

A second relationship between ϕ_x' and ϕ_y' is obtained by adding eq 1 and 2. Letting $s = x + y$ represent the total concentration of photoreactive material and $f_x = x/s$ and $f_y = y/s$ represent the fraction of each species, the differential equation

$$ds/dt = -I_0 l \bar{\epsilon} \bar{\phi} / (VF(D)) = -I_0 \bar{\phi}' (1 - e^{-D}) / V$$

is obtained where $D = l \bar{\epsilon} s$, $\bar{\epsilon} = (\epsilon_x + \epsilon_y r) / (1 + r)$ and

$$\bar{\phi}' = (\epsilon_x \phi_x' + r \epsilon_y \phi_y') / (\epsilon_x + \epsilon_y r) \quad (5)$$

Note that $\bar{\phi}'$ and $\bar{\epsilon}$ lie between ϵ_x and ϵ_y and ϕ_x' and ϕ_y' depending on the value of r . As t increases, $s \rightarrow 0$ but during the period in which r has nearly reached r_∞ (for compounds such as the alkyldiazenes with small ϕ 's, long before s has vanished), the decrease in $\ln s$ is essentially linear if one considers a short enough interval such that $F(D)$ is nearly constant. In that span $\bar{\epsilon}$ and $\bar{\phi}'$ approach constant values, $\bar{\epsilon}_\infty$ and $\bar{\phi}'_\infty$:

$$(d \ln s / dt)_\infty = -I_0 l \bar{\epsilon}_\infty \bar{\phi}'_\infty / (VF_\infty) \quad (6)$$

Expressing experimental data in terms of r and s may provide a physically more tangible description of a molecule's photochemistry since the two variables can be thought of as separately characterizing the kinetics of $X \leftrightarrow Y$ interconversion and those of irreversible photo-reaction when both types of processes occur simultaneously. As in completely reversible transformations, prolonged irradiation produces a fixed ratio of interconverting species (eq 3); however, once the limiting composition is approached, the mixture described by r_∞ continues to decompose, absorbing light as if it were a single compound with extinction coefficient $\bar{\epsilon}_\infty$ and quantum yield $\bar{\phi}'_\infty$. Accordingly, the system is said to be in a "quasi-steady state".

From measurement of s in the quasi-steady-state region of a compound for which the irreversible products are the same (e.g., N_2 and hydrocarbons in azoalkanes) or are not observed, only $\bar{\phi}'_\infty$ can be obtained. Measuring s in the initial or "transient" region starting with either pure isomer and measuring initial slopes allows determination of both ϕ_x' and ϕ_y' . However, initial (or any) slopes are notoriously difficult to obtain accurately from experimental points²⁵ and we preferred to test the mathematical model by fitting experimental data recorded over a longer period.

For azomethane, the four quantum yields are evaluated from optical density data. First r_∞ and $\bar{\phi}'_\infty$ are obtained from the quasi-steady state using eq 6. (Note, however, that in the same region eq 4 can be integrated exactly and explicitly.) Then values of ϕ_x and ϕ_x' are guessed and the other two ϕ 's are computed from eq 3b and 5. The functions $r(t)$ and $s(t)$ are generated using a Runge-Kutta program to solve the appropriate differential equations, and ϕ_x and ϕ_x' are varied until the best agreement between calculated and experimental kinetics is obtained. For azoisopropane, the irreversible ϕ 's are too small to separate with any accuracy using the above procedure. Instead they are obtained from initial rates of total N_2 production (starting with pure trans isomer) combined with the value of $\bar{\phi}'_\infty$ taken from optical density measurements.

Experimental Section

Materials and Spectral Characterization. *trans*-Azomethane, synthesized according to the method of Renaud and Leitch,²⁶ was flushed with helium through Drierite into a vacuum system where it was purified by degassing and fractionation at 77 and 195 K. *trans*-Azoisopropane of high purity was obtained from Merck Sharp and Dohme, Canada, and degassed and fractionated prior to usage.

Phenylazomethane was prepared by the method of E. Fischer.²⁷ Spectrograde isooctane and benzene- d_6 and reagent grade benzene, dried over molecular sieves, were used as solvents after spectroscopic purity was confirmed.

