

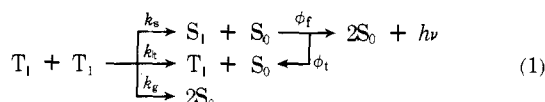
Delayed Fluorescence Efficiencies of Anthracene and Phenanthrene

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Abstract: The flash technique of Kikuchi, Kokubun, and Koizumi has been used to determine the efficiencies of excited singlet production in the homopolar triplet-triplet annihilations of anthracene and phenanthrene. The results for anthracene agree very closely with the earlier data of Kikuchi et al. and Tfibel and Lindqvist. The phenanthrene annihilation produces singlets only 25% as efficiently as the corresponding anthracene reaction and just 4% as efficiently as the same process for naphthalene. A simple rationale for the strong dependence of this efficiency on molecular structure is presented. It is based on a comparison of Franck-Condon factors for all paths of energy disposition available to a given annihilation process, and it is qualitatively successful with the three cases at hand.

Homopolar triplet-triplet annihilation is the simplest observed interaction between two excited molecules.^{1,2} As such, it is intrinsically interesting, but studies of the process are more generally appealing because they may illuminate the broader issue of energy disposition in fast, energetic, solution-phase reactions. At least three parallel branches must be considered in kinetic descriptions of triplet annihilation:



Here S_0 , S_1 , and T_1 represent molecules in their ground, first excited singlet, and triplet states, respectively. The rate constants k_s , k_t , and k_g refer to the individual branches, which are denoted below as the s, t, and g pathways. The quantum efficiencies of fluorescence and intersystem crossing are shown respectively as ϕ_f and ϕ_t . Quantitative information about the distribution of available energy among the pathways is necessary for the description of any given annihilation reaction. Of particular interest is the effect of molecular properties on that distribution.

If ϕ_f is significantly large, the s channel yields P-type delayed fluorescence,^{1,2} as eq 1 shows. This emission is frequently observed from solutions of aromatic hydrocarbons, and Parker's studies of it^{1,3-5} have provided much of the available information about branching efficiencies in triplet-triplet annihilation. By a phosphorescopic technique, he and Joyce measured k_s values and calculated s-channel encounter efficiencies, p_c , and k_s/k_d , where k_d is the diffusion-limited rate constant computed from the Smoluchowski-Debye formula.^{6,7} The efficiencies varied quite widely among similar compounds, and they notably failed to correlate with any of the usual triplet parameters.

Later, Kikuchi et al. devised a flash technique that allows a more direct measure of s-pathway efficiencies, and they applied the method to a detailed study of anthracenes.^{3,9} More recently, Tfibel and Lindqvist have employed a variant of this flash method¹⁰ to corroborate the results of Kikuchi et al. for anthracene⁸ and to obtain new data for naphthalene. The efficiencies from flash measurements differ somewhat from Parker's results, but they confirm his observation of wide variations in efficiency among structurally similar species. Tfibel and Lindqvist recognized the importance of this variation and advanced a hypothesis to explain it. We shall examine their ideas more fully below.

In our laboratory, we have implemented the method of Kikuchi et al. to obtain new data for the s-channel efficiencies in the anthracene and phenanthrene systems. The results of these studies are presented below. In addition, we note that the order

of the efficiencies in the naphthalene, anthracene, and phenanthrene systems can be predicted by a simple argument relating the available annihilation energy to the highest accessible states in the singlet and triplet manifolds. The success of this approach may signal a major role for Franck-Condon factors in controlling energy disposition in these reactions.

