The Sensitized Photolysis of a Bicyclic Azo Compound in Solution

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Abstract: The photosensitized decomposition of 2,3-diazabicyclo[2.2.1]heptene-2 (1) in hydrocarbon solutions at 20° has been investigated. Aromatic hydrocarbons whose singlet excited state lies higher than that of 1 cause singlet sensitized decomposition. Evidence is cited that the singlet of 1 does not cross to the triplet before decomposition. The triplet of 1 is also photolabile and, although it does not emit, its energy has been determined as 59.3-61 kcal using a graded series of sensitizers.

In a preliminary report,[1] we demonstrated that a sharp cutoff in efficiency of the photosensitized decomposition of 2,3-diazabicyclo[2.2.1]heptene-2 (1) could be seen as the sensitizer triplet energy fell below a certain value which we suggested was the triplet energy of 1. The line of reasoning which led to the choice of 1 as substrate was that its rigid structure would preclude nonvertical energy transfer, which was presumably the reason for the confused quantum yields[2] in acyclic systems. It will be shown in this paper that the more fundamental reason why 1 is a suitable substrate is that in sharp contrast with acyclic azo compounds, the triplet state of 1 decomposes very efficiently.

It has recently been demonstrated[3] that acyclic azo compounds can decompose by accepting singlet energy from certain sensitizers, and 1 will be shown to behave similarly.[4] The occurrence of both triplet- and singlet-sensitized decomposition complicates the interpretation of our data but does not substantially alter our estimate of the triplet energy of 1.[5]

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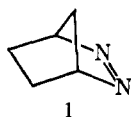
Results and Discussion

In Table I are presented the nitrogen quantum yields for sensitized decomposition of 1. Any given sensitizer triplet state must lie above or below that of 1 and is therefore expected on the basis of our original explanation to be efficient or inefficient with regard to nitrogen formation. However, an observation which appears inconsistent with this interpretation is the fact that 2-acetonaphthone and acenaphthene, which both have a triplet energy of 59.3 kcal, give vastly different quantum yields. Knowing that singlet energy transfer occurs in other azo compounds,[3] we can explain the high quantum yield of the acenaphthene sensitized reaction on the basis of singlet energy transfer to 1. The singlet of acenaphthene lies at 89.1 kcal, more than 5 kcal above that of 1 (see below) and has a lifetime of 46

Table I. Photolysis of 0.02 M 2,3-Diazabicyclo[2.2.1]heptene-2 at 20°

Sensitizer	E_T,[a] kcal mol^{-1}	E_S,[d] kcal mol^{-1}	ϕ_{N_2}[g]
Anthracene	42.6[b]	75.5	<0.00017
Pyrene	48.7	77.0[e]	<0.00029
Chrysene	56.6[b]	79.4	0.027
1-Naphthyl phenyl ketone	57.5	<76[e]	0.0096
2-Acetonaphthone	59.3	~79[e]	0.013
Acenaphthene	59.3[c]	89.1[e]	0.76
Naphthalene	60.9	90.8	1.0[h]
Michler's ketone	61.0	~77[e]	0.77
Phenanthrene	62.2	83.0	0.90
Thioxanthone	65.5	~76[e]	0.96
Triphenylene	66.6	83.5	0.73
Triphenylene	66.6	83.5	0.73[i]
Benzophenone	68.5	76.5[f]	0.97
Benzophenone	68.5	76.5[f]	0.075[i]

[a] Triplet energy from J. Calvert and J. Pitts, "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 298, unless otherwise noted. [b] Reference 15. [c] A. P. Marchetti and D. R. Kearns, J. Am. Chem. Soc., 89, 768 (1967). [d] Singlet energy from footnote a, p 254, unless otherwise noted. [e] Estimated from the uv spectrum. [f] N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., New York, N. Y., 1967, p 48. [g] Values not corrected for light directly absorbed by azo compound; however, in all cases this was small. [h] I. Abram, G. Milne, B. Solomon, and C. Steel, J. Am. Chem. Soc., 91, 1220 (1969). [i] With 0.1 M piperylene added.

nsec.[6] At an azo concentration of 0.02 M, diffusion-controlled energy transfer is readily calculated to be an order of magnitude faster than sensitizer decay so that singlet sensitized decomposition is expected.

