthalene in the energy-transfer experiments was that only a small photochemical disappearance competed with the triplet energy transfer process, *i.e.*, $k_r/k_{et} < 0.1$. It was also observed that nitrobenzene was not sensitive to oxygen concentration (consistent with short-lived triplet), whereas 1-nitronaphthalene did show an oxygen dependence. If an additional reaction is included for oxygen quenching in the energy-transfer experiments with 1-nitronaphthalene, *i.e.*

$$S^{*3} + O_2 \xrightarrow{k_q} S + O_2^{*3}$$

then the isomerization quantum yield can be determined for degassed solutions, Φ_0', and for air-saturated solutions, Φ'. The relationship relating these two quantities is given by

$$\frac{1}{\Phi'} - \frac{1}{\Phi_0'} = (1/\phi_T)\frac{k_q(O_2)}{k_{et}(cis\text{-P})} \qquad (12)$$

where k_q is the rate constant for the oxygen quenching ($\sim 10^9\ M^{-1}\ \text{sec}^{-1}$).[22,23] The quantum yields for isomerization which were determined for air-saturated and degassed solutions of 1-nitronaphthalene in 0.065 M *cis*-piperylene are 0.462 and 0.557, respectively. Substitution in the expression above, using $10^{-3}\ M$ for the concentration of oxygen in solution,[24] leads to $k_{et} = 6.8 \times 10^7\ M^{-1}\ \text{sec}^{-1}$. This value for the endothermic

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energy transfer of 1-nitronaphthalene ($E_T = 55$ kcal) to *cis*-piperylene ($E_T = 57$ kcal) is in the general range of rate constants reported by Hammond, *et al.*[18]

From the data for 1-nitronaphthalene presented in Figure 1 it can be estimated that the slope, which is equal to $(1/\phi_T)(k_{dt}/k_{et})$, is <0.01 *M*. This approximation together with the value for ϕ_T and k_{et} leads to $k_{dt} < 4 \times 10^5$ sec^{-1}, which corresponds to a significantly longer lived triplet relative to nitrobenzene.

Discussion

It is quite evident from the data presented that nitrobenzene and 1-nitronaphthalene are characterized by relatively large triplet yields ($\phi_T > 0.6$). In view of the absence of significant photochemistry observed with nitrobenzene in pure isopropyl alcohol, it appears that rapid radiationless decay from the triplet is of prime importance. This implication is especially evident from the concentration dependence of piperylene in the energy transfer experiments with nitrobenzene. With 1-nitronaphthalene, however, decay of the triplet is less rapid ($<4 \times 10^5$ sec^{-1}), but the π,π^* character of the lowest triplet accounts for the inefficiency with respect to the hydrogen-abstraction reaction. Since the photoreduction of 1-nitronaphthalene in isopropyl alcohol has a quantum yield $<10^{-3}$, it follows that $k_H < 10^2$ M^{-1} sec^{-1}. Consequently, the lack of photochemical reactivity of 1-nitronaphthalene arises from a slow hydrogen abstraction rather than a rapid radiationless decay of the triplet.

The results indicate that radiationless deactivation from the singlet is not unimportant in these aromatic compounds. The lack of fluorescence from these compounds is well known.[25] It follows then that for aromatic nitro compounds $\phi_F + \phi_T < 1$, whereas in many cases the sum is very close to unity.[1,3,4]

The relatively large triplet yield in the case of nitrobenzene supplies an answer to the query concerning its photochemistry. It is very likely that rapid deactivation of the nitrobenzene triplet is the cause of inefficient photoreduction. The photochemical disappearance yield, Φ, of nitrobenzene in isopropyl alcohol (IPA) *via* the hydrogen-abstraction reaction is represented by the expression

$$\Phi = \frac{\phi_T}{[1 + k_{dt}/k_H(\text{IPA})]} \tag{13}$$

where ϕ_T is the triplet yield, currently available from this work to be 0.67, and k_{dt} and k_H are the rate constants for radiationless decay and hydrogen abstraction for the nitrobenzene triplet. Substituting $\Phi = 1.14 \times 10^{-2}$ from our earlier investigation and the value for the triplet yield, the ratio $k_{dt}/k_H = 753$; in contrast, the value for benzophenone is 0.39. The high ratio for nitrobenzene indicates that the deactivation of the triplet is very rapid relative to hydrogen abstraction. If the assumption is made that the hydrogen-abstraction rate constant for the nitrobenzene triplet from isopropyl alcohol is equal to that for benzophenone, 1.28×10^6 M^{-1} sec^{-1},[8] then the radiationless decay constant for the nitrobenzene triplet is estimated to be $\sim 10^9$ sec^{-1}. It is interesting that both the energy-transfer experiments and the photochemical disappearance quantum yields for nitrobenzene in pure isopropyl alcohol predict $k_{dt} \sim 10^9$ sec^{-1}.

In pure isopropyl alcohol we have observed no photochemistry for 1-nitronaphthalene despite the high triplet yield. Although rapid radiationless decay can explain the observation, another possibility is to consider a reversal of states such that the π,π^* triplet is lower than n,π^*. This explanation has been used to explain the lack of photoreduction in 1-naphthaldehyde.[26]

In summary the inefficient photoreduction of nitrobenzene is attributed to a rapid radiationless deactivation of the triplet. The lack of photoreduction with 1-nitronaphthalene, however, is due to a slow hydrogen-abstraction process, *i.e.*, $k_H < 10^2$ M^{-1} sec^{-1}. Although radiationless decay of the nitrobenzene triplet is rapid, the availability of a reasonably fast reaction or an environmental perturbation in solution may lead to substantial photochemical quantum yields. An application of the latter possibility to nitrobenzene using protonation in the excited state has resulted in significant quantum yield enhancement.[27,28]

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