Experimental Section

Phenanthrene, obtained from Eastman Organic Chemicals, was treated with maleic anhydride in order to remove the anthracene impurity.^{1,11} The purified phenanthrene was recrystallized from absolute ethanol. The anthracene (Aldrich Chemical Co., gold label, blue-violet fluorescence grade) was used without further treatment. Absolute ethanol was treated by the method described by Leighton, Cray, and Schipp.¹²

Ethanol solutions of anthracene and phenanthrene ($\sim 10^{-4}$ M) were prepared and transferred to a deaerating flask attached to the quartz photolysis cell. The cell assembly was then connected to a high-vacuum line through a ground glass joint, and the solution was deaerated by the freeze-pump-thaw method, with a 5-min reflux period following each thaw. After five or six cycles, the cell was flooded with high-purity helium and the cycles were recommenced. Following deaeration, approximately 0.5 atm of high-purity helium was added, and the cell assembly was sealed by a Teflon stopcock and removed from the vacuum line.

The kinetic spectrometer used for this study has been described.^{13,14} The excitation source employed EG&G FX-142C-4.5 or Xenon Corp. FP-100C flashlamps having output pulse widths (fwhm) of 10 and 24 μ s, respectively. Transient absorption or emission data were acquired via a computer-based recording system that obtained points digitally at a 7- μ s spacing.¹⁴

We obtained transient absorption spectra that were identical with those attributed in earlier papers to the anthracene and phenanthrene triplets.¹⁵⁻¹⁷ For kinetic studies, the anthracene triplet was monitored at its 424-nm absorption maximum, where its molar absorptivity ϵ_T was taken to be¹⁸ 64 000 $M^{-1} cm^{-1}$. The phenanthrene triplet was followed at its 485-nm maximum, where ϵ_T was assumed to be^{19,21} 23 000 $M^{-1} cm^{-1}$. The absorption path length, b , was 10 cm. Delayed and prompt fluorescences were recorded at the 400- and 367-nm emission maxima for anthracene and phenanthrene, respectively.

Emission and triplet absorbance decay transients were obtained from the deaerated solution. With the analyzing beam off, the emission and scattered light from the flash were also measured at the triplet monitoring wavelength as a background correction for the absorbance data. The solution was then exposed to a limited amount of air,¹³ and a second emission transient, comprising mostly prompt fluorescence, was recorded. The difference between the corresponding emission decays for aerated and deaerated solutions was taken to be the delayed fluorescence intensity.

All measurements were carried out at room temperature, 21-23 $^{\circ}C$.

Results and Discussion

Kinetic Analysis. The triplet decay following flash excitation

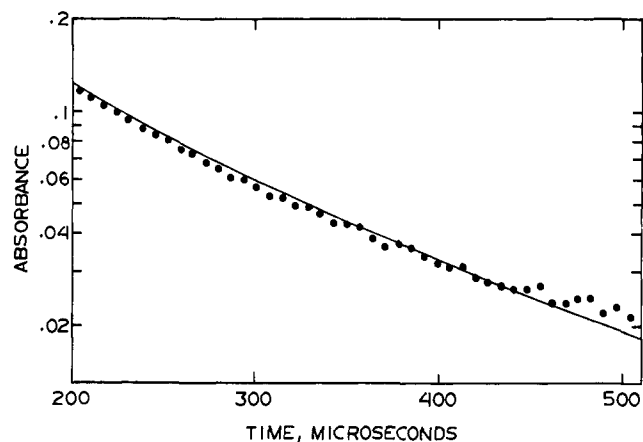


Figure 1. Semilogarithmic plot of the absorption transient at 485 nm following flash excitation of an ethanolic phenanthrene solution (1.6×10^{-4} M). Solid curve calculated from fitting procedure. Flash energy 150 J.