The singlet of 2-acetonaphthone, on the other hand, lies below that of 1 and is too short lived[7,8] to be involved in energy transfer. 2-Acetonaphthone gives a low quantum yield, we postulate, simply because its triplet lies below that of 1.

The difference between acenaphthone and 2-acetonaphthone suggests that we divide the sensitizers into two groups. Those with long singlet lifetimes, the aromatic hydrocarbons, can engage in singlet energy transfer in addition to triplet transfer and should not be used for estimating the triplet energy of 1 unless this complication is shown to be absent. The ketones, when con-

(1) P. S. Engel, J. Am. Chem. Soc., 89, 5731 (1967).
(2) J. R. Fox and G. S. Hammond, ibid., 86, 4031 (1964).
(3) P. D. Bartlett and P. S. Engel, ibid., 90, 2960 (1968).
(4) A similar case of singlet energy transfer involving alkyl azides has recently been discovered: see F. D. Lewis and W. H. Saunders, Jr., ibid., 90, 7033 (1968); F. D. Lewis and J. C. Dalton, ibid., 91, 5260 (1969).
(5) The fact that our initial value for the quantum yield of the phenanthrene sensitized reaction was incorrect lowers our estimate by a few kilocalories; see footnote 14 of ref 3.

(6) I. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965.
(7) F. Wilkinson and J. T. Dubois, J. Chem. Phys., 39, 377 (1963).
(8) Also by analogy with benzophenone; see W. Moore, G. Hammond, and R. Foss, J. Am. Chem. Soc., 83, 2789 (1961).

sidered alone, constitute a graded series of triplet sensitizers which locate the triplet of **1** at about 60 kcal.

The effect of piperylene upon some of the quantum yields further delineates the difference between sensitizers with long and short singlet lifetimes. At the bottom of Table I the results for **1** sensitized by triphenylene and by benzophenone are given. It is to be noted that addition of 0.1 *M* piperylene to the aromatic hydrocarbon causes no change, while in the case of the aromatic ketone, the quantum yield is drastically reduced. Since 0.1 *M* piperylene is sufficient to quench nearly all triphenylene triplets,[9,10] the fact that decomposition of **1** continues unabated rules out triphenylene triplet as the sensitizing species under these conditions. Thus the hydrocarbon singlet is left as the most likely species involved in energy transfer. The recent discovery[11] that dienes can quench certain hydrocarbon singlet states does not enter the argument because this type of quenching would lead to a drop in quantum yield, which was not observed. As a double check, though, it was ascertained that 0.25 *M* piperylene does not affect the fluorescence of triphenylene. The unlikely possibility that the short-lived piperylene triplet sensitizes decomposition of **1** is ruled out by the benzophenone experiment where triplet piperylene is certainly produced yet azo decomposition proceeds only slowly. Because of the short lifetime of the benzophenone singlet,[8] we interpret the effect of added piperylene in this case as competing with **1** for benzophenone triplets. Energy transfer from triplet **1** to piperylene cannot be an important process, for at such a high quencher concentration the quantum yield would have been zero.

Further evidence that hydrocarbon sensitizers can engage in singlet energy transfer to **1** is shown in Table II. The efficiency with which **1** quenches sensitizer

Table II. Quenching of Sensitizer Singlets by
2,3-Diazabicyclo[2.2.1]heptene-2

Sensitizer	τ_S, nsec[a]	E_S, kcal[b]	M^c	$k_q{}^d$
Naphthalene	96	90.8	~1100	~1.14 × 10¹⁰ [e]
Phenanthrene	56[f,g]	83.0	390[i]	7.0 × 10⁹
Triphenylene	36.6[g]	83.5	450[i]	1.2 × 10¹⁰
Triphenylene	28.8[h]	83.5	185	6.4 × 10⁹ [h]
Chrysene	44.7[g]	79.4	1.1[i]	2.5 × 10⁷
Pyrene[j]	15.7[k]	77.0	<3.1	<2.0 × 10⁸
Anthracene	4.9	75.5	<0.2[i]	<4.0 × 10⁷

