Figure 6. A perspective of the H_2FeP_4 skeleton for the molecule $H_2Fe[P(OC_2H_5)_2C_6H_5]_4$, taken from an X-ray crystal structure determination.[27]

trans species are attractive possibilities as intermediates in the exchange processes. Several permutational alternatives exist for this type of mechanism and will not be discussed in detail here.[5] Suffice it to say that for one case the permutational analysis gives the linear combination 2E + I + IV (E is the identity set and has no effect on the line shapes).[5] This combination gives fair agreement with the observed line shapes although it is less satisfactory than with IV alone. At this point in time, it is not possible to distinguish unambiguously between the concerted and two-step alternatives; in fact, strong arguments can be advanced, indicating that these closely related alternatives merely represent two extremes of a continuum of potential surfaces, many of which may be actually realized in practice.[5]

Conclusion

It is clear, with the introduction of the new mathematical approaches to computation, and with the application of group theoretical methods to the determination of the mechanistic information potentially present in the line shapes for a given exchanging system, that the field of nmr in dynamic systems has entered a new and exciting phase. Transition metal hydrides have been used as examples since this is the area in which the bulk of our research has so far been done. The methods can clearly be applied to any system undergoing mutual intramolecular exchange on the nmr time scale, provided it contains magnetic nuclei. The example of $(CH_3)_2NPF_4$ has been mentioned; we have analyzed the spectra for, and are currently studying, cationic transition metal ML_5 species where mechanistic information can be obtained.

Aside from the area of mutual intramolecular exchange it is likely that further diversification of the field will lead to mechanistic studies of non-mutual intramolecular exchange and of intermolecular exchange.

Photochemistry of Aliphatic Azo Compounds in Solution

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Irradiation of aliphatic azo compounds with ultraviolet light may lead to any of three unimolecular chemical reactions: elimination of nitrogen, cis-trans isomerization, or tautomerization to a hydrazone.[1] Although bimolecular hydrogen abstraction has been observed in the aromatic series[4] and in azo esters,[5] the evidence for its occurrence in the azoalkanes is only very tentative.

Mechanistic investigations to date have focused primarily upon the first two reactions, nitrogen extrusion and cis-trans isomerization. In some instances these have been complemented by studies of such photophysical processes as fluorescence and energy transfer. It is the purpose of this Account to present and evaluate some of the existing solution-phase photochemical data. Both the gas-phase photochemistry[6] and the thermal chemistry[7] of azo compounds are also under active investigation, and our

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Paul Engel's research is likewise in the area of organic photochemistry, with special interest in the reactions of azo compounds, β,γ-unsaturated ketones, and peroxides. He received his Ph.D. in 1968 with Paul D. Bartlett at Harvard, spent the following 2 years at the National Institutes of Health, Bethesda, Md., and then assumed his present position of Assistant Professor of Chemistry at Rice University.

(1) The recently reported photoisomerization of certain pyrazolines to diazo compounds should also be included:[2,3] M. Franck-Neumann and C. Buchecker, *Tetrahedron Lett.*, 2659 (1969).

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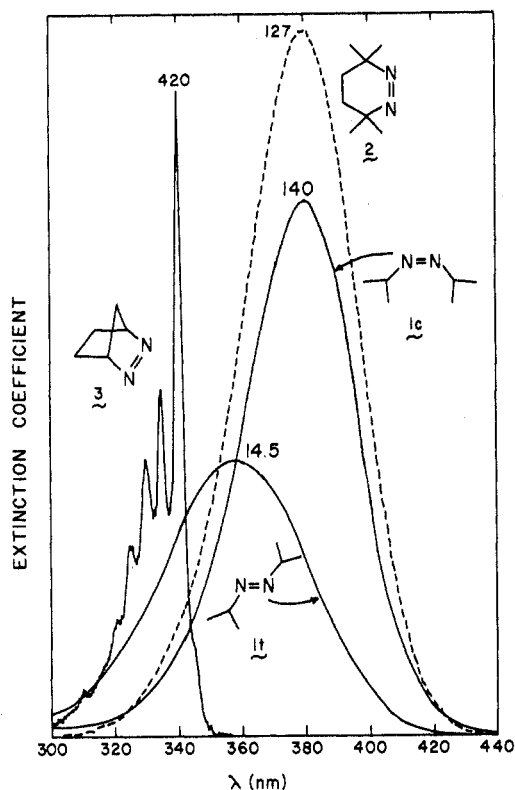
Figure 1. The $n \rightarrow \pi^*$ absorption spectra of selected azo compounds in saturated hydrocarbon solvents. The ordinates are on different scales; for each compound the extinction coeffcient (M^{-1} cm^{-1}) at the wavelength of maximum absorbance is given.

omission of these areas is due more to limitations of space than to our lack of interest in them.