All UV-visible spectra were measured on a Cary Model 14 recording spectrophotometer. The absolute absorbances of *trans*-azomethane in benzene and in isooctane²⁸ were determined by measuring spectra of several solutions of known concentration. A mixture of both isomers in benzene was prepared by irradiating, with a band centered at 313 nm, a solution of *trans*-azomethane in C_6D_6 (with 3 mol % of C_6H_6 added for an internal NMR standard); the absolute absorbance of the *cis* isomer was determined by measuring both electronic and NMR spectra of this solution before and after photoisomerization. The two isomers have distinct proton chemical shifts (*trans*-azomethane +3.66 ppm and *cis*-azomethane +4.23 ppm), and the fraction of each isomer following irradiation was computed from NMR peak heights including a resonance for the decomposition product ethane.

Absorption spectra of both isomers of azoisopropane and phenylazomethane were obtained similarly except for *cis*-azoisopropane where the spectrum was supplied by Steel.^{3c} Spectra for *cis*-azoisopropane and phenylazomethane were also checked using a procedure developed by Fischer²⁹ and also by Sutin.²⁷ For phenylazomethane in benzene the chemical shifts are 1.84 ppm for the *trans* isomer and 1.32 ppm for the *cis* isomer relative to cyclohexane; the *cis*-*trans* difference is nearly the same as for azomethane.

Photochemical Procedure and Actinometry. The source for irradiations was a Hanovia medium-pressure 60-Hz ac mercury-arc lamp operated with a constant-voltage power supply. (For irradiation to produce *cis*-azomethane for measurement of the absolute UV spectrum, an Oriel xenon lamp was used.) Conventional filters³⁰ were used to isolate the 313-, 365-, 405-, and 436-nm mercury "lines". The incident intensity for azomethane and phenylazomethane irradiations was determined by chemical actinometry from the *cis*-*trans* isomerization of azobenzene in isooctane.²¹ At the azobenzene concentrations employed ($(8.5\text{--}8.7) \times 10^{-5}$ M) absorption at 365 and 436 nm is so small that I_0 can be calculated from the limiting linear form of the photochemical equation²¹ where the fraction of *cis*-azobenzene, $f_{y,t}$, is determined from its optical absorption. For azoisopropane, uranyl oxalate actinometry³⁰ was used.

Pure *trans*-azoalkane solutions were irradiated with continuous stirring at 25 °C with frequent spectroscopic monitoring in the S_1 band for a minimum of 5 h. The light intensity was monitored throughout the course of each run, either simultaneously or alternately irradiating the actinometric and azoalkane solutions. The lamp output was constant within the precision (2–4%) of the actinometric methods used. After each run the irradiated azoalkane solution was stored in the dark at room temperature and the UV spectrum was recorded periodically; for all three compounds the rate of any dark reaction was too slow to affect the photochemical kinetics.

Results

The UV-visible absorption spectra of azomethane in benzene and phenylazomethane in isooctane appear in Figure 1. Typical of diazenes, the intensities of the $n \rightarrow \pi^*$ transition in the *cis* isomers are much stronger than for the *trans*.^{3c,31}

The kinetics of photoisomerization and photodecomposition were determined by calculating the concentrations of each isomer and the ratio r ($y/x = [cis]/[trans]$) and sum s from absorbance at two wavelengths using simul-

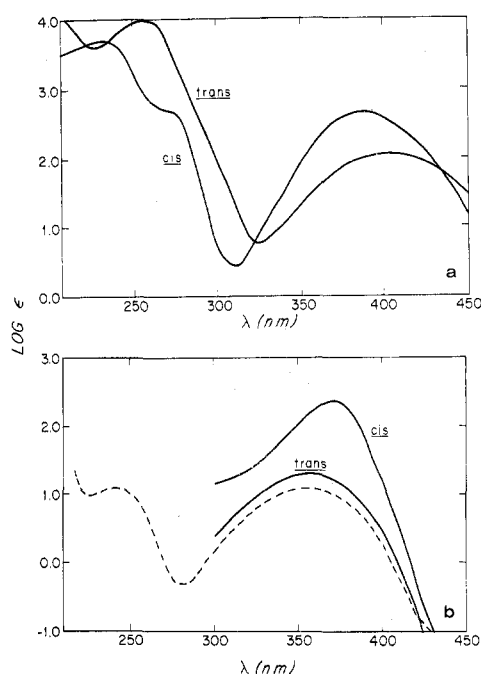


Figure 1. UV absorption spectra of (a) phenylazomethane in isooctane and (b) azomethane in benzene (—) and isooctane (---).

