However, quantum yields drop to less than 0.1 in EGW, MCH-SiO_2, and 85% H_3PO_4, highly polar solvents in which only long-lived component phosphorescence is observed at 77°K (Table II). This long-lived emission, as in acetophenone and certain substituted aryl ketones, must be predominantly $\pi^* \rightarrow \pi$ in character, indicating that the lowest excited state is predominantly the *relatively* (see, however, ref 5 and 14) unreactive $^3(\pi,\pi^*)$. Further increases in triplet lifetime, from 0.075 sec in MCH-SiO_2 to 0.8 sec in 85% H_3PO_4 (at 77°K) are caused by decreasing perturbations from n,π^* states,[4] and we observe correspondingly that butyrophenone in phosphoric acid is essentially photostable (Table III) at room temperature under normal irradiation conditions.

The difference between ϕ_B and ϕ_A, or alternatively, the quantity $-(\Delta$acetophenone/Δbutyrophenone) is a measure of the extent the Norrish type II elimination, and is smallest in solvents capable of donating radical hydrogen. Irradiation of solutions of butyrophenone in ethanol shows a marked decrease in ϕ_B when 0.5% concentrated HCl is added and an even greater decrease when 1 and 5% concentrated HCl is added. These results are fully expected in light of the increase in lifetime of the long-lived triplet state in butyrophenone upon the addition of small amounts of hydrogen ion. (This effect was also observed by Lamola in the case of acetophenone.[4]) However, the *relative* extent of the Norrish type II elimination shows little change with increasing acidity, the decrease in ϕ_B being nearly proportional to the decrease in ϕ_A. Unexpectedly the over-all reaction goes quite efficiently in glacial acetic acid, in 50% EGW–acetic acid, and in 1:1:2 ethanol–ethylene glycol–acetic acid solution; glacial acetic acid, like *t*-butyl alcohol, apparently provides optimal reaction conditions for reasons that are not readily explained. The quantity $-(\Delta$ acetophenone/ Δbutyrophenone) is relatively high in all three cases, but lowest when ethanol is present, since ethanol, an excellent donor of radical hydrogen, tends to promote photoreduction.

Acknowledgments. We are deeply indebted to Drs. T. R. Evans, A. A. Lamola, and N. C. Yang for stimulating discussion about this work, and to the latter two men, in addition, for preprints of their related work. Financial support was provided by the Petroleum Research Fund of the American Chemical Society and by Grant GM 13592 from the National Institutes of Health.

Primary Processes in the Photochemistry of Bicyclic Azo Compounds[1,2]

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Abstract: The primary processes in the photochemistry of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) and of 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) have been investigated. In the gas phase the quantum yields of decomposition are 0.85 ± 0.1 and 0.50 ± 0.1, respectively. In isooctane solution the yields are 1.0 ± 0.1 (DBH) and 0.08 ± 0.01 (DBO). Both molecules fluoresce in the gas phase with yields of 0.014 ± 0.0015 (DBH) and 0.56 ± 0.10 (DBO). In solution, however, DBH does not fluoresce. This is consistent with the existence of a pressure-induced dissociation, DBH* + X → products + X, which can also be observed in the gas phase when "inert" gases X are added to the system. In the case of DBO there is still strong emission in solutions such as isooctane and water, $\phi = 0.20 \pm 0.02$ and 0.22 ± 0.02, respectively, and "inert" gases are ineffective quenchers in the gas phase. However, the emission can be quenched both in the gas phase and in solution by oxygen, dienes, and olefins, DBO* + Q → DBO + Q. In the direct photolysis of both DBO and DBH there is no evidence for the intermediacy of a triplet state, although molecules in their triplet states, which have been produced by energy transfer, do dissociate. The emission lifetimes of DBO* both in the gas phase and in isooctane solution have been measured, yielding $\tau = 1.0 \times 10^{-6}$ and 0.33×10^{-6} sec, respectively.

Although the production of radicals by the photochemical decomposition of aliphatic azo compounds has been widely studied,[4–6] relatively little is known of the details of the primary processes involved in the photochemistry of azo compounds. This is in sharp contrast to the extensive investigations into the detailed photochemistry of ketones, both cyclic and acyclic,[7,8] to which azo compounds have several strong analogies. During recent studies into the production of vibrationally excited molecules by the photodecomposition of cyclic azo compounds,[9–11] it became of

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[1] Research sponsored by Directorate of Chemical Sciences, Air Force Office of Scientific Research Grant 583-66.

[2] A preliminary report on this work was given at Division of Physical Chemistry, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966.

[3] Author to whom inquiries should be addressed.

[4] H. Zollinger, "Azo and Diazo Chemistry," Interscience Publishers, Inc., New York, N. Y., 1961, p 279 ff.

[5] D. E. Hoare and G. S. Pearson, *Advan. Photochem.*, 3, 83 (1964).

[6] E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., New York, N. Y., 1954, p 376.

[7] R. Srinivasan, *Advan. Photochem.*, 1, 83 (1963).