Spectroscopy

Azo compounds show a characteristic $S_0 \rightarrow S_1$ absorption band in the region 320–380 nm. This lowest energy transition is of the $n \rightarrow \pi^*$ type which, according to group theory, is symmetry forbidden in trans compounds but not in cis.[8] As shown in Figure 1, the experimental facts nicely support this conclusion, for the extinction coefficient jumps almost by an order of magnitude in going from *trans*-azoisopropane (1t) to the cis isomer (1c). Incorporation of the azo group into a relatively flexible ring (2) does not change the spectrum from that of the acylic cis compound. However, a distinct change occurs with increasing rigidity of the ring system, namely, the absorption band sharpens and structure appears. This can be seen particularly well when the spectra of 2 and 3 are compared.

In compounds such as 3, the rigid skeleton forces the excited state to have the same geometry as the ground state, so that by the Franck–Condon principle the $0 \rightarrow 0'$ transition is the most strongly allowed, with the $0 \rightarrow 1'$, $0 \rightarrow 2'$, ..., transitions occurring with lesser probabilities. On the other hand, the relatively symmetric absorption band observed in

flexible cyclic and in acyclic azo compounds indicates that the first excited singlet state, S_1, has an equilibrium geometry which is significantly different from that of the ground state. The lack of vibrational fine structure even in the gas phase may mean that several vibrational modes couple into the transition and that at least one of these is associated with a rather shallow potential in the upper state.

In rigid cyclic compounds where the absorption envelope is generally markedly asymmetric and in which vibrational structure is often clearly seen, the $0 \rightarrow 0'$ transition can be assigned with some certainty. Thus the adiabatic singlet energy E_S, which is the energy difference between the $v = 0$ levels of S_0 and S_1, can be determined accurately. However, the shape of the bands and the lack of structure in the acyclic compounds allow only an upper limit to be placed on E_S.

Fluorescence has been observed from rigid cyclic azo compounds,[9-11] and the lifetime of 4 (Table I) is in accord with calculations based upon the integrated absorption coefficient.[10,12] In such cases, the singlet energy assignment can be confirmed by observing the wavelength onset of emission. Oxygen quenches the fluorescence of 4 by enhancing intersystem crossing,[12] while dienes apparently quench *via* an exciplex.[9b] To the frustration of many investigators,[13,14] fluorescence has never been detected in acyclic and flexible cyclic azo compounds.

Although several workers[15,16] have attempted to calculate the location of various electronic states of azo compounds, the most complete calculation was on *cis*- and *trans*-diimide (6).[17] As can be seen in Table I the values are in fair agreement with the results on azoalkanes. Higher excited states of azo compounds have been considered by spectroscopists,[17-19] but for most photochemical studies in solution involving direct excitation, only the $S_0 \rightarrow S_1$ transition is important (see ref 12, 17, 20–23).

Triplet Energies

The most direct method of determining the triplet energy of a compound is by observing the $0' \rightarrow 0$ band of phosphorescence. Indeed, this method has been used successfully on a wide variety of aromatic hydrocarbons and ketones which have since found use as photosensitizers.[24] Unfortunately not all sub-

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Table I
Excited-State Energies of Selected Azo Compounds

Compd	E_S, kcal	E_T, kcal	E_{S-T},[a] kcal	Ref
1t	<68	54	<14	20, 21
3	84.3	60 ± 1	24	12, 22
4	76.0	54.5 ± 1	21.5	20
5	80[b]	55	25	23
6t	90.5[c]	69.5[c]	21.0	17
6c	77.6[c]	47.8[c]	29.8	17

[a] Energy gap from lowest excited singlet to lowest triplet state.
[b] Estimated from the 358-nm absorption band origin in 3,6-bis(p-methoxyphenyl)-1-pyrazoline. [c] Calculated values from ref 17.

stances phosphoresce, and azo compounds fall into this uncooperative category. Since it is of considerable interest, both from a theoretical and practical viewpoint, to know the triplet energy of azo compounds, indirect methods have been attempted.