TABLE I: Quantum Yields for Diazene Photochemistry in Solution^a

	phenylazo- methane ^c		azome- thane ^b	azoisopropane ^c		
	365 ^d	436	365	313	365 ^f	405
ϕ_x	0.42	0.53	0.42	0.40	0.48	0.44
ϕ_y	0.51	0.60	0.45	0.31 ^e	0.60	0.59
ϕ_x'	0.0	0.0	0.090	0.027	0.025	0.016
ϕ_y'	0.0	0.0	0.008	0.048	0.016	0.012
ϕ_∞'	0.0	0.0	0.050	0.035	0.020	0.010

^a Values reported are ± 0.01 . ^b In benzene. ^c In isooctane. ^d Wavelengths are given in nm. ^e This value does not seem to be due to an experimental artifact but probably reflects a greater uncertainty in the absorptivities at 313 nm and possibly small absorption by secondary photolysis products (see Discussion). ^f These values are in reasonable accord with Steel's:^{14,15} starting with *trans*-azoisopropane, $\phi_x = 0.53 \pm 0.04$, $\phi_y = 0.46 \pm 0.04$, and $\phi_x' = 0.021$.

taneous equations. Best values of x and y were obtained by restricting monitoring wavelengths to the region of greatest spectral change (345–390 nm).

Only reversible isomerization was found for phenylazomethane (see Table I); its behavior resembles that of typical aryl diazenes.³² For the other two compounds the kinetics of a representative photoisomerization are shown in Figure 2. From the decrease in $s(t)$ it is seen that a significant amount of irreversible reaction competes with *cis*–*trans* isomerization, and the quasi-steady-state behavior predicted for such a system is evident in Figure 2b. After a rapid initial rise, r remains constant throughout the irradiation during which time $\ln s$ decreases linearly. From r and the slope of $\ln s$ in the quasi-steady state (eq 6), quantum yields for the photoreactions are calculated as described above. It is found that although the agreement between computed and observed values of s and $\ln s$ for azomethane (Figure 2) is not very sensitive to small variations in the individual quantum yields ϕ_x' and ϕ_y' , a reasonable fit to the experimental kinetics can only be obtained when ϕ_x' is much greater than ϕ_y' . The means of best fit quantum yields for each of the three diazenes appear in Table I.