Table I. Delayed Fluorescence Rate Parameters

Compd	k_2/ϵ_T , cm/s	p_e	p_0	
			Min	Max
Anthracene ^a	6.0×10^4	0.077	0.077	0.14
Anthracene ^b	6.0×10^4	0.08	0.08	0.15
Anthracene ^c	6.3×10^4	0.080	0.082	0.15
Naphthalene ^b	7.0×10^5	0.52	0.58	0.74
Phenanthrene ^c	2.13×10^5	0.020	0.020	0.040

^a Reference 8. ^b Reference 10. ^c This work.

is described by^{8,10,22,23}

$$-\frac{d[T_1]}{dt} = k_1[T_1] + k_2[T_1]^2 \quad (2)$$

where k_2 is an experimental bimolecular rate constant, which can be interpreted via eq 1 as

$$k_2 = (2 - \phi_t)k_s + k_t + 2k_g \quad (3)$$

The rate law for decay of triplet absorbance A_T is then

$$-\frac{dA_T}{dt} = k_1A_T + \frac{k_2}{\epsilon_T b} A_T^2 \quad (4)$$

In this work, k_1 and k_2/ϵ_T were extracted from absorbance transients via Marquardt's algorithm for nonlinear least-squares curve fitting.²⁴⁻²⁶

Points from a typical phenanthrene absorption decay are shown in Figure 1 for times greater than 200 μ s after the start of the flash. The solid curve was calculated from the rate parameters extracted from the fitting procedure. The anthracene system gave more intense, longer lived transients with more pronounced curvature due to the bimolecular process. They could be fitted essentially perfectly. Table I shows the fitted values for k_2/ϵ_T . The corresponding values of k_2 were 4.0×10^9 and 4.9×10^9 $M^{-1} s^{-1}$.

The first-order rate constants k_1 implied triplet lifetimes of 3.2 ms and 155 μ s, respectively, for these two molecules. The shorter lifetimes for phenanthrene triplets probably indicate the presence of trace triplet quenchers that could selectively quench the higher energy species.^{1,2}

Branching efficiencies for the s channel were obtained via the method of Kikuchi et al., which required evaluation of an instrumental parameter, α , relating the recorded intensities of emission to total rates of emission from the sample per unit volume.⁸ The delayed fluorescence intensity is

$$I_{DF} = \alpha\phi_f k_s [T_1]^2 \quad (5)$$

and the prompt fluorescence intensity is given by

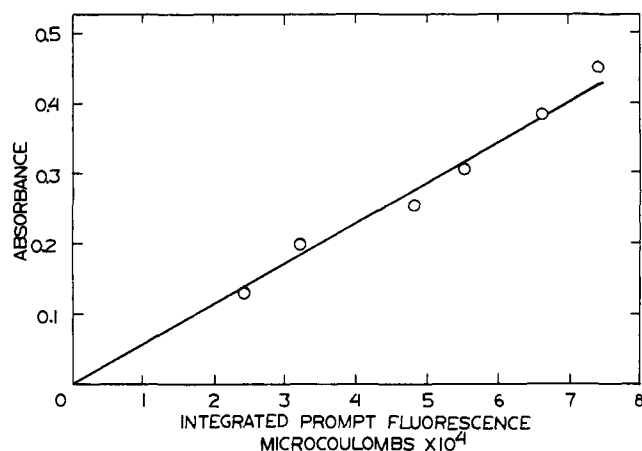


Figure 2. Initial triplet absorbance $A_{T,0}$ of anthracene vs. integrated prompt fluorescence intensity.

$$I_F = \alpha\phi_f I_a \quad (6)$$

where I_a is the rate of light absorption by the sample.

The parameter α is evaluated by measuring the triplet concentration immediately following the flash, $[T_1]_0$. It reflects the total number of flash excited triplets, but is smaller by the number that decay during the flash itself. If the flash intensity is made low enough that purely first-order decay is observed, then the rise and fall of the triplet concentration obeys

$$\frac{d[T_1]}{dt} = \frac{\phi_t}{\alpha\phi_f} I_F - k_1[T_1] \quad (7)$$

which can be solved exactly to give²⁷

$$[T_1]_0 = \frac{\phi_t}{\alpha\phi_f} \int_0^{t_f} e^{-k_1(t_f-t)} I_F dt \quad (8)$$

where $[T_1]_0$ applies to a time t_f after the start of the discharge at $t = 0$. We consider t_f to be twice the full width at half-maximum of the excitation pulse, i.e., 20 μ s for the EG&G lamps and 48 μ s for the Xenon Corp. lamps. At these times, the excitation pulses were complete, except for a low-level afterglow.