[a] Reference 6. [b] See Table I. [c] Slope of Stern–Volmer plot. [d] $k_q = M/\tau_S$. [e] *Cf.* Table I, footnote *h.* [f] C. Amata, M. Burton, W. Helman, P. Ludwig, and S. Rodemeyer, *J. Chem. Phys.*, **48**, 2374 (1968). [g] We have shown that the decay time of our sensitizer solution with no added quencher is within experimental error of these values. [h] We are indebted to Mr. Carl C. Wamser for determining this value by fluorescence lifetime quenching. [i] Result of determinations at 0.107 *M* **1** only. [j] Solutions not degassed before measurement. [k] J. Birks and I. Munro in "Luminescence of Organic and Inorganic Materials," H. Kallmann and G. Spruch, Ed., John Wiley and Sons, Inc., New York, N. Y., 1962. Corrected for quenching by oxygen[6] and excimer formation. [i] Stern–Volmer plots with five points from 2 × 10⁻³ to 1 × 10⁻² *M* **1** were good straight lines.

(9) Triphenylene transfers energy to isoprene, whose triplet lies above that of piperylene, at a diffusion-controlled rate; see A. Fry, R. Liu, and G. Hammond, *J. Am. Chem. Soc.*, **88**, 4781 (1966).

(10) We observed that triphenylene is an efficient sensitizer for the *cis–trans* isomerization of piperylene.

(11) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 3665 (1966).

fluorescence drops sharply in the region of 82 kcal, and the nitrogen quantum yield shows similar behavior in this region (*cf.* Table I).[12] We suggest that the drop in sensitization efficiency occurs when the hydrocarbon no longer has sufficient energy to promote **1** to its singlet state. The 0–0 singlet state of **1** has been accurately located by Steel[13] at 83.9 kcal in solution. However, as shown by a hot band in the absorption spectrum of **1** at 82.7 kcal (29,120 cm⁻¹), the first vibrationally excited level of the ground state is partially populated at room temperature. It is not presently known whether slightly endothermic transfer into the $v = 0$ level of the ground state or exothermic transfer into the $v = 1$ level obtains.

Coincidentally, those hydrocarbons in Table II with a singlet above that of **1** also have their triplet higher than **1**. Since **1** quenches triphenylene triplets at a rate[14] of 3.4 × 10⁹ M^{-1} sec⁻¹ and since triplet **1** is unstable, hydrocarbon-sensitized decomposition can occur from both states. In this framework, the fact that the first three sensitizers in Table I give low quantum yields is evidence that their triplets and singlets are less energetic than those of **1**.

In agreement with Steel,[13] we see no reason to invoke crossing from singlet **1** to triplet before decomposition. In the gas phase 1000 Torr of oxygen does not lower the rate of photolysis of **1**.[13] Addition of oxygen decreases the quantum yields of fluorescence and decomposition of **2** by the same extent in the gas phase, which is evidence that both processes initiate from the singlet state.
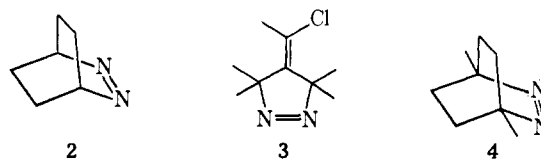
Similarly, addition of piperylene to the photolysis of **3** decreases the fluorescence intensity to the same extent as it lowers the initial rate of photolysis.[16]

From the calculated natural radiative lifetime and the fact that **1** does not fluoresce in solution, Steel[13] has concluded that the lifetime of singlet **1** (τ_S) in solution is <2 × 10⁻¹⁰ sec. Since the efficiency of intersystem crossing is equal to τ_S times the rate of intersystem crossing (k_{ic}), it follows that k_{ic} would have to exceed 5 × 10⁹ sec⁻¹ in order to get quantitative intersystem crossing. In view of the large (24 kcal) value of the singlet–triplet splitting (E_{S-T}) which we find,[17] such a high value of k_{ic} seems unlikely. Saunders[19] has used a similar argument to show that intersystem crossing in an azide with the same value of E_{S-T} ought to be inefficient. The

(12) Fluorescence quenching of acenaphthene was not done because its fluorescence emission is strongly absorbed by **1**.

(13) B. Solomon, T. Thomas, and C. Steel, *J. Am. Chem. Soc.*, **90**, 2249 (1968).