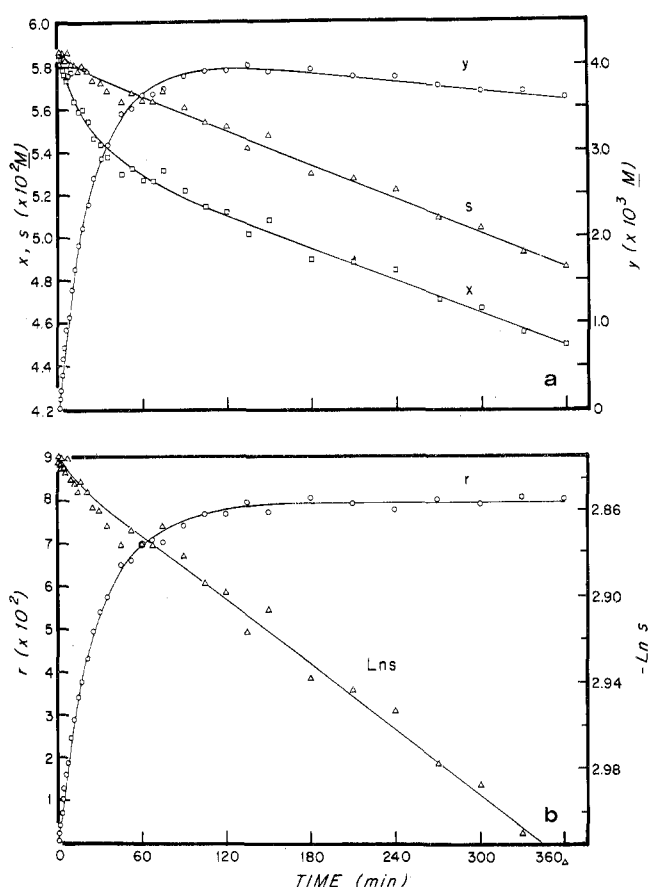


Figure 2. Photochemical kinetics of azomethane in benzene irradiated at 365 nm: (a) $[trans] = x$, $[cis] = y$, $s = x + y$; (b) $[cis]/[trans] = r$. The curves represent simulated kinetics ($\phi_x = 0.41$; $\phi_y = 0.44$; $\phi_x' = 0.095$; $\phi_y' = 0.00$).

Discussion

(I) *Spectra*. The UV spectrum of *trans*-azomethane consists of a broad, structureless band centered at 356 and 354 nm in benzene and isooctane, respectively, in good agreement with solution-phase spectra reported previously.^{6,33} The absolute spectrum of *cis*-azomethane is consistent with those measured for other *cis*-azoalkanes^{3c,31,34} and for *cis*-azomethane in D_2O .⁶

The spectra of azomethane in isooctane and benzene differ from each other (see Figure 1b) and from those measured in D_2O and to a lesser extent in hexane.³³ The blue shift of the maximum in D_2O relative to other solvents is to be expected³⁵ but the cause of intensity variation, as with solvent influence on the quantum yield for photodecomposition noted by other investigators,^{6,12,36,37} remains unexplained. Judging from Nodelman and Martin's⁵ theory, for example, there seems to be no simple relationship between the amount of photolysis and the solvent properties which determine the extent of cage reaction^{36–38} in azomethane. This is understandable since the former effect is related to the dissociation process whereas the latter concerns the fate of methyl radicals once they are formed. A comparison of solution-phase decomposition quantum yields^{6,12,36,37} and absorption intensities³³ suggests that there may be an inverse connection between absorbance and photodissociation; it is not unreasonable to suppose that a solute–solvent interaction could distort the azomethane molecule in a way that would both enhance the $n \rightarrow \pi^*$ transition probability and stabilize the excited molecule with respect to decomposition.

The absorption spectrum of phenylazomethane in isooctane, as might be expected, resembles neither that of a purely alkyl nor that of a purely aromatic diazene. Both

the n, π^* and π, π^* bands are intermediate in intensity and position between azomethane³⁹ and azobenzene.²¹

(II) *Photochemistry: Major and Minor Reactions.* Quantum yields for azomethane and azoisopropane photoreaction determined from analysis of the spectroscopic quasi-steady state are consistent with values obtained from direct measurement of gaseous products.^{6,12,14,15,36} Cis-trans isomerization accounts for 90% or more of the photochemical reaction observed in the S_1 irradiation of azomethane in benzene and azoisopropane in isooctane; the remaining fraction of absorbed energy causes free-radical decomposition to N_2 and hydrocarbons. The unimolecular nature of the decomposition reaction^{3d} is evident in the energy dependence of ϕ_{∞}' in azoisopropane (see Table I) and in the greater amount of azomethane dissociation at 365 nm.⁴⁰

Both azomethane and azoisopropane on prolonged irradiation give rise to a small additional absorbance at wavelengths less than 310 nm. This probably results from a nitrogen-containing product formed in a secondary free-radical reaction,⁴¹ but its presence does not affect analysis of the photochemistry except possibly at the lowest wavelength. In one experiment, azoisopropane was irradiated until none of either isomer of the parent compound remained; the resulting spectrum displayed a small maximum at about 290 nm. Of several possible decomposition products, the most chemically reasonable known spectrum we could find with a comparable maximum was for tetraisopropyltetrazene studied by Lemal⁴² which has a maximum absorbance at 291 nm ($\log \epsilon_{\max} = 4.05$). If this type of compound is indeed formed from the dimerization of $\cdot N=N(i-C_3H_7)_2$ (in this case to the extent of approximately 0.1% of the original diazene), it would suggest that the primary dissociation of azoisopropane is a one-bond scission.⁴³

The inequality of the decomposition quantum yields in azomethane—indeed, *cis*-azomethane may not photolyze at all in solution—signifies that a different excited state is responsible for the decomposition of each isomer, states which must also be distinct from the one leading to isomerization. This is also implied by the energy dependence of ϕ_{∞}' in azoisopropane since *cis*-trans isomerization in a condensed phase is expected to follow vibrational relaxation of the initially excited molecule (*vide infra*). The fact that the sum of the four quantum yields is close to unity in both cases (see Table I) means that the species leading to the various reactions share some common pathways and strongly suggests that isomerization proceeds through a common intermediate.