An exact evaluation of the integral in eq 8 requires a shape function for the flash intensity, which would be manifested by the prompt fluorescence intensity, I_F . However, a good approximation can be made for $k_1 t_f \leq 0.4$. For virtually any symmetrical discharge function (e.g., Gaussian) centered on $t_f/2$, the integral is very nearly equal to $e^{-k_1 t_f/2} \int I_F dt$. If $[T_1]_0$ is expressed in terms of an absorbance $A_{T,0}$ at $t = t_f$, we therefore have

$$e^{k_1 t_f/2} A_{T,0} = \frac{\epsilon_T b \phi_t}{\alpha\phi_f} \int_0^{t_f} I_F dt \quad (9)$$

A plot of $e^{k_1 t_f/2} A_{T,0}$ vs. $\int I_F dt$ for various flash energies ought to give a straight line with a slope inversely proportional to the calibration factor α . As Kikuchi et al. showed,⁸ this slope is useful in the evaluation of k_s .

Equation 9 differs from their analogous relation only by the exponential factor accounting for triplet decay during the flash itself. For stable triplets and short discharges, as we observed with anthracene under excitation by the EG&G lamps, it is essentially unity. However, it becomes larger when short-lived triplets and long discharges are involved. For phenanthrene excited by the Xenon Corp. lamps, the mean value of $e^{k_1 t_f/2}$ was 1.23.

Figures 2 and 3 show the correlations between $A_{T,0}$ values and $\int I_F dt$ for our two systems. The absorbances were extrapolated from Marquardt fits of transients observed at reduced flash energies, and the corresponding fluorescence intensities were recorded from the aerated solutions at the same

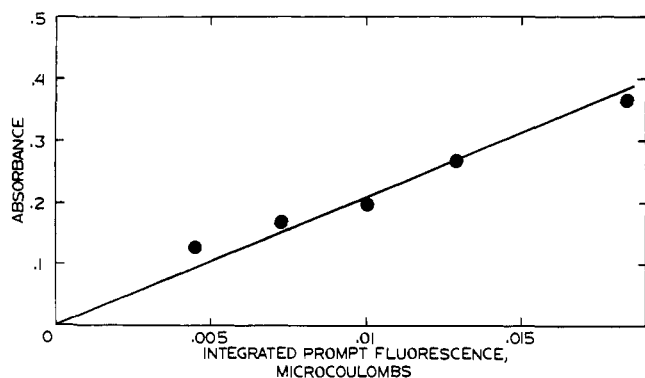


Figure 3. Corrected initial triplet absorbance of phenanthrene vs. integrated prompt fluorescence intensity.

reduced energies. The photomultiplier was operated under standardized conditions, and its anode currents were integrated with fast analog circuitry.¹⁴ The slopes, m , of these plots were computed by a linear least-squares method with a forced zero intercept.

If α is expressed in terms of m , and $[T_1]$ is given via the absorbance, eq 5 becomes

$$I_{DF} = \frac{\phi_t}{mb\epsilon_T} k_s A_T^2 \quad (10)$$

Since I_{DF} and A_T are given directly by the flash experiment, k_s may be determined if ϕ_t and ϵ_T are available from the literature. However, triplet molar absorptivities are not often known accurately, so it is more desirable to report the s -pathway rate constant as a fraction, p_e , of the experimental bimolecular decay constant. That is, $p_e \equiv k_s/k_2$, and eq 10 becomes

$$I_{DF} = \frac{\phi_t}{mb} \left(\frac{k_2}{\epsilon_T} \right) p_e A_T^2 \quad (11)$$

Since the transient fitting procedure provides k_2/ϵ_T directly, p_e can be evaluated from a plot of $I_{DF}^{1/2}$ vs. A_T without knowledge of ϵ_T .