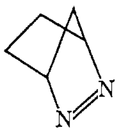
[8] W. A. Noyes, Jr., J. E. Jolley, and G. B. Porter, *Chem. Rev.*, **56**, 49 (1956).

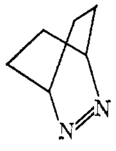
[9] C. Steel, *J. Phys. Chem.*, **67**, 1779 (1963).

[10] T. F. Thomas and C. Steel, *J. Am. Chem. Soc.*, **87**, 5290 (1965).

[11] T. F. Thomas, C. I. Sutin, and C. Steel, *ibid.*, **89**, 5107 (1967).

interest and importance to us to learn something about the processes which precede or compete with dissociation. In this paper we report on our studies on 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) and on 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO).


DBH


DBO

Experimental Section

Materials. The preparation of DBH, DBO, and azoisopropane (AIP) has been described previously.[12] Since the AIP prepared in this manner was found to contain a small amount of acetone (~2%), it was further purified by preparative gas chromatography. The hydrocarbons *n*-pentane, 2,2,4-trimethylpentane (isooctane), piperylene, 1,3-cyclohexadiene, benzene, cyclopentene, cyclohexene, 1-hexene, 1-octene, and *cis*-2-butene were all best grade commercial compounds. The cyclopentadiene was prepared by distillation from dicyclopentadiene and used within half an hour.

The oxygen was Matheson Extra Dry grade 99.6% and the nitrogen Matheson Prepurified grade 99.997%.

Samples were carefully degassed on a mercury-free greaseless high-vacuum line before filling the fluorescence, absorption, and reaction cells. Gas pressures below 1 atm were read on a quartz spiral manometer (Texas Instrument); those above 1 atm were read on a metal Bourdon gauge (Matheson).

Emission and Excitation Spectra. Fluorescence spectra were run on a spectrofluorimeter (Zeiss Model ZFM4C) equipped with quartz prisms, whose dispersion varied from 8.5 mμ/mm at 325 mμ to 28 mμ/mm at 450 mμ, and a 500-W xenon arc light source. Both emission and excitation spectra were corrected for the sensitivity of the fluorimeter as a function of wavelength and for scattering where necessary, after the manner of Parker and Rees[13] and of Melhuish.[14] Rhodamine B was used as a fluorescent screen of constant quantum efficiency.[15] Thus the emission spectra are in terms of an intensity which is porportional to the number of quanta emitted per unit frequency interval, and the excitation spectra are in terms of an intensity which is proportional to the emission signal per incident quantum. Therefore in the latter case if the emission quantum yield is independent of the exciting frequency and the absorbance of the sample is less than 0.05, the excitation spectrum should correspond to the absorption spectrum. Since the recorder and prism drives were directly coupled, the original spectra were not linear in frequency and the spectra shown in Figures 1 and 3 have been replotted from original data. In the case of the gas phase spectra, especially of DBH where the emission yield is so low, the noise level was quite high and the size of the points reflects this uncertainty. Fluorescence quantum yields were determined by comparison with biacetyl for the gas phase and with quinine sulfate (0.8 mg/100 cc) in 0.1 *N* H_2SO_4 for the solution phase. The biacetyl yield was taken to be 0.145 in the limit of zero pressure for λ_{exc} = 405 mμ,[16,17] and for quinine sulfate the yield was taken as 0.55 independent of exciting wavelength.[13,14] In one case, gaseous DBH, the use of either standard gave the same quantum yield within experimental error.

Spectra and Extinction Coefficients. Ultraviolet absorption spectra were run on a Cary 14 spectrophotometer. Most spectra were run at 24°, but in the case of DBO in the gas phase the cell compartment was thermostated at 62° in order to get sufficient vapor pressure to obtain the spectrum. Low temperature solution spectra were run using a cell with insulated dewar flask construction. The extinction coefficients of DBH and DBO in solution and of DBH in the gas phase could be determined from direct absorbance readings at room temperature. However, because of the low vapor pressure, the absorbance of DBO in the gas phase at 22° was too small for direct measurement. We therefore determined the vapor pressure of DBO as a function of temperature using a specially designed Bourdon gauge. Our results were fitted by the equation $\log P$ (torr) = 9.51 − 14,100/2.303*RT*. We then measured the absorbance as a function of temperature for various samples at their saturation vapor pressures and hence obtained the extinction coefficients.

Infrared spectra were run on a Perkin-Elmer 621 grating spectrophotometer, and nmr spectra on a Varian A-60A.

Photochemical Apparatus and Actinometry. Photolyses were effected by a high-pressure mercury arc (PEK 100 W) and by a xenon arc (PEK 75 W) in conjunction with a grating monochromator (Bausch and Lomb) and a quartz lens system which produced a collimated beam. All photolyses were carried out at 24 ± 2°. Quantum yields were determined using ferrioxalate actinometry to determine the incident light intensity.[18] The fraction, *F*, of the total incident light absorbed by the sample is given by

$$F = \sum I_{\lambda_i}[1 - 10^{-A_{\lambda_i}}]/\sum I_{\lambda_i}$$

where A_{λ_i} is the absorbance of the sample at wavelength λ_i as determined using the Cary spectrophotometer and I_{λ_i} is the intensity of light of wavelength λ_i emerging from the monochromator, that is, the intensity emitted by the source suitably corrected by the triangular "slit function."

