Involvement of Hydrocarbon Singlet States in Azo Compound Photolysis

Sir:

Several recent studies[1–6] have been concerned with differences between radical pairs in solution having their electron spins coupled or uncoupled ("singlet" or "triplet" radical pairs). This has been done by observing the competition between spin inversion in the radical pair from a triplet precursor, preliminary to recombination of the radicals, and either intramolecular rotation or diffusion from the solvent cage.

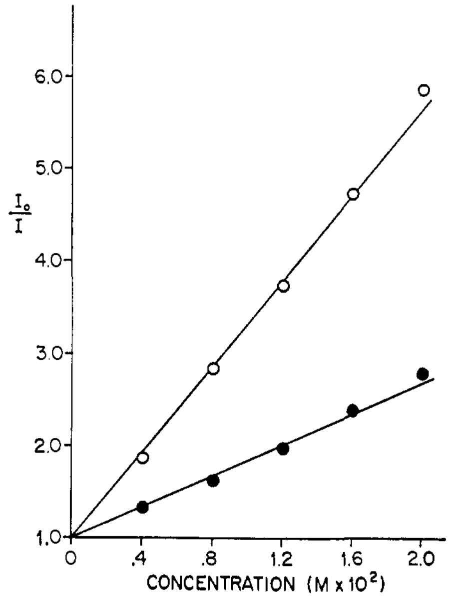
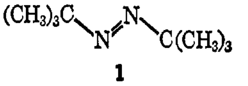


Figure 1. Quenching of sensitizer fluorescence with azo-2-methyl-2-propane: ○, triphenylene; ●, 9,10-diphenylanthracene.

When spin inversion is slow relative to the competing process, radical pairs of different multiplicity may lead to different products. We shall refer to this situation as showing a spin correlation effect. Although this effect has been seen in some cases,[3,5,6] attempts to observe it with an acyclic azo compound as the radical pair precursor have not been successful. In particular, we were unable to detect any difference in the amount of ethane formed in a solvent cage from azomethane by direct or sensitized photolysis. Since we had considered azomethane the compound most likely to show a spin correlation effect, we wondered whether there was a merging of paths in the sensitized and direct photolysis. It is the purpose of this communication to point out such a complication which is relevant to some of the studies of spin correlation effects, namely, involvement of hydrocarbon singlet excited states.



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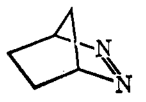

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We have noted that azo-2-methyl-2-propane (**1**) is an efficient quencher of the fluorescence of anthracene, pyrene, phenanthrene, 9,10-diphenylanthracene, and triphenylene. Stern–Volmer plots for the last two cases are shown in Figure 1. Since 0.02 *M* azo compound quenches triphenylene fluorescence to 18% of its initial value, we calculate[7] from the known[8] intersystem-crossing yield that the maximum possible quantum yield for a triphenylene triplet-sensitized azo decomposition under these conditions is 0.17. That the experimental value is about 0.40 implies that at least part of the decomposition is due to triphenylene singlets.

Table I. Photolysis of Azo-2-methyl-2-propane at 20°

Sensitizer (*M*)	E_T, kcal	E_S,[a] kcal	Azo concn, *M*	Solvent	λ, mμ	% $h\nu$[b]	Φ_{N_2}[c]
None			0.022	Hexane	366	100	0.46
Acetophenone (0.11)	73.6	79	0.0204	Hexane	313	0.83	0.012
Benzophenone (0.050)	68.5	76.5[d]	0.0206	Toluene	366	5.8	0.024
Benzophenone (0.050)	68.5	76.5[d]	0.0106	Hexane	313	0.63	0.013
Phenanthrene (0.050)	62.2	82.8	0.0215	Hexane	313	0.46	0.46
Pyrene (0.050)	48.7	77.0	0.018	Hexane	366	3.2	0.18
Anthracene (0.0135)	42.6	76.4	0.0207	Toluene	366	0.94	0.058
Anthracene (0.0138)	42.6	76.4	0.020	Toluene	366	0.89	0.062
Triphenylene (0.050)	66.6	81.2	0.020	Toluene	313	0.14	0.39
Triphenylene (0.050)	66.6	81.2	0.020	Toluene	313	0.14	0.42
Triphenylene (0.050)	66.6	81.2	0.020	Toluene	313	0.14	0.44[e]
Triphenylene (0.050)	66.6	81.2	0.020	Toluene	313	0.14	0.37[e]
Triphenylene (0.050)	66.6	81.2	0.00475	Toluene	313	0.034	0.18
Triphenylene (0.10)	66.6	81.2	0.0104	Toluene	366	3.0	0.019[f]
9,10-Diphenylanthracene (0.0054)	?	73.0	0.0202	Toluene	366	0.55	0.27
9,10-Diphenylanthracene (0.0055)	?	73.0	0.0192	Toluene	366	0.51	0.25

[a] Estimated from the longest wavelength band in the ultraviolet absorption spectrum. [b] Per cent light absorbed directly by the azo compound during sensitized photolysis calculated from the extinction coefficients. [c] Not corrected for simultaneous direct photolysis. [d] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1967, p 48. [e] With 0.1 *M* piperylene added. [f] With 0.050 *M* benzophenone added.

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

(2) S. F. Nelsen and P. D. Bartlett, *ibid.*, **88**, 143 (1966).

(3) S. D. Andrews and A. C. Day, *Chem. Commun.*, 667 (1966).

(4) P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967).

(5) P. Scheiner, *J. Am. Chem. Soc.*, **90**, 988 (1968).

(6) E. Allred and R. Smith, manuscript in preparation.

(7) Assuming that azo compound does not enhance intersystem crossing of triphenylene.