A square-law plot for phenanthrene is shown in Figure 4. Anthracene gave equivalent results, and the corresponding values of p_e for both molecules are summarized in Table I. In the calculations, ϕ_t was taken as 0.70 for anthracene and 0.80 for phenanthrene.¹ Our p_e ratio for anthracene agrees very well with the values reported previously by Kikuchi et al.⁸ and by Tfibel and Lindqvist.¹⁰ Their results for anthracene and naphthalene are also shown in Table I for comparison. Of further interest is the agreement among the three values of k_2/ϵ_T for the anthracene system. This ratio itself is evidently very reproducible; the broad range of reported k_2 values come almost wholly from differences in the extinction coefficients used by the various authors. The consistency of our results for the well-characterized anthracene system with respect to those from earlier flash studies serves as a standard by which the reliability of our results for phenanthrene may be judged.

Probabilities of Singlet Production. Parker's^{1,3-5} investigations of branching in triplet-triplet annihilation involved the s -channel encounter reaction probability $p_e = k_s/k_d$, where k_d is the bimolecular limiting rate constant $8RT/3000\eta$.^{6,7} For ethanol at 20 °C,¹ $k_d = 5.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The p_e values given by Parker for the substances of interest here are listed in Table II. They differ from the originally reported data by a factor of 2, for the reasons given by Naqvi²⁸ and by Parker.⁵ Although they are not directly comparable, flash photolytic p_e ratios are also shown in Table II. From the probabilities p_e and p_c , one can calculate rate constants k_s that do allow comparison. The results in Table II show that the phosphorescopic and flash

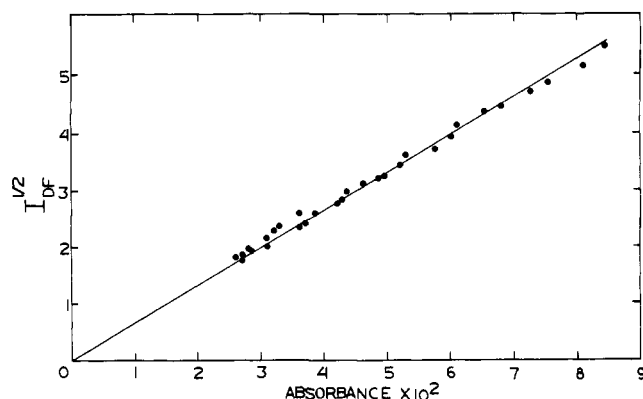


Figure 4. Square root of delayed fluorescence intensity vs. phenanthrene triplet absorbance. These data correspond to the transient shown in Figure 1.

Table II. Comparison of s -Pathway Rate Constants

Compd	Flash photolytic ^a		Parker ^b	
	p_s	$k_s, \text{M}^{-1} \text{s}^{-1}$	p_c	$k_s, \text{M}^{-1} \text{s}^{-1}$
Anthracene	0.08	3.2×10^8	0.04	2.2×10^8
Naphthalene	0.52		0.28	1.5×10^9
Phenanthrene	0.020	1.0×10^8	0.025	1.4×10^8

^a Data from this work, except for those of naphthalene, which come from ref 10. Naphthalene was studied in cyclohexane, the others in ethanol. ^b Reference 5, all for ethanolic solutions.

photolytic data agree reasonably well, especially when one takes into account (1) the effect of uncertain molar absorptivities upon the flash results and (2) the fact that Parker's original results were reported only to a single significant figure.