These solution-phase quantum yield data may constitute the first evidence for two excited intermediates in the direct irradiation of azomethane since the efficiency of its gas-phase photolysis has prevented their detection by more conventional methods.^{6,7,18,20,41a} In addition, they support the concept of a general two-state model for diazene photochemistry.^{3d,13-16,19,20} Among the specific mechanisms which have been proposed to explain azoalkane photochemistry are

A**	A*	A ⁺	ref
T_{1N}	T_{1R}	T_{1R}	20
$S_0^*(cis)$	$S_0^*(trans)$	S_1	15
S_1	T_{1R}	T_{1R}	20

where A* and A** are short-lived decomposing states of different lifetime and A⁺ is the isomerizing form of A*.^{3d} The subscripts N and R refer to species in which vibrational energy is nonrandomly and randomly distributed throughout the excited molecule.^{19,20} Each of the above

mechanisms will be considered in view of the quantum yield data for azomethane (first) and for azoisopropane (second).

(III) *Mechanism for Azomethane Photochemistry. $S_0^*-S_1$ Mechanism.* In this model, which is favored by Steel¹⁵ to explain the gas-phase photochemistry of azoisopropane, decomposition follows isomerization; in solution, which is considered to be the limiting case of a high-pressure gas, decomposition would be presumed to come from the shorter lived of the two species $S_0^*(trans)$ and $S_0^*(cis)$. Thus, if isomerization occurs from a common intermediate as it appears to in azomethane ($\phi_x + \phi_y = 1$), subsequent dissociation of $S_0^*(cis)$ or $S_0^*(trans)$ would demand that the decomposition quantum yields be equal. On the contrary, the photodecomposition of azomethane in solution results almost exclusively from the *trans* isomer (see Table I) so that the shorter lived species (A**) is identified with a pathway that is associated with only one isomer. This together with the probably higher barrier for thermal decomposition relative to isomerization^{44,51,52} tends to rule out a mechanism in which decomposition follows isomerization and the likelihood that dissociation in solution comes from a vibrationally excited ground state molecule.

Unimolecular Calculation (Classical). The two other mechanistic alternatives shown above are derived from Chervinsky and Oref's²⁰ unimolecular treatment of high-pressure collisional quenching data for four simple azoalkanes. In both models, photolysis at low pressures is ascribed to a randomized triplet, T_{1R} , of a configuration intermediate between the *cis* and *trans* ground states, which at higher pressure is collisionally deactivated. In solution, T_{1R} can be identified with the species responsible for *cis*-*trans* isomerization and decomposition could occur through a shorter lived species S_1 or T_{1N} . Either singlet or triplet decomposition is consistent with the quantum yields for azomethane photodecomposition. On the basis of a classical model of unimolecular dissociation of a molecule in solution,⁴⁵ the observed quantum yields correspond to values computed from decomposition of an excited molecule ($E(00) = 55-63$ kcal mol⁻¹) with a vibrational minimum of 6-10 kcal mol⁻¹ for which the energy is distributed among 6-8 degrees of freedom. Although such a classical picture is certainly oversimplified, the values of $E(00)$ and the minimum vibrational energy required for dissociation compare favorably with those obtained from more sophisticated unimolecular calculations^{18,20} and support a model of decomposition through S_1 or T_1 in which the vibrational energy is non-randomized (confined to the CNNC chromophore).

T_{1N} - T_{1R} Mechanism. A "two-triplet" mechanism would offer a straightforward explanation of the unity sum of azomethane quantum yields since formally only one electronic state would be responsible for all of the photochemistry. However, the inequality of ϕ_x' and ϕ_y' and the near-unity sum of ϕ_x and ϕ_y require that both $S_1(cis)$ and $S_1(trans)$ would have to cross quickly²⁰ to their respective triplet states (with only $T_{1N}(trans)$ decomposing significantly) before they could relax to the isomerizing intermediate.