(14) We thank Mr. Carl C. Wamser for determining this value by kinetic spectroscopy.[15]

(15) W. Herkstroeter and G. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966).

(16) S. Andrews and A. Day, *Chem. Commun.*, 477 (1967). This is an example of "exiplex" formation between a fluorescent substance and a diene; see ref 11 and 13.
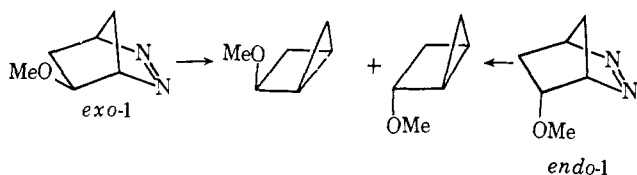
(17) This value, the difference between the 0–0 n–π* absorption band at 341 mμ and the 60-kcal triplet energy, agrees well with the 29.7 kcal calculated for *cis*-diimide.[18]

(18) M. Robin, R. Hart, and N. Kuebler, *J. Am. Chem. Soc.*, **89**, 1564 (1967).

(19) F. D. Lewis and W. H. Saunders, Jr., *ibid.*, **90**, 7031 (1968).

objection might be raised that several factors determine k_{ic}[20] and the validity of estimating its magnitude solely from E_{S-T} is questionable. It is perhaps better to compare the azo group with an aliphatic ketone whose lowest triplet state is also n–π*. Here k_{ic} is estimated[21] to be only about 10^7 sec^{-1} despite the fact that E_{S-T} is considerably smaller than 24 kcal. The conclusion, then, is the same; namely, the value of E_{S-T} in 1 is too large for rapid intersystem crossing to precede decomposition of the singlet. The possibility that intersystem crossing is faster than expected due to the interposition of a ^{3}π–π* state between the lowest ^{3}n–π* and ^{1}n–π* states[21] is rendered unlikely by the high energy calculated for the ^{3}π–π* state.[18]

Perhaps the best evidence against the S–T crossing is the fact that different product ratios have been observed in sensitized *vs.* direct photolysis of several cyclic azo compounds.[22–26] The most relevant study is that of Allred and Smith[23] who compared the direct and triplet sensitized photolysis of *exo*- and *endo*-1. Since the sensi-

tized reaction gave different ratios of *exo*: *endo* product than direct photolysis, both cannot proceed exclusively through the triplet state of the azo compound. The methoxyl group serves only as a stereochemical label and is not expected to alter the electronic properties of the azo group.

We have observed that the vpc peak area ratio of cyclopentene to bicyclo[2.1.0]pentane, the products from decomposition of 1 in solution, is about 1:10 in both direct and sensitized photolysis. This, of course, is not inconsistent with the results from *exo*-1 and *endo*-1 since the presumed hydrogen shift which leads to cyclopentene may not be sensitive to the multiplicity of the initially formed diradical in solution.

Calvert[27] has raised the possibility that triplet 1 may decompose with an activation energy. In this case the triplet energy of about 60 kcal determined using a graded series of sensitizers would be higher than the true 0–0 triplet energy.

A possible means of checking this suggestion would be to measure the rate of energy transfer to 1 from sensitizers whose triplets lie above and below 60 kcal. Although this is most elegantly done by kinetic spectroscopy[15] as earlier suggested,[1] we lacked the necessary equipment and therefore resorted to a simpler method. If the true triplet were below 60 kcal, 1 should quench phosphorescence of sensitizers whose energy is below this value. Using 1 as a quencher of biacetyl phospho-

rescence in hexane at room temperature, we found that the quenching rate constant was below 4×10^4 M^{-1} sec^{-1}, which is strong evidence that the lowest triplet of 1 lies above that of biacetyl ($E_T = 54.9$ kcal).[28] Since energy transfer endothermic by a few kilocalories proceeds at a faster rate than this,[15] no substantial activation energy for decomposition of triplet 1 can exist.[31]

The most common way of detecting an activation energy in a photoreaction is to measure the quantum yield as a function of temperature. An experiment in which photolysis using one of the low-energy group of sensitizers is conducted at a higher temperature is expected to increase the quantum yield whether there is an activation energy or not because the sensitizer becomes effectively more energetic and because energy transfer to ground-state vibrational levels above $v = 0$ becomes more probable. On the other hand, if triplet 1 reaches thermal equilibrium with the surroundings before decomposition, lowering the temperature of the Michler's ketone sensitized reaction may cause a drop in efficiency if the activation energy exists. In fact, the quantum yield was the same at +18° as at −18°.