If lack of intersystem crossing were the whole problem, triplet-sensitized phosphorescence ought to produce emission. Compound 4 and its bridgehead dimethyl analog (7, Table III) appear ideal for such experiments because their triplet state shows relatively little photochemical reactivity in solution. However attempts to observe sensitized phosphorescence of 7 met with failure;[22] moreover, the triplet state of 4 could not be intercepted with appropriate quenchers.[20] Thus it appears that some form of radiationless decay is exceptionally rapid in these cases.

Another approach is to use some characteristic chemical reaction of the azo triplet to monitor the efficiency of energy transfer. Diazabicycloheptene (3) is an ideal case for it has been shown that triplet 3 loses nitrogen with near unit efficiency.[22] Thus the triplet-sensitized quantum yield of nitrogen will equal the product of the probability of intersystem crossing of the donor times the probability that the triplet energy is transferred to 3. The first quantity is a constant for a given donor and is generally known. The second quantity equals $k_t[\text{Azo}]/(k_t[\text{Azo}] + k_d)$, where k_d is the first-order rate of disappearance of the triplet donor in the absence of azo accepter and k_t is the rate constant for triplet energy transfer from the donor to the acceptor. In going from Michler's ketone (E_T = 61.0 kcal)[25] to 2-acetonaphthone (E_T = 59.3 kcal) the quantum yield of nitrogen falls from nearly unity to almost zero.[22] This precipitous drop is associated with the rapidly decreasing value of k_t and locates the triplet of 3 at 60 ± 1 kcal. Further discussion of the fate of excited

(25) For the sake of brevity, energies are expressed in kcal rather than kcal mol^{-1}.

triplet azo compounds will be deferred until chemical processes arising from direct irradiation have been considered.

If the triplet acceptor does not undergo a well-defined chemical reaction, the triplet energy may still be determined if k_t can be measured for a series of donors of differing energy. Since 1,1'-azoisobutane (8) quenched triplet biacetyl at essentially the collision-controlled rate in the gas phase, Collier, et al.,[13] were able to conclude that the upper limit to the triplet energy of 8 was 55 kcal. More recently[21] for benzil, biacetyl, and benzophenone, E_T = 53.7, 54.9, and 68.5 kcal, the following quenching constants by 1t in isooctane solution were obtained: 1.5 × 10^8, 1.4 × 10^9 and 2.8 × 10^9 M^{-1} sec^{-1}. This would place the triplet energy of 1t at 54 ± 1 kcal.

Conceivably one might locate the triplet energy of an unknown substance by measuring the transfer rate from one donor and then noting where the value fell on a plot of transfer rates *vs.* triplet energy of known acceptors.[13] This technique may be inaccurate, however, because it has recently been demonstrated[26] that steric hindrance in azo compounds influences the transfer rate. Thus azo-*n*-butane quenched triplet triphenylene at a rate of 6 × 10^9 M^{-1} sec^{-1} while the tertiary compound, azo-2-methyl-2-propane (9), was 20 times slower.

Cis–Trans Isomerization

The usual synthetic routes to aliphatic acyclic azo compounds produce the trans isomers, and their pyrolysis results in decomposition without cis–trans isomerization.[21] However, irradiation into the n,π* band of azo compounds causes efficient isomerization, as detected by uv and nmr spectroscopy.[27] It was recently discovered[28] that many of the cis isomers undergo remarkably facile thermal decomposition to give nitrogen and free radicals. Thus *cis*-azo-2-methyl-2-propane (9) decomposes with an activation energy of 23 kcal, some 20 kcal less than that of the trans isomer. *cis*-Azoisopropane (1c), on the other hand, is relatively stable,[21] the activation energy in this case being 40 kcal, only about 8 kcal less than that of the trans isomer. In addition to this powerful steric effect, the nature of the incipient radical greatly influences the stability of cis azo compounds. 11c, for example, decomposes at −120°.[29]