(8) (a) A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965); (b) C. A. Parker and T. A. Joyce, *Trans. Faraday Soc.*, **62**, 2785 (1966).

Included in Table I are four further lines of evidence which point toward the involvement of sensitizer singlets: (1) adding 0.1 M piperylene, an effective quencher of triphenylene triplets but not singlets, does not alter the quantum yield of decomposition of **1**; (2) decreasing the concentration of **1** from 0.02 M to 0.00475 M causes the quantum yield to fall by over 50%, which is consistent with energy transfer from a short-lived excited state; (3) producing triphenylene triplets by benzophenone sensitization results in virtually no azo decomposition; and (4) using 9,10-diphenylanthracene whose fluorescence quantum yield[9] is 1.0 leads to quite efficient decomposition. The high efficiency of hydrocarbon sensitizers is best explained either by singlet energy transfer or by a mechanism wherein azo compound complexes with excited singlet sensitizer and the complex breaks up by partitioning enough energy into the azo moiety to cause decomposition.

Aromatic ketones which undergo extremely rapid intersystem crossing[10] are inefficient sensitizers for decomposition of **1**. We have found that **1** is capable of quenching the benzophenone–benzhydrol photoreduction[11] with a Stern–Volmer slope of 760. Furthermore azomethane is efficiently photoisomerized[12] by benzophenone. These observations prompt us to suggest that triplets of acyclic azo compounds undergo geometric changes rather than decomposition in solution, at least up to the highest energy sensitizer which we have tried.

In light of the ideas that hydrocarbon singlets can be important in sensitized decompositions and that the triplet of **1** does not decompose under our conditions, the data in Table I become understandable. The efficiency of sensitizers, such as anthracene, whose triplet energy lies considerably below estimates of the azo compound triplet[13] can be rationalized by involvement of the singlet instead of nonvertical triplet energy transfer. The lack of a spin correlation effect in azomethane and other cases[1,2,4] can be explained by saying that triplet-sensitized decomposition did not occur.

Our results have led us to reexamine the sensitized decomposition of 2,3-diazabicyclo[2.2.1]heptene-2 (**2**). Indeed this compound was found to be an efficient quencher of the fluorescence of triphenylene and phenanthrene[14] but not of anthracene and pyrene. Addition of 0.1 M piperylene to the triphenylene-sensitized decomposition did not alter the quantum yield. Thus sensitizer singlets apparently can be involved here also, and triphenylene and phenanthrene should not be included in the list of triplet sensitizers. Further investigation with other sensitizers continued to reveal a cutoff in quantum yield as reported,[13] though about 3 kcal lower. Singlet energy transfer is probably absent with the ketonic sensitizers used since 0.1 M piperylene reduces the quantum yield of the benzophenone-sensitized reaction of **2** by a factor of 10. Thus the behavior of **2** constrasts with that of **1** in that its triplet is exceedingly unstable toward decomposition. This may be a consequence of its ring strain and the fact that geometric changes are virtually excluded by its rigid structure. The interpretation here presented explains why a spin correlation effect was not seen in solution photolysis of acyclic azo compounds,[1,2] whereas it was readily observed in the cases of a ketenimine[1] and of rigid cyclic azo compounds.[3,5,6]

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[10] W. M. Moore, G. S. Hammond, and R. P. Foss, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

[11] *Cf.* P. J. Wagner, *ibid.*, **89**, 2820 (1967), and references cited therein.

[12] R. F. Hutton and C. Steel, *ibid.*, **86**, 745 (1964).

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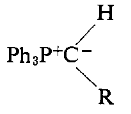
[14] The published[13] value for phenanthrene is incorrect on account of an impurity in our sample and should actually be 0.90. Zone-refined phenanthrene which was used in subsequent work does not absorb significantly at 366 mμ.

An Observation of Facile Transylidation by Nuclear Magnetic Resonance Spectroscopy

Sir:

An unusual and unexplained temperature and solvent dependency of P–C–H coupling in the nmr spectrum of an ylide has recently been reported.[1] Since temperature variation of a P–C–H coupling has no precedent or theoretical basis,[2] this problem has been reexamined, and evidence is presented which defines the source of the apparent effect and provides a rational mechanism for the process.


Ig, R = CO$_2$CH$_3$

[Ph$_3$P$^+$CH$_2$R]X$^-$
IIa, R = CO$_2$Et; X$^-$ = Br
b, R = H; X = Br
c, R = Ph; X = Cl
d, R = CO$_2$Et; X = OH

Low-temperature nmr spectra of ylide Ig[3] (Figure 1) were taken at both 60 and 100 Mc and at each frequency $\Delta\nu = 21$ cps for the methine proton; therefore, this must be a coupling constant (the double doublet observed is the net result of hindered rotation and P–C–H coupling).[1,4] Adding D$_2$O to a solution of the ylide Ig in CDCl$_3$ and shaking for 5 sec result in almost complete exchange of the α proton for deuterium (Figure 1). Addition of 0.5 equiv of IIa (δ 5.42 ppm, $J_{\mathrm{PH}} = 13$ cps) to Ig in CDCl$_3$ results in the appearance of a single extremely broad peak (25°) for the α protons of Ig and IIa (δ 4.00 ppm). Cooling this solution to $-76°$ gives for Ig a double doublet (δ 3.00 ppm, $J = 21$ cps) and a broad peak for IIa (δ 5.45 ppm, $W_{1/2} = 30$ cps). Upon heating, the broad peaks for the two types of protons merge into a single broad peak, but decomposition takes place at 110° before complete coalescence occurs ($\Delta G^{\ddagger}$ for transylidation > 17.5 kcal).

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[2] J. A. Pople, W. G. Schneider, and H. J. Berstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

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