A great deal about the nature of the triplet electronic states could be learned by examining the phosphorescence of 1. However, triplet emission from a directly irradiated azo compound has never been observed,[27,32] and, of course, this is what prompted us to use an indirect method for determining the triplet energy. This failure to observe emission from azo compounds could be due to inefficient intersystem crossing, rapid nonradiative decay, or a short dissociative lifetime of the triplet state. It must be emphasized that the photochemical and spectroscopic behavior of azo compounds depends very much upon their structure so the explanation need not be the same for all of them.

In fluid solution at room temperature 1 does not sensitize biacetyl phosphorescence so that any or all of the above reasons may obtain in this case. If, however, inefficient intersystem crossing were the key reason that phosphorescence from 1 could not be observed, populating the triplet state by energy transfer may allow emission to be seen. Using benzophenone and *p*-methoxyacetophenone[33] as triplet sensitizers in an alcohol–ether glass at −196,[34] as triplet sensitizers in an alcohol–ether glass at −196°,[34] we failed to see any new emission although sensitizer phosphorescence was strongly quenched. This result is not too surprising since triplet 1 can decompose with unit efficiency (*cf.* Table I). Compound 4, on the other hand, has a

(20) K. Lower and M. El-Sayed, *Chem. Rev.*, **66**, 199 (1966).

(21) M. El-Sayed, *Accounts Chem. Res.*, 1, 8 (1968).

(22) S. Andrews and A. Day, *J. Chem. Soc.*, B, 1271 (1968).

(23) E. L. Allred and R. L. Smith, *J. Am. Chem. Soc.*, 89, 7133 (1967). Photosensitization experiments on this system have been submitted for publication.

(24) P. Scheiner, *J. Am. Chem. Soc.*, 88, 4759 (1966); 90, 988 (1968).

(25) H. Kato, *Chem. Commun.*, 496 (1968).

(26) P. D. Bartlett and N. A. Porter, *J. Am. Chem. Soc.*, 90, 5317 (1968).

(27) J. Calvert, "Nature of the Excited States of Organic Molecules," Symposium at Riverside, Calif., Dec 18–20, 1967; S. Collier, D. Slater, and J. Calvert, *Photochem. Photobiol.*, 7, 737 (1968).

(28) A referee has suggested that the inability of 1 to quench biacetyl phosphorescence may be accounted for if the transition to triplet 1 is Franck–Condon forbidden due to a change in geometry upon excitation. Two arguments against this possibility can be adduced. The first is that 1 is an extremely rigid system in which the only reasonable geometric changes of the azo group, twisting about the N=N bond and straightening of the C—N=N angle,[29] are severely restricted. It is known that the geometry of the ^{1}n–π* state is essentially the same as that of the ground state.[13] Secondly, the sharpness of the cutoff in Table I is inconsistent with the postulated geometric change.[30]

(29) M. S. Gordon and H. Fischer, *J. Am. Chem. Soc.*, 90, 2471 (1968).

(30) E. F. Ullman and W. Henderson, Jr., *ibid.*, 88, 4942 (1966).

(31) The author is grateful to Professor D. R. Herschbach, Dr. E. Charney, and Dr. R. McDiarmid for helpful discussion on this point.

(32) R. E. Rebbert and P. Ausloos, *J. Am. Chem. Soc.*, 87, 1847 (1965).

(33) N. C. Yang, D. S. McClure, S. L. Murov, J. J. Houser, and R. Dusenbery, *ibid.*, 89, 5467 (1967).

(34) V. L. Ermolaev, *Opt. Specty.* (USSR), 6, 417 (1959).

remarkably stable triplet state since its quantum yield for direct or triplet sensitized decomposition is less than 0.03. Benzophenone transfers triplet energy to both **1** and **4**, as shown by quenching of the benzophenone–benzhydrol photoreduction.[35] The slopes of the Stern–Volmer plots were 1330 and 1410, respectively, which indicates nearly diffusion-controlled quenching. Since **4** accepts triplet energy from benzophenone yet decomposes only inefficiently, we hoped that it might be induced to emit following energy transfer. Unfortunately, we were unable to detect sensitized emission under the same conditions as used for **1** although again sensitizer phosphorescence was strongly quenched. Apparently radiationless processes rapidly degrade the triplet state of **4**.