For DBO photolysis in isooctane solution the degassed solutions were contained in a 1-cm optical cell and the extent of photolysis measured by following the change in absorbance. For DBO in the gas phase the reaction vessel was a 1-cm fluorescence cell so that the emission intensity could be followed as a function of photolysis time. Because of the low vapor pressure, 0.1 torr at 22°, the A_λ's were too small to measure directly at room temperature and the values had to be estimated from the corresponding extinction coefficients, ϵ_λ, and the known pressure. The uncertainties associated with the quantum yields of decomposition and of fluorescence of gaseous DBO, Tables I and II, largely reflect the uncertainty associated with the values of ϵ_λ.

For DBH in the gas phase, a 10-cm optical cell was employed, the progress of the photolysis being monitored by the change in absorbance. The uncertainties in the decomposition and fluorescence yields for gaseous DBH mainly reflect the uncertainty in the percentage of absorbed light. This is largely due to the low over-all absorbance and the sharply structured spectrum. For example, at a pressure of DBH = 0.803 torr, the calculated percentage of absorbed light is 7.85%. However, a change in the absorbance readings of −0.005 decreases the percentage of light absorbed to 6.0% resulting in a 30% change in the quantum yield. Because of the large possible error, the quantum yield of gaseous DBH was also measured by a second more direct method. Two cadmium sulfide photocells were incorporated in the arms of a Wheatstone bridge; one photocell monitored the incident light intensity and one the intensity of the beam after passage through the cell. The change in transmittance due to the presence of DBH in the photolysis cell was determined by balancing the bridge with DBH in the cell and then observing the off-balance signal due to the increased transmittance when DBH was frozen into the side arm of the cell. The off-balance signal was then calibrated by using filters of accurately known absorbance.

Emission Lifetime Measurements. The degassed samples, contained in a 1-cm path-length rectangular fluorescence cell, were irradiated by light from a 6.5-W-sec air-flash (Edgerton, Germeshausen and Grier No. 549) which decayed from its peak intensity to 1/*e* times that value in 0.30 ± 0.04 × 10^{-6} sec. The exciting and the emitted light were monitored by a photomultiplier–oscilloscope circuit, care being taken that the time constant of response of the detection circuitry was at least tenfold smaller than the time constants of the events being measured. This was done by also monitoring the flash light with a fast response photodiode which had a response time of 1.5 × 10^{-8} sec (Edgerton, Germeshausen and Grier SD100). The light from the flash lamp, after being passed through a Corning 7-39 filter, was collimated by a series of baffles before being incident on the sample cell. The light emitted by the sample was viewed at right angles to the exciting beam, provision being made so that filters could be placed in the path of the former before it struck the 1P-28 photomultiplier. These filters included a

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[12] R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954); S. G. Cohen and R. Zand, *J. Am. Chem. Soc.*, **84**, 586 (1962).

[13] C. A. Parker and W. T. Rees, *Analyst*, **85**, 587 (1960).

[14] W. G. Melhuish, *J. Opt. Soc. Am.*, **52**, 1256 (1962).

[15] G. Weber and F. W. J. Teale, *Trans. Faraday Soc.*, **53**, 646 (1956).

[16] G. Ishikawa and W. A. Noyes, Jr., *J. Chem. Phys.*, **37**, 583 (1962).

[17] G. M. Almy and P. R. Gillette, *ibid.*, **11**, 188 (1943).

[18] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc.* (London), **A235**, 518 (1956).