11c
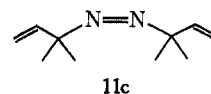
The mechanism by which cis and trans azo compounds are interconverted is not well understood, but any satisfactory model must account for the fact that even bulky azo compounds are readily isomerized at low temperatures in rigid matrices. Thus Φ_{t-c} for azoisopropane (1t) is invariant over the temperature range 20 to −196°,[21] and even *trans*-azocumene (12) is readily converted to the cis isomer in a poly(methyl methacrylate) matrix at −196°.[29]

It is therefore unlikely that there are significant barriers to isomerization. The only excited states of

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azoalkanes which should decrease in energy as rotation is carried out about the $N=N$ bond are the ethylene-like π,π^* states;[30] the n,π^* states retain considerable double bond character and so should offer significant resistance to rotation. Since the $^1\pi,\pi^*$ state lies at very high energy, the isomerization of 1 was initially postulated as proceeding *via* the $^3\pi,\pi^*$ state.[31] Intersystem crossing from $^1n,\pi^*$ to $^3\pi,\pi^*$ could well be rapid[32] and would explain the lack of fluorescence from acyclic azoalkanes.

Despite certain appealing aspects of this explanation, the experimental facts require isomerization with a minimum of nuclear motion. An alternate mechanism involving inversion through one nitrogen
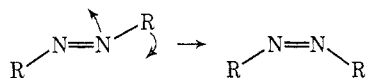
atom better meets this criterion, but little is known about the electronic states through which it might occur. Since it is difficult to conceive experiments which would resolve the problem, theoretical calculations are perhaps the best approach.[15,16,33]

Nitrogen Elimination

Table II lists a number of nitrogen quantum yields for acyclic azo compounds in nonpolar hydrocarbon solvents (see ref 7d, 21, 27, 29, 34–37). It is immediately apparent that the values rarely exceed 0.5, suggesting that some process common to all of them limits the quantum yield. Since the cis isomer of azo-2-methyl-2-propane is known to be unstable,[28] we can accommodate these data by saying that in general acyclic azo compounds are excited to a state which decays with nearly equal probabilities to trans and cis ground states, and that the cis isomer, if thermally unstable, decomposes. Two facts support this scheme: (a) the quantum yield for isomerization of *trans*-azoisopropane in isooctane and water is 0.5 but the cis isomer of azoisopropane is thermally stable;[31] (b) the cis forms of compounds 9, 11, 12, 13, and 16 have been observed by low-temperature uv spectroscopy and have been found to be thermally labile.[28,29]

Many acyclic azo compounds show a remarkable difference in behavior between solution and the gas phase, where decomposition occurs with unit efficiency at sufficiently low pressures. The results of many gas-phase studies are in accord with an excited molecule mechanism; that is, an electronically and/ or vibrationally excited molecule either decomposes or is collisionally deactivated.[38] Larger azoalkanes have more vibrational modes in which to distribute

Table II
Nitrogen Quantum Yields for Photolysis of Acylic Azo Compounds in Nonpolar Solvents

Compd[a]	R in RN=NR	$\Phi_{N_2}{}^b$	$\Phi_{N_2}(\text{sens})^c$	Ref
10	CH_3	0.15	0.009	21, 27, 34
14	C_2H_5	0.023		35
15	$n\text{-}C_3H_7$	0.007		21
1t	$i\text{-}C_3H_7$	0.025	0.001^d	21, 31
9	$t\text{-}C_4H_9$	0.46	0.016	34
12	$C_6H_5CMe_2$	0.36	0.31	29
13	$NCCMe_2$	0.44	0.11	29, 36
11	$H_2C=CHCMe_2$	0.57	0.54	7d, 29
16	$HC\equiv CCMe_2$	0.47	0.27	7d, 29
17	$EtOOCCMe_2$	0.42	0.06	37

a All compounds are trans isomers. *b* Direct irradiation. *c* Benzophenone sensitized. *d* Quantum yield for hydrocarbon formation.