Experimental Section

Materials. Phenanthrene, anthracene, and acenaphthene were zone refined. We should point out that most samples of phenanthrene contain anthracene as an impurity; however, uv and fluorescence spectra showed ours to be pure. Triphenylene (Aldrich) was chromatographed on silica gel with 50% benzene–chloroform. Thioxanthone (Aldrich) was chromatographed on alumina with chloroform and was then recrystallized from ethanol. Benzophenone and 2-acetonaphthone (Eastman White Label) were recrystallized from hexane. Michler's ketone (4,4′-bisdimethylaminobenzophenone, Eastman White Label) was recrystallized from ethanol. The procedure of Fieser[36] was followed for the preparation of 1-naphthyl phenyl ketone. It was treated with activated charcoal and recrystallized three times from ethanol. Eastman White Label chrysene was treated with maleic anhydride[37] to remove anthracene and was then recrystallized from benzene. Eastman White Label pyrene was used without further purification.

Biacetyl was Matheson Coleman and Bell material which was fractionally distilled under nitrogen through a small packed column. It was pure by vpc. Aldrich mixed piperylenes were distilled shortly before use.

2,3-Diazabicyclo[2.2.1]heptene-2 (**1**) was prepared by the procedure of Cohen, Zand, and Steel.[38] 1,4-Dimethyl-2,3-diazabicyclo[2.2.2]octene-2 (**4**) was synthesized with Askani's modification[39] by the procedure used for the normethyl compound (**2**)[40] from 1,4-dimethyl-1,3-cyclohexadiene[41] and ethyl azodicarboxylate. Formation of considerable amounts of ene adduct could not be avoided. The nmr spectrum of the cycloadduct purified by column chromatography was at first quite puzzling since the olefinic protons appeared as a temperature-dependent AB pattern. We now recognize this as a fine example of the effect of two slowly inverting nitrogen atoms.[42] After repeated sublimation, the spectral properties of **4** were found to be very similar to those of **2**. The compound melted at 70.5–71.5°, and the mass spectrum showed a parent peak at mass 138.

Fisher reagent grade toluene was shaken twice with concentrated sulfuric acid, once with sodium carbonate solution, and once with water. It was then dried over magnesium sulfate and distilled from sodium. Benzene was treated similarly except that it was distilled from phosphorus pentoxide. Fisher Spectrograde hexane was used without further purification.

Quantum Yields. Quantum yields were determined on an optical bench consisting of a 1000-W xenon–mercury lamp, a Bausch and Lomb uv monochromator, two collimating lenses, and a thermostated water bath. A portion of the beam was reflected by a quartz plate to a phototube connected to a chart recorder for monitoring the relative light intensity during a run. The bath, which was fitted with quartz windows, contained a holder for two closely spaced cells, the second of which was filled with actinometer solution[43]

Table III. Experimental Conditions for Photolysis of **1**[a]

Sensitizer	Concn, M[b]	Solvent	Wavelength, $m\mu$
Anthracene	0.053	Toluene	366
Pyrene	0.050	Hexane	366
Chrysene	0.0152	Toluene	313
1-Naphthyl phenyl ketone	0.0509	Toluene	366
2-Acetonaphthone	0.10, 0.10	Hexane	366
Acenaphthene	0.0507	Toluene	313
Michler's ketone	0.0505	Toluene	366
Phenanthrene	0.099	Hexane	313
Thioxanthone	0.052, 0.047	Toluene	366
Triphenylene	0.108, 0.068	Toluene	313
Triphenylene	0.051	Toluene	313
Benzophenone	0.100	Hexane	366
Benzophenone	0.0509	Toluene	366

[a] Listed in the same order as in Table I. [b] Where two runs were done, the concentration is listed for each.