Apart from the quantum yield data, it is difficult to find evidence for a two-triplet mechanism in the direct photolysis of azomethane since the molecule does not phosphoresce. However, efficient quenching of sensitizer phosphorescence by azomethane argues for some triplet participation^{7,12,15} in its photochemistry, and triplet-sensitized photodecomposition of azomethane is well-established. There may be some evidence for two triplets

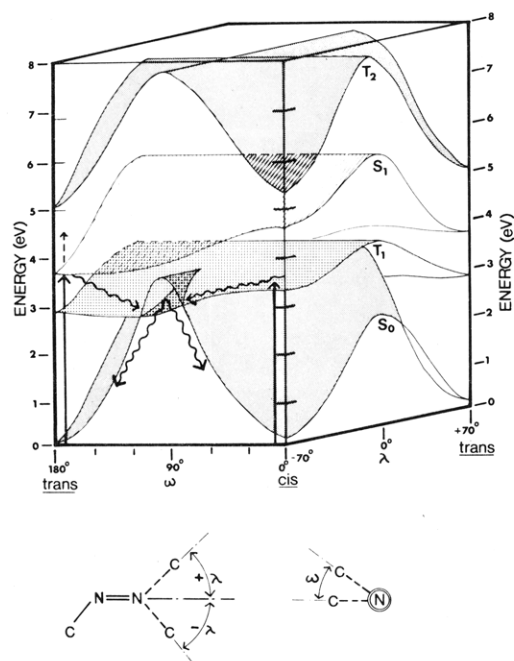


Figure 3. Potential energy surfaces for the S_0 , S_1 , and $T_1(n\pi^*)$ and $T_2(\pi, \pi^*)$ states of azomethane.⁶³ Baird and Swenson's⁶⁰ correlation diagrams for the model compound N_2H_2 have been used on the ω and λ axes, and a smooth variation between planes has been assumed.⁶⁴ Calculated curves have been shifted to coincide with experimental energies of *trans*-azomethane taken from electronic absorption⁵³ and electron-impact spectra.⁵⁴

in photosensitization data (curvature in ϕ_{N_2} (sensitized) at low pressure⁷), but it is not conclusive.⁴⁶

S_1 - T_1 Mechanism. The most obvious choice for the shorter lived species in azomethane photolysis is vibrationally excited S_1 ,⁴⁷ and the quantum yields measured in benzene can be explained by an S_1 - T_1 mechanism in which decomposition competes with collisional deactivation and intersystem crossing to T_1 more effectively for S_1 (*trans*) than for S_1 (*cis*). Although details of specific solute-solvent interactions are not well understood, it is reasonable to expect that together with collision such effects might stabilize the polar *cis* isomer more efficiently than the *trans*,⁴⁸ giving $\phi_x' > \phi_y'$. Isomerization is presumed to occur as T_1 (*cis*) and T_1 (*trans*) relax to a minimum energy at some intermediate configuration, intersecting the ground-state potential surface to return rapidly to S_0 (*cis*) and S_0 (*trans*) with a slight preference ($\phi_y/\phi_x = 1.1$) for the more stable isomer (vide infra). A common isomerizing triplet would account for the near-unity sum of the quantum yields and the absence of an energy barrier to its relaxation would explain the temperature independence of azomethane photoisomerization in condensed phases.⁶

There is support for an S_1 - T_1 mechanism in solution-phase azomethane photosensitization data¹²—singlet-sensitized decomposition comparable in magnitude to direct photolysis and triplet-sensitized isomerization with negligible decomposition.⁶⁶ More recently singlet dissociation has been observed in the direct irradiation of azomethane in solution using low-field CIDNP.⁵⁰ Thus, it appears that experimental evidence is strongest for a model of azomethane photochemistry based on two excited states which probably both decompose in the gas phase whereas only S_1 (*trans*) decomposes appreciably in solution and T_1 isomerizes.