their excitation energy so that their rate of dissociation is smaller. In the case of azoisopropane, increasing pressure of inert gas enhances cis–trans isomerization at the expense of decomposition.[31] Two possible explanations are (a) collision aids intersystem crossing from a dissociative to an isomerizing state, (b) dissociation occurs from an upper vibrational state which is deactivated by collision. Both mechanisms predict virtually no decomposition in solution where the effective pressure is very high; however, the quantum yields for azoisopropane (1) and azoethane (14) do not reach zero in solution and azomethane (10) decomposes considerably more efficiently than these higher homologs. One explanation is as follows. If after excitation to S_1 the azomethane relaxes to ground-state cis and trans sufficiently rapidly that the excess vibrational energy of any intermediate states is not transferred to the solvent, then the vibrationally excited ground-state molecules would have some 80 kcal of vibrational energy. A unimolecular RRKM calculation[6c,39] shows that the cis isomer should have a sufficiently short lifetime, $10^{-12}\text{--}10^{-13}$ sec, for decomposition to compete favorably with vibrational energy transfer to the solvent. For the more complex azo compounds, vibrational transfer should dominate.

Although the decomposition quantum yield for 1 is very small, it is interesting to note that the value is significantly influenced by the nature of the solvent. Thus 1t shows $\Phi_{dec} = 0.00$ in water and $\Phi_{dec} = 0.02$ in isooctane.[31] This effect, which has also been observed for azomethane,[27,40] may be due to an increase in the effective size of the molecule caused by association with polar solvents. The resulting increase in the rate of vibrational relaxation would lower the probability of dissociation.

Phototautomerism

It is generally appreciated that azo compounds bearing α hydrogen atoms tend to tautomerize thermally to the more stable hydrazone.[41,42] An increasing number of reports indicate that this process also occurs photochemically; for example, tautomerism is the major photoreaction of compounds 18–21.

(30) Y. Kaldor and I. Shavitt, *J. Chem. Phys.*, 48, 191 (1968).

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(37) G. S. Hammond and J. R. Fox, *J. Amer. Chem. Soc.*, 86, 4031 (1964).

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(39) Reference 38, p 616.

(40) S. Kodama, *Bull. Chem. Soc. Jap.*, 35, 658 (1962).

(41) C. G. Overberger, *Rec. Chem. Progr.*, 21, 21 (1960).

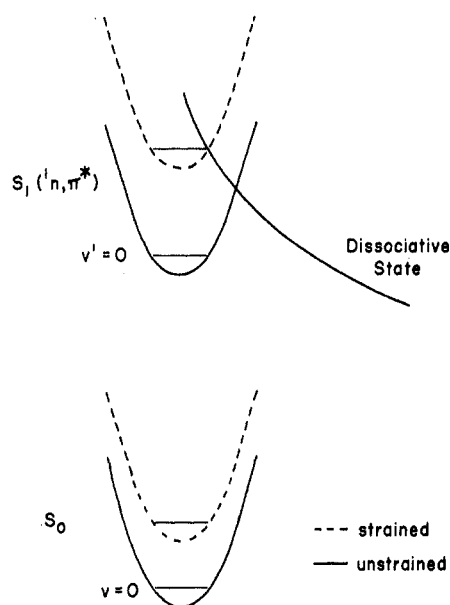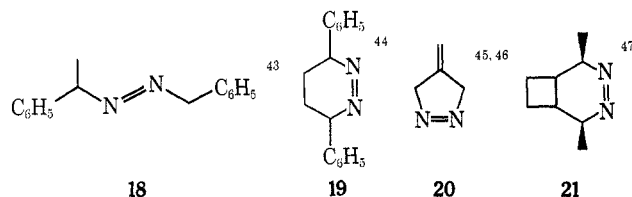(42) B. V. Ioffe and V. S. Stopskij, *Tetrahedron Lett.*, 1333 (1968).

Figure 2. Dissociation of cyclic azo compounds.