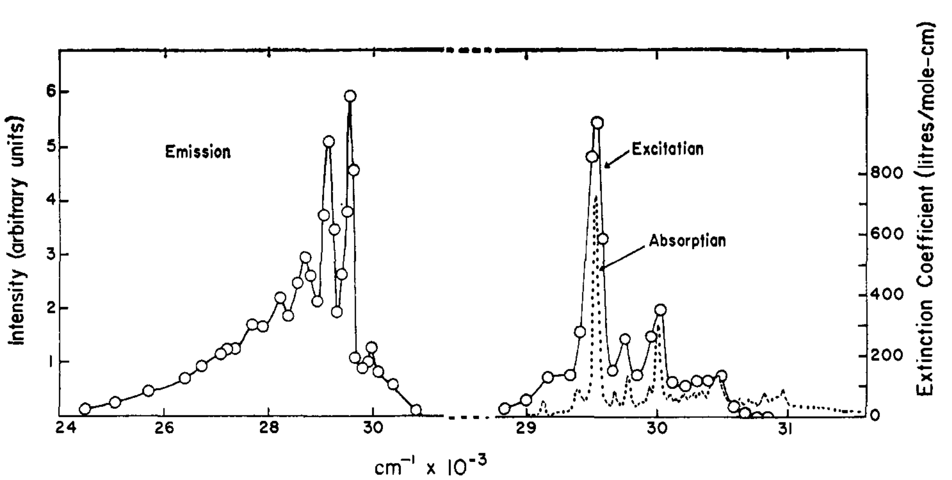

Figure 1. Absorption, excitation, and emission spectra of DBH. The absorption curve, which is referred to the right-hand ordinate, was obtained using a spectral band width of 14 cm^{-1}, DBH in the gas phase at 0.83 torr, and 22°. The excitation and emission spectra were obtained under similar conditions. For the former ν_{em} = 28,570 cm^{-1}, $\Delta\nu_{em}$ = 1700 cm^{-1}, and $\Delta\nu_{exc}$ = 100 cm^{-1}. For the latter ν_{exc} = 30,030 cm^{-1}, $\Delta\nu_{exc}$ = 800 cm^{-1}, and $\Delta\nu_{em}$ = 200 cm^{-1}, where $\Delta\nu_{em}$ and $\Delta\nu_{exc}$ are the spectral band widths of the emission and excitation monochromators. Both the excitation and emission spectra are corrected after the method of Parker and Rees.[13]

Corning 3-73 which passes wavelengths greater than 410 mμ and interference filters with peak transmittances at 402, 436, 503, and 602 mμ and band passes of about 10 mμ. The concentration of DBO in isooctane was 3.48 × 10^{-3} *M*, while the pressure of DBO was 1.16 × 10^{-1} torr in the gas-phase experiments. For solution the ratio of scattered to emitted light was so low that under the conditions in which DBO emission was observed we could see no signal when the sample cell was replaced by one containing only the solvent isooctane. Because of the lower azo concentration in the gas phase and the consequent low level of light emitted, the contribution of scatter to the total signal was appreciable, in this case approximately 25%, and had to be allowed for. All experiments were carried out at 24 ± 2°.

Results and Discussion

The primary processes involved in the photochemistry of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) and of 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) can be represented by the mechanism shown in eq 1-5, where Azo* represents the (n,π*) singlet excited state of the azo compounds.

$$\text{Azo} + h\nu_a \xrightarrow{I_{abs}} \text{Azo*} \qquad (1)$$

$$\text{Azo*} \xrightarrow{k_f} \text{Azo} + h\nu_f \quad \text{(fluorescence)} \qquad (2)$$

$$\text{Azo*} \xrightarrow{k_d} N_2 + \text{hydrocarbons} \quad \text{(dissociation)} \qquad (3)$$

$$\text{Azo*} + X \xrightarrow{k_{q,4}} \text{Azo} + X \quad \text{(``physical'' quenching)} \qquad (4)$$

$$\text{Azo*} + X \xrightarrow{k_{q,5}} N_2 + \text{hydrocarbons}$$
$$\text{(quenching by collision-induced dissociation)} \qquad (5)$$

Absorption, Excitation, and Emission Spectra. Although n–π* fluorescence, including fluorescence of nitrogen-containing compounds, is known,[19] aliphatic azo compounds have not been previously observed to fluoresce.[20,21] This is generally believed to be due to the fact that either azo compounds have short photodissociative lifetimes relative to their natural radiative lifetimes or other radiationless processes such as intersystem crossing and internal conversion can favorably compete. We have, however, observed emission from both DBH* and DBO*.

DBH. The emission spectrum of gaseous DBH shown in Figure 1 shows a reasonably good mirror-image relationship to the sharply structured n–π* absorption spectrum, while the excitation spectrum closely parallels the latter. The coincidence of the emission, absorption, and excitation maxima at 29,540 ± 10 cm^{-1} indicates that this corresponds to the (0′–0″) transition. It is clear that a single progression dominates in both the absorption and the fluorescence spectra. The main absorption peaks are at 29,530, 30,010, 30,480, and 30,970 cm^{-1}, while the excitation maxima are at 29,540, 30,030, and 30,490 cm^{-1}. The excitation band which should have occurred at 30,970 cm^{-1} was too weak to see on our apparatus. Since there is a relatively large uncertainty, approximately ±50 cm^{-1}, in our fluorescence measurements, the excellent agreement is partly fortuitous. Emission maxima occurred at 29,550, 29,140, 28,680, and 28,240 cm^{-1}. Although the relatively low resolution and weak signal from the fluorimeter precludes great accuracy, separation of the two largest emission peaks is 410 ± 20 cm^{-1}, a value close to the frequency of a strong peak at 403 ± 2 cm^{-1} seen in the infrared absorption spectrum (KBr disk). Transitions in this region are usually assigned to ring deformation modes.[22] The strength of the (0′–0″) band relative to the other bands indicates that the electronic transition is not symmetry forbidden and that vibronic interaction is not effective in aiding the transition. Indeed, although X-ray analysis has not been carried out for DBH, it should belong to the C_s point group so that an n–Π* transition is not symmetry forbidden. In terms of Platt's local symmetry requirements,[23] the transition is allowed, though not strongly, by virtue of the partial s character of the n orbitals.