Table IV. Sensitizer Fluorescence Quenching in Hexane at Room Temperature

		λ, $m\mu$	
Sensitizer	Concn, M	Excitation	Emission
Triphenylene	1.86×10^{-5}	290	366
Phenanthrene	1.02×10^{-4}	290	368
Chrysene	3.5×10^{-5}	262	382
Anthracene	4.9×10^{-6}	250	400
Pyrene	6.3×10^{-4}	287	390

to determine the amount of light not absorbed. The cells were of 2 × 2 cm square Pyrex tubing and were provided with magnetic stirring.

The solutions to be irradiated were thoroughly degassed, and the cell was removed from the vacuum line and placed in the bath. After photolysis, the cell was reconnected through a series of traps to a Toepler pump and gas buret. The solution was allowed to distill from trap to trap at −78° while the nitrogen was being pumped off. Knowing the light intensity absorbed, the photolysis time, and the amount of nitrogen formed, it was possible to calculate the quantum yield. Further data on the quantum yield runs are given in Table III.

Spectra. Fluorescence quenching was done using round tubes in an Aminco fluorimeter fitted with an adapter to handle them. Solutions were generally thoroughly degassed and sealed before measurement. Because of the unusual window in the absorption spectrum of **1**, careful choice of wavelengths allowed light absorption by quencher to be kept negligible.

Quenching of biacetyl phosphorescence was done similarly on a Hitachi–Perkin-Elmer fluorescence spectrometer.[44] The intensity of biacetyl phosphoresence in tubes containing **1** was found to decrease with time so these solutions were run immediately after making them up. Attempts to observe sensitized phosphorescence from **1** and **4** were also made on this instrument with and without the light beam chopper in place.

Lifetime measurements on phenanthrene, triphenylene, and chrysene were carried out on a TRW nanosecond flash apparatus.[45] For biacetyl, the apparatus was modified by using a 50-kΩ load resistor on the photomultiplier tube. Our value of the decay time was 0.65 msec, in good agreement with that obtained by Bäckstrom and Sandros.[46] Further data on the fluorescence quenching experiments are given in Table IV.

(35) P. J. Wagner, *J. Am. Chem. Soc.*, **89**, 2820 (1967); G. S. Hammond and P. A. Leermakers, *J. Phys. Chem.*, **66**, 1148 (1962).

(36) L. F. Fieser, "Laboratory Experiments in Organic Chemistry," 1st ed, Edwards Bros., Inc., Ann Arbor, Mich., 1933, p 142.

(37) C. S. Marvel and W. S. Anderson, *J. Am. Chem. Soc.*, **76**, 5434 (1954).

(38) S. Cohen, R. Zand, and C. Steel, *ibid.*, **83**, 2895 (1965).

(39) R. Askani, *Ber.*, **98**, 2551 (1965).

(40) S. Cohen and R. Zand, *J. Am. Chem. Soc.*, **84**, 586 (1962).

(41) K. Alder and H. von Brachel, *Ann.*, **608**, 195 (1957).

(42) J. Anderson and J. Lehn, *J. Am. Chem. Soc.*, **89**, 81 (1967).

(43) C. G. Hatchard and C. A. Parker, *Proc. Royal Soc.* (London), A235, 518 (1956).

(44) We are grateful to Dr. Lin Tsai for the use of his spectrofluorimeter.

(45) We thank Dr. Raymond Chen for allowing us to use this instrument.

(46) K. Sandros and H. Bäckstrom, *Acta Chem. Scand.*, **16**, 958 (1962).

Quenching of the benzophenone–benzhydrol photoreduction was done in the conventional manner[35] with a photochemical merry-go-round.

Effect of Water on the Dissociation and Dissociation Constant of Picric Acid in Acetonitrile[1]

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Abstract: Previously (ref 2) picrate buffers have been recommended to calibrate the glass electrode in acetonitrile. The dissociation constant, K^d_{HPi}, of picric acid used for the calculation of pa_H involved calculated pa_H values in other acid–base systems. In the present investigation the degree of dissociation of picric acid was increased by addition of various amounts (up to 1 M) of water, and the value of pK^d_{HPi} was found from the pa_H's measured with the glass electrode and the total picrate ion concentration determined spectrophotometrically. The latter type of determination does not involve any assumption. The pK^d_{HPi} found was equal to 10.9 as compared to the previous value of 11.0 ± 0.1. Formation of neither the ion pair $H_3O^+Pi^- \cdot 3H_2O$ nor of any other picric acid hydrate ion pair has been found. The predominant species of the proton in the presence of 1 M water are $H(H_2O)_3^+$ and $H(H_2O)_4^+$, while a small fraction of the picrate ions is present as $Pi^- \cdot H_2O$. From infrared measurements it could be concluded that picric acid is not hydrated in acetonitrile while $K^f_{Pi^- \cdot H_2O}$ was found equal to 0.3 ± 0.1.