Table III
Nitrogen Quantum Yields for Direct Photolysis of Cyclic
Azo Compounds in Nonpolar Solvents

	Compd	Φ_{N_2}	Ref
2		0.002	49
22		0.52	29
23		0.45	29
4		0.022	20
7		0.014	45
3		1.0	50

18   19   20   21

Although phototautomerization may be a primary photoprocess of azo compounds, other mechanisms must be considered. Acyclic cases may first photoisomerize to cis form, whose tautomerization is readily catalyzed by traces of base.[27] Abstraction of an α hydrogen by the free radicals produced may lead to a resonance-stabilized species which reprotonates on nitrogen.[48]

The meager data presently available suggest only that phototautomerism is favored when a conjugated hydrazone can be produced, but further studies are currently under way.[29]

## Photolysis of Cyclic Azo Compounds

Cyclic azo compounds, like their acyclic counterparts, show varying degrees of photolability. Many representatives have been irradiated but, as is shown in Table III, only a few quantum yields have been determined (see ref 20, 29, 45, 49, 50). From the rather scanty data it would appear that five-membered ring compounds have higher decomposition yields than do six-membered rings. The former, including 3, have their n → π^* absorption maxima at considerably shorter wavelengths than do the latter.[11,12,51,52] Furthermore, recent thermochemical

studies[53] show that 3 possesses about 6 kcal more ring strain than 2 and 7. Taken together, this means that the energy gaps between the S_1 state and that of the products of dissociation are significantly greater for five-membered than for six-membered rings. As is shown in Figure 2, it is thus possible that a dissociative surface crosses the S_1 state of the former rather close to $v' = 0$, but only at higher energies for the latter. It is known, for example, that 3 dissociates from S_1 while the predominate fates of the S_1 state of 4 are emission and intersystem crossing.

It would be very interesting if the ring strain associated with compounds such as 24[51] and 25[52] in-

24   25
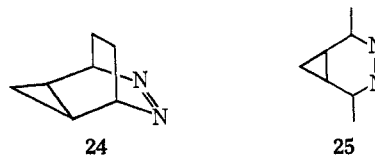
fluenced their photolability. It is possible, however, that in these cases dissociation does not occur from S_1 but that rather, after intersystem crossing, relaxation to S_0^{vib} occurs. Since the compounds are extremely unstable thermally, decomposition may compete with vibrational relaxation. This idea gains some support from the observation that photolysis of each stereoisomer of 25 leads to the same products as does thermolysis.[52]

Because of their flexibility, large-ring azo compounds behave rather like their acyclic counterparts;[54] thus, photochemical cis–trans isomerization has recently been observed in the unsubstituted eight-membered compound.[55]

(43) K. R. Kopecky and T. Gillan, *Can. J. Chem.*, 47, 2371 (1969).
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(45) P. S. Engel, unpublished results.
(46) P. Dowd, *Accounts Chem. Res.*, 5, 242 (1972).
(47) J. A. Berson and E. W. Petrillo, private communication.
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(49) N. A. Porter, Ph.D. Thesis, Harvard University, 1969.
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(52) J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, 92, 1086 (1970).