The absorption at 29,120 cm^{-1} is believed to be due

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[19] J. Heicklen, *J. Am. Chem. Soc.*, **81**, 3863 (1959); S. R. LaPaglia and B. C. Roquitte, *Can. J. Chem.*, **45**, 287 (1963); B. J. Cohen, H. Baba, and L. Goodman, *J. Chem. Phys.*, **43**, 2902 (1965); L. M. Logan and I. G. Ross, *ibid.*, **43**, 2903 (1965).

[20] C. Steel and T. F. Thomas, *Chem. Commun.*, 900 (1966).

[21] H. Cerfontain and K. O. Kutschke, *Can. J. Chem.*, **36**, 344 (1958).

[22] A. R. Katritsky and A. P. Ambler, "Physical Methods in Heterocyclic Chemistry," Vol. II, Academic Press Inc., New York, N. Y., 1963, p 173.

[23] J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

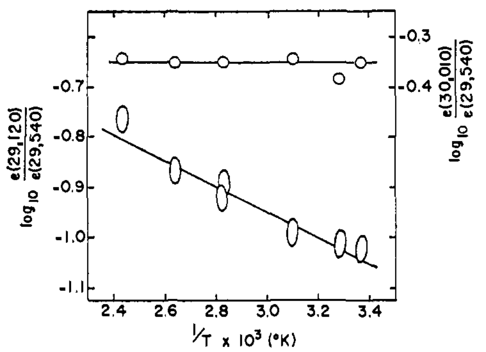

Figure 2. Relative absorption intensities of DBH as a function of temperature. The ellipses refer to the left-hand ordinate where ϵ(29,120) is the extinction at the 29,120-cm^{-1} maximum and ϵ(29,530) is the extinction at the 29,530-cm^{-1} maximum. These absorptions are believed to be due to the transitions (0′ ← 1′′) and (0′ ← 0′′), respectively. Similarly the circles, which refer to the right-hand ordinate, give the ratio of the intensities of the transitions (1′ ← 0′′) and (0′ ← 0′′).

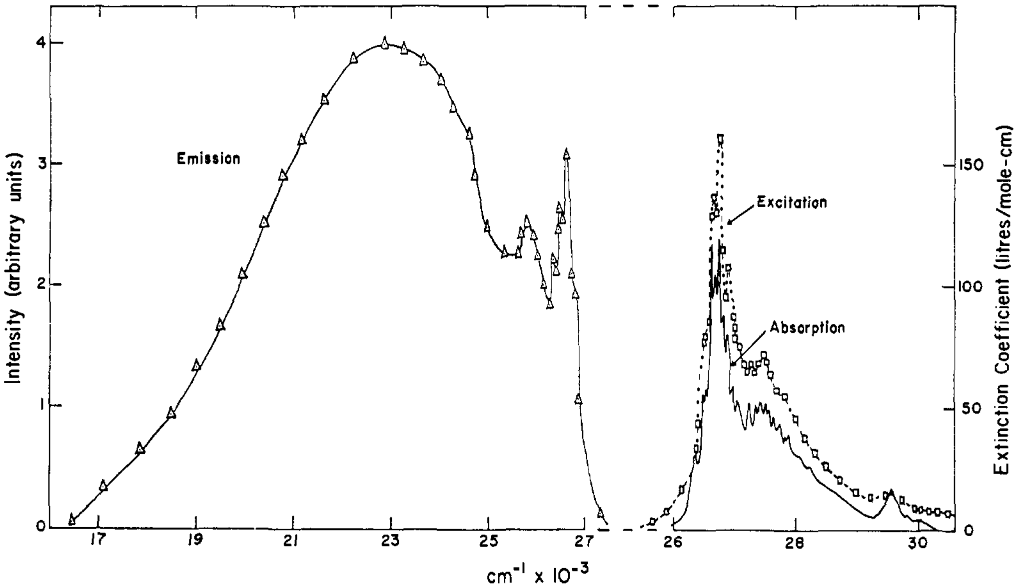

Figure 3. Absorption, excitation, and emission spectra of DBO. The absorption curve, which is referred to the right-hand ordinate, was obtained using a spectral band width of 25 cm^{-1}, DBO at its saturation vapor pressure at 62° (~1.95 torr). The excitation and emission spectra were obtained at 75°, DBO pressure approximately 4.4 torr. For excitation, ν_{em} = 22,200 cm^{-1}, $\Delta\nu_{em}$ = 3000 cm^{-1}, and $\Delta\nu_{exc}$ = 30 cm^{-1}. For emission, ν_{exc} = 26,700 cm^{-1}, $\Delta\nu_{exc}$ = 1800 cm^{-1}, and $\Delta\nu_{em}$ = 100 cm^{-1}, where $\Delta\nu_{em}$ and $\Delta\nu_{exc}$ are the spectral band widths of the emission and excitation monochromators. Both excitation and emission spectra are corrected after the method of Parker and Rees.[13] There was also a weak fine structure to the emission in the region 26,000–25,000 cm^{-1} which has not been represented because it was just above our noise level.