In establishing a pa_H scale in acetonitrile (AN) we calculated the pa_H of mixtures of 2,5-dichlorobenzenesulfonic and methanesulfonic acids with their tetraalkylammonium salts and of o-nitroaniline (I) with its perchlorate, knowing pK^d_{HA} or $pK^f_{IH^+}$, and thus found at 25° $E°$ of the glass electrode $vs.$ 0.01 M AgNO₃–Ag in AN.[2] The data covered a pa_H range between 4.0 and 8.0. A plot of the pa_H $vs.$ potential had the theoretical slope. The plot was then extrapolated to potentials of the glass electrode measured in mixtures of picric acid with its tetrabutylammonium salt, and it was concluded that the pK^d_{HPi} of the picric acid was 11.0 ± 0.1. The picric acid–picrate mixtures in AN have the same buffer capacity as corresponding mixtures in water and therefore are ideally suitable for the calibration of the glass electrode in AN. Since the extrapolation was made from a pa_H range between 4 and 8 to values of the order of 11 and since the pa_H values of the mixtures used in the calibration were calculated, involving various assumptions, it appeared desirable to check in some independent way the value of 11.0 for the dissociation constant of picric acid, K^d_{HPi}. Picric acid is such a weak acid that the measurements of pa_H or picrate ion concentration in solutions of the acid in AN cannot provide reliable values of pK^d_{HPi} because of the almost unavoidable presence of traces (2 × 10⁻⁶–2 × 10⁻⁵ M) of ammonia and possibly weaker basic impurities in the solvent.

The over-all dissociation constant of picric acid in AN is increased by addition of a base. In the present study we have used the weak base water to increase the dissociation of picric acid in AN, and we have measured a_{H^+} with the glass electrode and the total picrate ion concentration spectrophotometrically.

Previously, it was found that the proton is hydrated by one to four molecules of water,[3] the formation constants of $H(H_2O)_x^+$ being defined as

$$K^f_{H(H_2O)_x^+} = [H(H_2O)_x^+]/[H^+]_s[H_2O]^x \quad (1)$$

the subscript s referring to the solvated species in the water-free solvent. The picrate ion is only slightly hydrated in AN upon addition of water. From solubility data of potassium picrate in presence of water, we have concluded that picrate can form at best a monohydrate[4]

$$Pi_s^- + H_2O \rightleftharpoons Pi_w^- \qquad K^f_{Pi_w^-} = [Pi_w^-]/[Pi_s^-][H_2O] \quad (2)$$
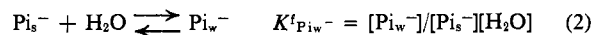
$K^f_{Pi_w^-}$ being of the order of 0.5. In the present paper the hydration constants of the picrate ion and of picric acid
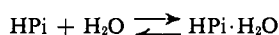
$$HPi + H_2O \rightleftharpoons HPi \cdot H_2O$$

$$K^f_{HPi \cdot H_2O} = [HPi \cdot H_2O]/[HPi][H_2O] \quad (3)$$

were estimated from the first overtone of the –OH stretch of free water at 1410 mμ in mixtures of the acid or salt and water. We regarded the hydrogen bonded H···OH stretching band not to overlap with that of the free –OH band. A similar assumption was made by Coetzee[5] in his study of hydration of some amines.

(1) This work was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, under Grant AF-AFOSR-1223-67.

(2) I. M. Kolthoff and M. K. Chantooni, Jr., *J. Am. Chem. Soc.*, **87**, 4428 (1965). $E°$ is the potential at unit hydrogen ion activity.

(3) I. M. Kolthoff and M. K. Chantooni, Jr., *ibid.*, **90**, 3320 (1968).

(4) M. K. Chantooni, Jr., and I. M. Kolthoff, *ibid.*, **89**, 1582 (1967).