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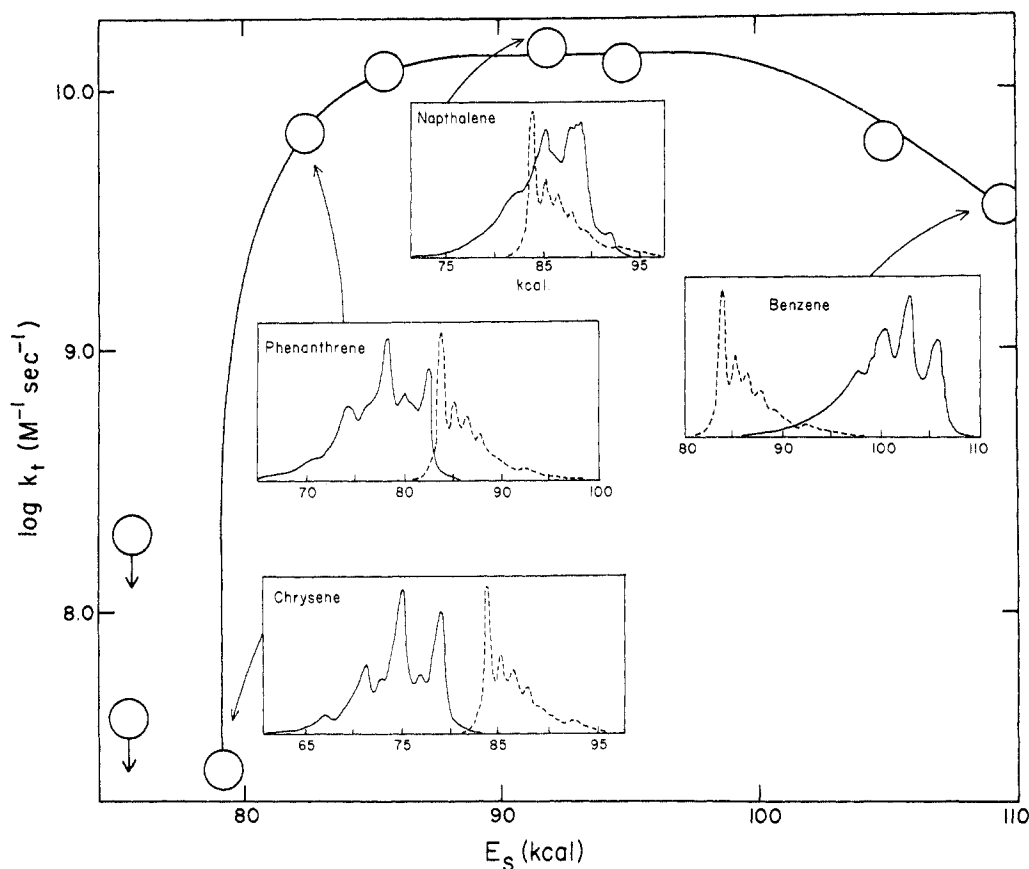(55) C. G. Overberger, M. S. Chi, D. G. Pucci, and J. A. Barry, *Tetrahedron Lett.*, 4565 (1972).

Figure 3. Rate constants for fluorescence quenching, k_t, by 2,3-diazabicyclo[2.2.1]heptene-2 (3) as a function of singlet sensitizer energy. Points with arrows are upper limits.[21,22,54,68] The absorption spectrum of 3 and the fluorescence spectra of selected donors are shown in the insets.

Photosensitization of Azo Compounds

Singlet Transfer. The great popularity of triplet sensitization[56] tends to obscure the fact that excited singlet states are also capable of energy transfer and that in any given case either or both mechanisms may operate.[57] In the earliest study of photosensitization of azo compounds[37] the quantum yield of ethyl azoisobutyrate (17) decomposition with various sensitizers could not be rationalized solely on the basis of triplet energy transfer. Triphenylene, for example, was much more efficient than benzophenone despite its lower triplet energy. Later it was shown[34] that triphenylene and other aromatic hydrocarbons interact with azo compounds through their singlet state. Of the several lines of evidence presented, the key one was that azo compounds are powerful quenchers of hydrocarbon fluorescence. Exchange-energy transfer[58] produces the excited singlet azo compound which either fluoresces[20] or decomposes, depending upon its structure.

The theoretical expression for $k_e(R)$, the rate constant for energy transfer from a donor to an acceptor separated by a distance R, is

$$k_e(R) = (2\pi/\hbar)U_e^2(R)J$$

where $U_e(R)$ represents the interaction energy between the donor (D) and the acceptor (A), and J is

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the overlap integral between the normalized donor emission and acceptor absorption bands. A similar expression holds for triplet transfer.[58] The overlap becomes small either if $E(D)$ is very much greater or very much less than $E(A)$; this results in a low value of k_e and hence k_t, the experimental second-order transfer constant. Figure 3 shows the effect of donor singlet energy on k_t, which becomes diffusion limited even for moderate spectral overlap. The actual sharpness in the fall-off of the quenching constant as a function of sensitizer energy depends strongly on the relative shapes of the absorption and emission bands, and this point should be borne in mind when quenching studies are used to locate energy levels. Even if the overlap integral J has a reasonable value, k_e, and hence k_t, may still be small if $U_e(R)$, which is a sensitive function of R, is small. This may well be the basis for the observed steric hindrance in the rate of quenching of triplet triphenylene by azo compounds.[26]