to a "hot" band, that is, to the (0′ ← 1′′) transition. The spacing between this band and the (0′ ← 0′′) band is 410 cm^{-1}, significantly different from the spacing in the main absorption progression, 480 cm^{-1}, but almost exactly equal to the frequency of the direct infrared transition (1′ ← 0′′). Also the intensity of the 29,120-cm^{-1} band is temperature sensitive. In Figure 2 we plot log ϵ(29,120)/ϵ(29,530) against $1/T$ where ϵ(29,120) is the extinction coefficient at the 29,120-cm^{-1} maximum. The plot shows that the energy difference is ΔE_{vib} = 390 ± 70 cm^{-1}, which is close to the energy difference between the v'' = 0 and v'' = 1 states. In contrast the ratio ϵ(29,530)/ϵ(30,010) shows no temperature dependence since both of these absorptions originate from v'' = 0.

Solution phase studies using 5:1 2-methylbutane: methylcyclopentane also indicate the presence of a "hot" band. Although the various vibrational bands are not so well resolved as in the gas phase, the main progression can still be seen and the "hot" band now appears as a shoulder, at 28,900 cm^{-1}, to the main (0′ ← 0′′) band which occurs at 29,310 cm^{-1}. At liquid nitrogen temperature this shoulder disappears.

The asymmetric, structured absorption band system of DBH is in sharp contrast to the structureless symmetrical n–π* absorption bands associated with acyclic aliphatic azo compounds.[24] Spectra of AIP, the acyclic analog of DBH, run under similar conditions to those for DBH gave no hint of structure. Symmetrical absorption envelopes are characteristic of electronic excitation to a state having a different equilibrium nuclear geometry from the ground state, while the asymmetric envelope indicates transition to a state which has essentially the same geometry as the ground state.[25] The latter is not unexpected for a rather rigid cyclic molecule like DBH. Indeed it should be noted that in most respects the absorption spectrum of DBH bears a very close relationship to the spectra of the azines which have been investigated in some detail by Mason and others.[26,27]

DBO. Even a qualitative explanation of the spectral characteristics of DBO appears, at present, subject to considerable uncertainty. The absorption spectrum of gaseous DBO, shown in Figure 3, shows the same asymmetric shape as the DBH spectrum, but the spectrum is more complex and no single dominant vibrational progression can be seen. In order to make sure that

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(24) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, N. Y., 1966, p 453.

(25) K. B. Wiberg, "Physical Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1964, p 174.

(26) S. F. Mason, *J. Chem. Soc.*, 1263 (1959).

(27) M. Ito, R. Shimada, T. Kuraishi, and W. Mizushima, *J. Chem. Phys.*, **26**, 1508 (1957).

Table I. Fluorescence Quantum Yields and Calculated Lifetimes for the First Excited Singlet State of Aliphatic Azo Compounds

Compound	Phase	Concn, M	ν_{exc}, cm^{-1}	φ_f	τ_{calcd}, sec
AIP	Gas	2.0×10^{-3}	27,320	$\leqslant 2 \times 10^{-5}$	$<4 \times 10^{-11}$
DBH	Gas	1.03×10^{-4}	30,770	$(1.4 \pm 0.15) \times 10^{-2}$	3.0×10^{-8}
DBO	Gas	4.93×10^{-6}	26,670	0.56 ± 0.10	4.3×10^{-6}
DBH	Isooctane soln	1.7×10^{-4}	30,770	$<2 \times 10^{-4}$	$<2 \times 10^{-10}$
DBO	Isooctane soln	1.9×10^{-4}	28,570	0.20 ± 0.04	5.9×10^{-7}
		2.0×10^{-3}	28,570	0.20 ± 0.02	5.9×10^{-7}
DBO	Aqueous soln	1.9×10^{-4}	28,570	0.22 ± 0.02	

there were no impurities present the DBO was recrystallized several times and the samples fractionated by vacuum distillation. The spectra obtained from all the samples both in the gas phase and in solution (isooctane) were virtually identical except that in solution the fine structure is smeared out. The nmr spectrum of DBO taken in carbon tetrachloride showed complex multiplets centered at 5 and 1.4 ppm to lower field from internal tetramethylsilane, whose areas were in the expected ratio of 1:4. No impurities could be detected.