This model is also consistent with what is known about the electronic structure of azomethane. Figure 3 shows experimentally observed states⁵³⁻⁵⁵ along the vertical axes and energies of S_0 and the three lowest excited states

calculated as a function of the geometrical parameters most likely to be modes for *cis*-*trans* isomerization.⁵⁶⁻⁶² The first, ω , is the dihedral angle between the two NNC planes, which corresponds to isomerization by rotation; the second mode, expressed by λ , the bending angle measured from the NN axis, represents inversion of one methyl in the plane of the molecule. Despite the approximations which have gone into their construction,⁶³ the essential features of the surfaces are consistent with orbital symmetry conservation rules and with a semiquantitative approach to the energy variations of the highest occupied molecular orbitals in each state.⁵⁸⁻⁶⁰ Accordingly, it is possible to make several observations concerning a photochemical mechanism for azomethane: (1) in 365-nm irradiation only S_1 and T_1 will be able to participate in photoreaction; (2) isomerization without irradiation can occur when an excited-state surface intersects S_0 ; (3) only intersection of S_0 with T_1 is illustrated, but isomerization through S_1 cannot be ruled out. In either case, however, intersection is seen only in the vicinity of the ω axis, which means that photoisomerization should proceed via a rotation about the double bond. (Note that thermal (S_0) isomerization is predicted to occur by inversion.⁵⁸⁻⁶²) From the representation of an S_1 - T_1 mechanism which has been included in Figure 3, it is possible to appreciate the lack of azomethane luminescence. Presumably decomposition and intersystem crossing from S_1 are so efficient that no fluorescence is seen and relaxation from T_1 to the ground state is fast enough to prevent phosphorescence from being observed.

(IV) Mechanism for Azoisopropane Photochemistry. The mechanism of azoisopropane photochemistry has been a subject of some controversy.^{13,15,20b} Arguments for isomerization through S_1 or T_1 are based partly on photosensitization data both singlet and triplet donors photosensitize isomerization,^{14,15} S_1 producing *cis* from *trans* more efficiently than T_1 does. The asymmetry of the isomerization quantum yields measured from quasi-steady state analysis ($\phi_y > \phi_x$; see Table I) supports isomerization through T_1 since it suggests that there is a barrier to *trans* \rightarrow *cis* isomerization in the direct excitation of azoisopropane as there appears to be in its triplet-sensitized isomerization.^{15,20b} Such a barrier is also consistent with the pressure dependence of azoisopropane gas-phase quantum yields determined by Fogel and Steel. The decomposition quantum yields for *cis*- and *trans*-azoisopropane are not the same although the difference between them borders on experimental uncertainty. A genuine inequality would indicate decomposition from S_1 (as in azomethane) giving an overall S_1 - T_1 mechanism for azoisopropane.

The increase in azoisopropane decomposition with irradiation energy has been mentioned as evidence for decomposition through S_1 . However, if the classical model of unimolecular decomposition described above is used, it is not possible to correlate the energy dependence of $\bar{\phi}_\infty'$ with dissociation from vibrationally excited S_0 , S_1 , or T_1 with any reasonable set of values for their energies and number of coupled vibrations. The assumptions made in the calculation are probably valid for azoisopropane and the lack of agreement may imply that UV irradiation of the molecule does not cause unimolecular decomposition of S_1 but instead leads directly to a predissociation.

Conclusion

The photochemistry of three diazenes—phenylazomethane, azomethane, and azoisopropane—has been determined by measuring changes in the solution absorption spectrum during UV irradiation. Mathematical

analysis based on the properties of a photochemical quasi-steady state has made it possible to extract from data of a single experiment quantum yields for both reversible and irreversible transformations of the molecules. For azomethane and azoisopropane, the results have been interpreted in terms of a mechanism in which each isomer decomposes through its S_1 state (in azoisopropane possibly by predissociation) and isomerizes by relaxing to a skewed form of T_1 capable of radiationless return to the ground state. Analysis of the quasi-steady state of other alkyldiazenes—especially those for which only irradiation in the solution phase or of one isomer is practical^{9,65}—may be able to give additional insight into their photochemistry as well.

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obtained a lower triplet-sensitized isomerization quantum yield using acetophenone. Since acetophenone is a higher energy donor than benzophenone, it seems likely that the lower amount of isomerization was accompanied by a greater amount of decomposition undetected in Steel's analysis for C_3 and C_6 hydrocarbon dissociation products. Further measurements of sensitized quantum yields for azomethane would help resolve the matter.