Triplet Transfer. Although azo compounds are effective energy acceptors from triplet donors,[13,14,20,22,26] the quantum yield of sensitized reaction can be very different from that of direct irradiation. Both **10t** and **1t**, for example, have quantum yields of isomerization ($\phi_{t \to c}$) of about 0.5 in direct irradiation, but the value falls to only 0.11 and 0.07, respectively, under acetophenone triplet sensitization. The quantum yield for sensitized isomerization of **9** is even smaller, as evidenced by the low decomposition quantum yield (*cf.* Table II). Any cis isomer which formed should have decomposed thermally to

nitrogen at the temperature employed (25°). The low efficiency of triplet-sensitized isomerization has been rationalized by saying that triplet transfer populates the $^3n,\pi^*$ (trans) state which encounters sizable barriers in going to a cis configuration.[31]

Triplet-sensitized decomposition of acyclic azo compounds such as **1, 9, 10,** and **17** also proceeds with low quantum yield. On the basis of these data, it was inferred that acyclic azo triplets did not decompose to radicals in solution.[34] However, one of us[29] has recently discovered that triplet-sensitized decomposition of acyclic azo compounds may in fact be as efficient as direct photolysis (e.g., compounds **11** and **12,** Table II). Perhaps the introduction of certain functional groups lowers the barrier to isomerization, and decomposition results from thermolysis of the cis isomer. More likely, the correlation between triplet-sensitized quantum yield and the stability of the incipient radicals is more than coincidence. Referring to the radicals as the zero of energy, a diagram like Figure 2 predicts that the dissociative surface would cross the triplet state at a lower energy when more stable radicals are produced.

Triplet-sensitized decomposition of cyclic azo compounds is well documented (see below). Although quantitative data are scarce, it appears that the quantum yield of sensitized decomposition parallels that of direct irradiation.

Spin Correlation Effects

Conservation of electron spin and energy considerations require that an excited singlet azo compound decompose to a singlet biradical plus ground-state nitrogen while an azo triplet should lead to a triplet biradical. Since triplet biradicals cannot form a bond without prior spin inversion, it is conceivable that some other process, which is faster than spin inversion, might occur prior to bond formation. The singlet radical pair, on the other hand, has no spin restriction to bond formation, so that the competing process should not be observed. Under these conditions decomposition from the singlet and triplet states of an azo compound will lead to different product distributions, a phenomenon which is referred to as a spin correlation effect.

A number of workers[34,37,59] have looked for a spin correlation effect in acyclic azo compounds where the competing process is diffusion of the radical pair from the solvent cage. Slow spin inversion of the triplet radical pair would be expected to decrease the cage effect in the sensitized reaction relative to that in direct irradiation. Although acyclic azo compounds appear to be ideal radical pair precursors, it

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is now known that in none of these studies was a genuine triplet radical pair ever produced, because the sensitizers which were employed transferred singlet instead of triplet energy.[34] Moreover, both direct and sensitized "photodecomposition" proceeded in most cases by thermolysis of unstable cis isomers.

On the other hand, spin correlation effects have been observed in many cyclic azo compounds.[60-66] Despite uncertainties in mechanistic details,[67,68] this argues against complete intersystem crossing in cyclic azo compounds.

Some Remaining Problems

Although the general features of azo photochemistry are recognized, a number of problems still exist. Perhaps the greatest need is for good theoretical calculations and photoelectron spectra in order to map out the energy levels and the shapes of the potential surfaces. Some excellent work on the photoelectron spectroscopy of *trans*-azomethane (**10**) has been reported,[69] but this must be expanded to include representatives of each class.

More specific problems include the "anomalous" behavior of azo compounds with the bicyclo[2.2.2]octane skeleton: the shape of the emission spectrum, the extremely short triplet lifetimes and the photoproducts are all poorly understood. Compound **3** undergoes pressure-induced dissociation from S_1,[12] a pathway which is apparently absent in the photolysis of **4,** but one is not sure which is the rule and which the exception.

In the case of acyclic compounds it is still not clear from which state(s) the photoreactions—decomposition, isomerization, and tautomerism—occur. The triplet-sensitized reactions of acyclic azo compounds are under active investigation. When compared with the data for direct photolysis, these results should allow a better understanding of the mechanisms involved.

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