As before, the excitation spectrum follows the absorption spectrum faithfully. In emission the first sharp peak coincides with the absorption peak at 26,610 cm^{-1} and probably corresponds to the (0′–0′′) transition. The next main emission peak is separated by 800 cm^{-1} from the first, matching the spacing observed in absorption, but at lower frequencies the mirror-image relationship is lost. This led us to believe originally that the emission might not simply be DBO* fluorescence but might also have a contribution from a triplet, an excimer,[28] or an impurity. The following experimental observations however do not support these possibilities. (1) The shapes of the emission spectra for both gas and solution phases are identical. (2) The shape of the emission is insensitive to the concentration of DBO in solution and to the pressure of DBO in the gas phase. (3) The emission can be quenched by oxygen and by olefins (*vide infra*), but no part of the emission is quenched selectively. (4) The (0′–0′′) bands in emission and in absorption correspond closely. (5) The excitation spectrum closely parallels the absorption spectrum in all cases. Results 1, 3, and 5 make it unlikely that the emission is due to impurity. Result 2 argues against excimer formation since from the lowest pressure in the gas phase where the concentration was 5×10^{-6} M to the highest concentration in solution, 7×10^{-3} M, the shape of the emission spectrum is essentially unchanged. From (4) it would appear that at least part of the emission is from the singlet state, while (3) argues against any emission from a triplet state, for it requires that if a second state is involved the product of its rate constant for quenching by oxygen times its lifetime in the absence of oxygen must be the same as for the singlet. The emission lifetime studies discussed below also argue against the involvement of impurity or excimer. Finally, the emission spectrum of DBO in 5:1 2-methylbutane:methylcyclopentane at 4.2°K was almost the same as the gas-phase emission spectrum shown in Figure 3, except that the weak fine structure mentioned in the caption was somewhat more sharp. One could rationalize the emission spectrum in two ways. First, the emission could be compounded from two transitions from the excited (n,π*) level, namely return to the ground state and a transition to some dissociative level. However, if this is so, it is hard to see why this level is not seen directly in absorption. Second, the (n,π*) level may be in rapid equilibrium with some other excited state with emission to the ground state coming from both these excited levels. However, the low-temperature studies require that this interconversion continues unabated in the glass at liquid helium temperatures. At present therefore, despite the somewhat unexpected nonmirror relationship between absorption and emission, the experimental evidence points to emission from a single state.

Quantum Yields of Fluorescence and Decomposition. The fluorescence quantum yields (φ_f) for DBH and DBO in the gas phase are given in Table I; the errors associated with these numbers are discussed in the Experimental Section. These yields should be compared with that for the acyclic analog azoisopropane (AIP). In the latter case we could detect no emission and estimate $\varphi_f < 2 \times 10^{-5}$.

In isooctane solution the absorption spectrum of DBH is practically the same as in the gas phase. However, no emission from DBH could be detected in solution, and the limit may be considerably lower than stated in Table I for scattering of exciting light made the uncertainty considerably greater than the usual case where absorption and emission are well separated. In contrast DBO still fluoresces strongly in a degassed isooctane solution. The emission spectrum is very similar to that obtained in the gas phase with the fine structure smeared out. In aqueous solution the absorption of DBO is broadened into a single envelope with a maximum at 27,590 cm^{-1} (ϵ 49.5 M^{-1} cm^{-1}). The emission spectrum also loses its banded structure, giving a maximum at 23,800 cm^{-1}. We shall see later that these solution-phase results are in agreement with out gas-phase quenching studies.

The quantum yields of decomposition (φ_d) are given in Table II. The yields for the acyclic compounds are in terms of nitrogen formation, while the yields for the bicyclic compounds are in terms of azo consumption. Since acyclic aliphatic azo compounds undergo a *cis–trans* photoisomerization in solution,[29] the quantum yields cannot be determined by simply measuring the change in absorbance as was done for the bicyclic compounds. In the case of DBH in isooctane, the quantum yield was measured for both azo consumption and for nitrogen formation and found to be 1.0 in both cases. From the results in Tables I and II it will be seen that for both DBH and DBO in the gas phase fluorescence

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(28) B. Stevens and E. Hutton, *Nature*, **186**, 1045 (1960).

(29) R. F. Hutton and C. Steel, *J. Am. Chem. Soc.*, **86**, 745 (1964).

Table II. Quantum Yields of Decomposition of Aliphatic Azo Compounds

Compound	Phase	Concn, *M*	λ_{irr}, mμ	Dispersion, mμ	φ_d	Ref
Azomethane	Gas	5.4×10^{-3}	365		1.0 ± 0.1	29, *a*
AIP	Gas	2.7×10^{-4}	365		0.73	*b*
DBH	Gas	4.6×10^{-5}	334	3.3	0.85 ± 0.10	This work
DBO	Gas	2.1×10^{-6}	365	6.6	0.50 ± 0.10	This work
Azomethane	Isooctane soln	5.0×10^{-3}	365		0.17 ± 0.01	29
DBH	Isooctane soln	1.23×10^{-3}	313		1.0 ± 0.1	9
			334		1.0 ± 0.1	9
DBO	Isooctane soln	3.2×10^{-3}	365	6.6	0.08 ± 0.01	This work

[a] M. H. Jones and E. W. R. Steacie, *J. Chem. Phys.*, **21**, 1018 (1953). [b] R. H. Riem and K. O. Kutschke, *Can. J. Chem.*, **38**, 2332 (1960).

and decomposition account almost quantitatively for the fates of the excited molecules. However, on the addition of a sufficient pressure of added gas, quenching reactions have to be taken into account; these are considered below. The solution phase quantum yields of DBH and DBO are also discussed later.