Triplet Deactivation in Benzotriazole-Type Ultraviolet Stabilizers

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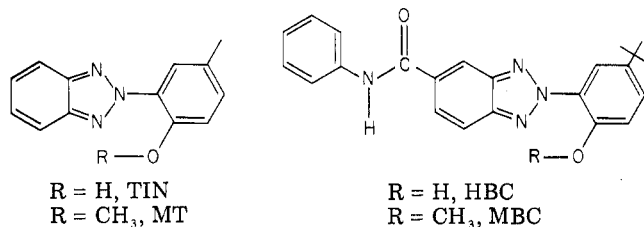
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The triplet-state properties of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole (TIN) and related compounds are investigated. It is shown by excitation spectra that molecules with an intramolecular hydrogen bond emit no slowly decaying phosphorescence. For the example of TIN, excited-state proton transfer is considered by application of the Förster cycle. The equilibrium constants between the tautomeric derivatives protonated at nitrogen or oxygen are estimated to be $pK_2(S_0) \leq 12$, $pK_2(S_1) \leq -3 (\pm 3)$ and $pK_2(T_1) \leq 0 (\pm 3)$ in the ground state, first excited singlet state, and triplet state, respectively. By a three-level energy-transfer experiment with nanosecond resolving time it is found that the triplet state shows no photosensitizing activity. A triplet decay time < 20 ns is concluded.

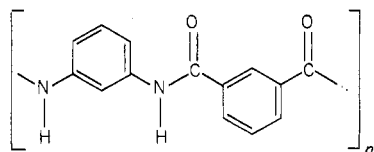
Introduction

Fast electronic deexcitation as a source of photostability is of great importance in molecules which are used as UV stabilizers in polymers. Some widely applied stabilizers are derivatives of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole (TIN). While compounds as TIN are used in



polyolefins, the 5-(carboxylic acid anilide) derivatives (HBC) proved to be particularly effective in aromatic polyamides.¹

In the near UV, these stabilizers are good light screens with extinction coefficients between 10^4 and $2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. In addition to screening, energy transfer can enhance the stabilizing efficiency of a given compound if the stabilizers are homogeneously distributed in a strongly absorbing polymer. As has been shown, TIN quenches excited ketones in solution.^{2,3} In preceding work, we detected triplet-triplet energy transfer from solid poly-(*m*-phenylenisophthalamide) (PPIA) to the methoxy



PPIA; $n = 200\text{--}300$

derivative MBC of HBC by sensitized phosphorescence of MBC and lack of sensitized fluorescence.⁴ This energy

transfer was also demonstrated by the phosphorescence depolarization of MBC in the polyamide films.⁵ It is assumed that triplet-triplet energy transfer occurs equally well between PPIA and HBC.

Up to now, however, it was uncertain whether triplet-triplet energy transfer could contribute to UV stabilization. UV stabilizers have to undergo rapid radiationless deactivation which interconverts the electronic energy into vibrational energy of the ground state, which is in turn rapidly equilibrated. So photochemical degradation of the stabilizer molecule itself and energy transfer to oxygen is inhibited.

Similar to the situation in *o*-hydroxybenzophenones,⁶ for stabilizers of the benzotriazole type the structural feature which is responsible for electronic deactivation is the internal hydrogen bond from the phenole group to the nitrogen atom of the heterocycle. For components of this type, Otterstedt⁷ proposed a deactivation mechanism, which is given in Figure 1. After the absorption of light, the next step is a proton transfer from O to N in the excited singlet state interchanging the main bond and the hydrogen bond. A process of this type was found for the first time by Weller⁸ in salicylic ester. In the benzotriazoles, the phototautomer undergoes rapid radiationless deactivation. The rapid rate of this process is explained by the decrease of the excitation energy in the N-protonated form which causes the Franck-Condon factors to increase exponentially.⁹ No statement concerning the lifetime of the triplet state is made in this model. In experimental work, some contradictory results have been reported. Lamola and Sharp¹⁰ estimate the triplet lifetime of *o*-hydroxybenzophenone to be smaller than 10 ns. Klöpffer¹¹ proposed a modification of the deactivation path for this compound, for which fast triplet decay is an essential process. On the other hand, Guillory and Cook³ report photosensitizing activity of TIN which is excited by triplet-triplet energy transfer. Merrill and Bennett¹²