Although the flash photolytic p_e ratios are apparently reliable, they are not as fundamentally significant as the ratio $p_0 = k_s/k_a$, where k_a is the total rate constant for triplet-triplet annihilation,

$$k_a \equiv k_s + k_t + k_g = 1/2(k_2 + \phi_t k_s + k_t) \quad (12)$$

Thus p_0 is the efficiency of the s pathway per annihilation event. Unfortunately, the t and g pathways are inseparable by the flash method, so precise p_0 values cannot be calculated from the available data.

However, estimates are still possible. Instinctively, one might expect that the g channel would be very infrequently exercised, because it requires the accommodation of the entire annihilation energy in mechanical modes. If so, then $k_2 = (2 - \phi_t)k_s + k_t$, and

$$p_0 = \frac{k_s}{k_2 - (1 - \phi_t)k_s} = \frac{p_e}{1 - (1 - \phi_t)p_e} \quad (13)$$

This simplification yields the lower limit for p_0 , because k_a reaches its maximum value when k_t is maximized for given k_2 and k_s . That condition is reached for $k_g = 0$.

An upper limit for p_0 can be obtained by considering the minimum value of k_a for given k_2 and k_s . Equation 12 shows that such a condition demands that $k_t = 0$, which would imply that annihilation takes place only through the s and g channels. Then

$$p_0 = \frac{2k_s}{k_2 + \phi_t k_s} = \frac{2p_e}{1 + \phi_t p_e} \quad (14)$$

These limiting values of p_0 are listed in Table I. The energy considerations stated above and the need for conservation of spin momentum suggest that the actual p_0 ratios are closer to the lower limit than the upper one. In any case, the ranges seem firm, and they allow one to order the compounds by increasing

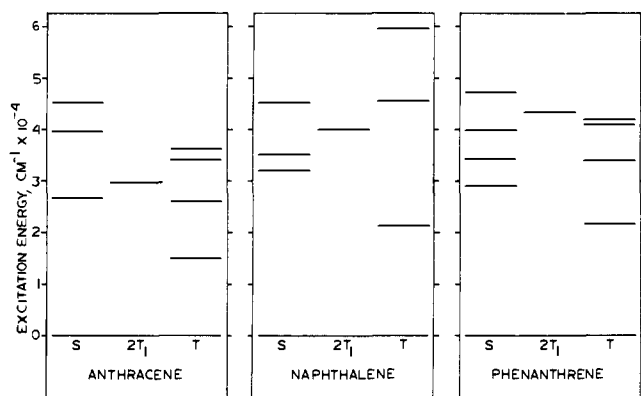


Figure 5. Observed singlet and triplet energies relative to the available annihilation energy.

s channel efficiencies as phenanthrene, anthracene, and naphthalene. The same relative order was given by Parker,^{1,5} albeit with a different set of numbers. The remaining question of interest is the molecular basis for this order and for the wide range of observed efficiencies.

A Simplified Reaction Model. Tfibel and Lindqvist proposed that annihilation via the s pathway takes place through a particular upper singlet excimeric state and that the relative branching efficiencies could be correlated with the formation and decay properties of the excimer.¹⁰ However, the experimental data suggest that the s channel is most favored when the formation of the excimeric state is moderately endothermic (by perhaps 3000 cm⁻¹), rather than the converse as one might expect. The energy required is somewhat more than that readily available by thermal activation, and in this respect the hypothesis is not completely satisfying.

Given the amount of energy available in an annihilation event, it seems likely that Franck-Condon factors would bear importantly on the problem of energy disposition. One can approach this possibility by considering the gaps between the total annihilation energy $2E(T_1)$ and the energies of the various states within the singlet and triplet manifolds of the isolated molecules. Two assumptions are made: (1) the main annihilation pathways are exothermic or thermonutral, and (2) Franck-Condon factors will favor those paths which lead to the lowest possible degrees of mechanical excitation. Thus s-channel efficiencies can be enhanced by reducing the gap between the annihilation energy and the energy of the highest accessible singlet, relative to the corresponding gap for the triplet manifold. Efficient production of S_1 would require a singlet state S_i with an energy $E(S_i)$ below the annihilation energy, but matching that energy more closely than the highest accessible triplet T_j does. More precisely, the values of p_0 should increase as $\Delta E_1/\Delta E_S$ increases, where $\Delta E_T = 2E(T_1) - E(T_j)$ and $\Delta E_S = 2E(T_1) - E(S_i)$. That the upper singlets may participate in annihilation has already been substantiated by observations of delayed fluorescence from these states in 1,2-benzanthracene and fluoranthrene.³⁰

Table III lists the annihilation energies, the $\Delta E_T/\Delta E_S$ ratios, and the triplet and singlet energy levels as observed in absorption spectroscopy for the three compounds discussed above. These data were taken from the critical reviews by Birks² and by McGlynn et al.²⁹ In Figure 5 the listed energy levels are shown schematically relative to the annihilation energies. From the ratios of the energy gaps $\Delta E_T/\Delta E_S$, one would predict that the order of increasing p_0 would be exactly that observed, viz., phenanthrene, anthracene, and naphthalene. Note also that the experimentally determined state structure of naphthalene is nearly ideal for a high p_0 value, if Franck-Condon factors are of overriding concern. Not only is there a huge gap between $2E(T_1)$ and $E(T_j)$, but there are

Table III. Upper Singlet and Triplet Energies^a

Compd	$2E(T_1)$, 10^3 cm^{-1}	$E(S_1 \cdots S_n)$, 10^3 cm^{-1}	$E(T_1 \cdots T_n)$, 10^3 cm^{-1}	$\Delta E_T/\Delta E_S$
Anthracene	29.8	26.7	14.9	1.2
			26.1	
			33.9	
Naphthalene	46.6	32.2	36.3	2.8
			45.2	
			35.0	
Phenanthrene	43.4	28.9	21.7	0.40
			34.2	
			39.9	
			41.0	
			47.3	

^a See ref 2 and 29. Experimentally observed transitions only.

also two singlets not far below the annihilation energy.³¹ In this framework, then, the exceptionally large s-channel efficiency in the naphthalene system can be understood.

This model is certainly oversimplified. Many additional molecular features, such as densities of states, spin statistical factors, and properties of excimeric structures, must enter into the determination of branching ratios. On the other hand, its success here is striking and may point to a central role for Franck-Condon factors in guiding energy disposition. The proposed model is a promising means of explaining the relative s-channel efficiencies, but one must await further studies with many more systems before its validity can be tested adequately.

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(31) Note also that only one triplet has been observed below these two singlets. This feature is an inconsistency that suggests the existence of other triplets between the T_1 and T_2 levels shown in Figure 5. They may not have been observed because they lie only slightly above T_1 or because the corresponding $T_1 \rightarrow T_1$ transitions are weak. See, e.g., T. Takemura, K. Hara,

and H. Baba, *Bull. Chem. Soc. Jpn.*, **44**, 977 (1971). The existence of such states might modify the extreme favor that our hypothesis gives toward the singlet channel in the case of naphthalene. On the other hand, it is possible that symmetry factors leading to low oscillator strength in $T_1 \rightarrow T_1$ transitions are also manifested in triplet-triplet annihilation.

Photochemical Extrusion of Nitrogen in Azo Compounds. An ab Initio SCF-CI Study

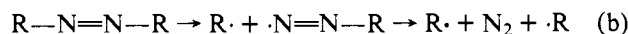
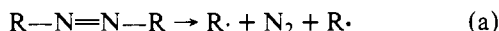
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Abstract: Ab initio SCF-CI methods have been used to simulate the behavior of the ground and low-lying excited states of *cis*-diazide when a nitrogen molecule is expelled via a concerted scission of the pair of NH bonds or a stepwise mechanism. The analysis of the states correlation diagrams shows that the successive rupture of the NH bond is the preferred pathway and might be initiated by the light-induced population of the lowest $n\pi^*$ singlet state of the azo chromophore.

Thermal nitrogen extrusion in azo compounds may proceed via concerted (a) or successive (b) scissions of the pair of N-C bonds coupling the N=N unit to the rest of the molecule.²

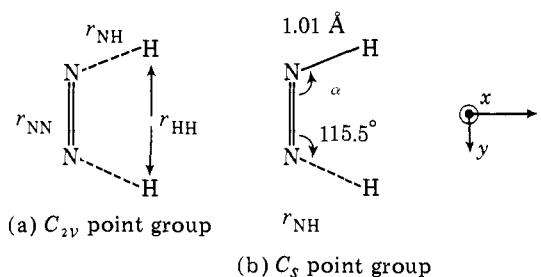


Of course these simple mechanisms have been improved to include, for example, cage effects, but nevertheless the refined versions retain their close parentage with (a) or (b). Recent ab initio SCF calculations³ have shown that no clear-cut choice can be made between (a) and (b) in the thermal decomposition of 1-pyrazolines. Simultaneous cleavage of both CN bonds leading to a planar trimethylene diradical has a calculated activation energy of 44.1 kcal/mol. On the other hand, a two-step reaction involving an intermediate diazenyl radical requires 44.5 kcal/mol. Undoubtedly small perturbations may favor one mechanism or its partner. This in turn might account for the conflicting interpretations of experimental results whether they favor concerted⁴ or successive⁵ scissions.

The same basic mechanisms have been invoked to rationalize the spin correlation effects noted in the photochemically induced expulsion of N_2 .⁶ The aim of this paper is to compare the behavior of the various excited states of azo compounds when pathways (a) and (b) are theoretically simulated. The prototype of this ab initio SCF study is *cis*-diazide.⁷ This choice requires a word of caution. In this model one or two N-H linkages will be broken whose bond energies (92 ± 2 kcal/mol) are notably different from those of the N-C bonds experimentally investigated (78 kcal/mol).⁸ In addition our scheme does not take into account the release of ring strain energy (~ 15 – 20 kcal/mol) which intervenes in the cleavage of cyclic azo compounds. Therefore these calculations will not provide us with an accurate estimation of the activation energies involved (which in turn might be compared with experimental values) but rather with the basic characteristics of the excited states correlation patterns in both alternatives (a) and (b). This approach closely parallels the study of acyclic and cyclic ketones with formaldehyde as a convenient model.⁹

Methodology

Mechanisms (a) and (b) have been treated in the following fashion. In the case of the concerted path (a), for each value of the elongated NH bonds we have minimized the SCF energy of the ground state (without CI) with respect to the r_{NN} and r_{HH} distances.¹⁰ In the second case we have restricted ourselves to the primary feature of the complete reaction, that is, the breaking of one of the NH linkages. For a given NH distance the ground-state energy has been optimized with respect to the NN bond length (r_{NN}) and the NNH angle (α).¹¹ The



ground-state energy was obtained using the ab initio SCF Gauss 70 series of programs¹² in its STO-3G minimum basis set version.¹³ The ground-state MOs were then used to carry out the CI segment of the complete calculation of the excited states wave functions. Singly and doubly excited configurations were constructed, that is, configurations obtained by promoting one or two electrons from the six highest occupied to the four lowest empty MOs.¹⁴ It is important to add that two theoretical procedures were tested at each point of the reaction path to ensure that, for each state under study, the best set of ground-state MOs was used to generate the Slater determinants to be included in the CI calculation. This forces the CI treatment, which, for practical reasons, had to be limited, to approach as closely as possible the results of a complete investigation. The first procedure is Roothaan closed-shell SCF formalism^{15a} which gives adequate MOs in the vicinity of the reactant; the second is Nesbet's brand of open-shell calculations^{15b} which is more adapted in regions where occupied and empty MOs eventually intersect. We accepted as final result