Emission Lifetime Measurements. The lifetime of the first excited singlet state (τ) is equal to the natural radiative lifetime of the state (τ_0) times the fluorescence quantum yield (φ_f). If φ_f is known, τ may therefore be estimated using the various formulas for the natural radiative lifetime;[30] this procedure was followed in obtaining the values of τ_{calcd} appearing in Table I, but, as has been pointed out by Strickler and Berg, the formulas may well not be exact for weakly allowed transitions. Direct measurements of the lifetimes of long-lived singlet states reached by symmetry-forbidden transitions have been reported in the cases of pyrene and benzene.[31-33] In the case of the latter the measured lifetime was 0.59 μsec, while the calculated value ($\tau_0\varphi_f$) is equal to 0.14 μsec. Because of these uncertainties and because it is likely that the n-π^* transitions are weak not because of over-all symmetry restrictions but rather because of local symmetry requirements, we undertook to measure the lifetime of the excited singlet state directly. With reliable data for these lifetimes, absolute rate constants could be determined from the quenching data reported in the next section (*cf.* eq 7). DBO was chosen for lifetime measurements because it emitted more strongly that DBH, its emission is better separated from the absorption, and its calculated lifetime was considerably longer (see Table I).

Lifetime measurements of DBO in isooctane solution have already been reported.[20] The data for a typical gas-phase emission are embodied in Figure 4. The emission at time t_i is calculated from the formula

$$I_{\text{em}}(t_i) = \alpha\sum_{j=0}^{i} I_{\text{ex}}(t_j) \exp\left(-\frac{t_i - t_j}{\tau}\right) \qquad (6)$$

where $I_{\text{ex}}(t_j)$ is the intensity of the exciting light at time t_j and is determined from the profile of the flash. The above equation assumes that, at each instant of time t_j after the initiation of the flash, a population of DBO* proportional to the exciting intensity $I_{\text{ex}}(t_j)$ is created and that this population decays with a characteristic lifetime τ. α is simply an arbitrary scaling factor which allows for the fact that the photomultiplier sees unknown and different fractions of the incident and emitted light. It is chosen so as to make the calculated maximum emission intensity match that for the experiment. The points are the experimental values, while the curves are computer determinations of $I_{\text{em}}(t_i)$ using τ = 1.00 and 0.75 μsec. The best fit would appear to be close to $\tau = 1.00 \times 10^{-6}$ sec. The data reported in Figure 4 refer to the case in which the emission filter was Corning 3-73; this is a sharp-cut yellow filter which passes frequencies below 24,400 cm^{-1}. We also measured the lifetime using interference filters with maximum transmittances at 22,950 and 19,950 cm^{-1} (band passes 400 cm^{-1}) and found no significant change in the measured lifetime.

In solution, because of the higher possible DBO concentration, the emission-to-scatter ratio was greater, and we were able to determine the emission lifetimes in solution over a more extended frequency range. For DBO in isooctane τ was measured for ν_{em} = 16,600, 19,950, 22,950, and 24,900 cm^{-1}, and the measured lifetime, $\tau = 0.33 \pm 0.05 \times 10^{-6}$ sec, was found to be independent of emission frequency. Unfortunately, because of interference from our exciting light, we were not able to measure the emission at 26,310 cm^{-1}, the position of the (0′-0′′) band in solution. But it appears that, if two states are involved in the emission from DBO*, they must have almost the same lifetime, which reinforces our belief that only one state is involved in the emission.

These data also rule out the possibility that emission is due to either impurity or excimer formed by the processes $\text{Azo}^* + \text{Im} \rightarrow \text{Im}^* + \text{Azo}$ and $\text{Azo} + \text{Azo} \rightarrow (\text{Azo,Azo})^*$ since at the pressures used, 116 μ, the time between Azo–impurity collisions would not be less than 10^{-4} sec, putting the maximum impurity level at 2%, while the time between Azo–Azo collisions is 10^{-6} sec. In both cases this would result in a delay between the initiation of the flash and the emission of light, which was not observed.

The experimental values of τ in solution and in the gas phase, 0.33×10^{-6} and 1.00×10^{-6} sec, respectively, are to be compared with the corresponding calculated values 0.59×10^{-6} and 4.3×10^{-6} sec. In the case of the gas-phase measurements, it should be noted that a 100% increase in the extinction coefficient of DBO would bring τ_{calcd} down to the experimental value; this strong dependence on ϵ results from its use in determining both τ_0 and φ_f. Despite the indirect method which we had to use to measure the gas-phase extinction coefficient, we believe it to be accurate to better than 20%; thus the discrepancy between the calculated and the observed lifetimes appears to be significant. In the case of DBO in solution, the extinction coefficients

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(30) S. J. Strickler and R. A. Berg, *J. Chem. Phys.*, 37, 814 (1962).
(31) R. G. Bennett, *ibid.*, 41, 3037 (1964).
(32) J. W. Donovan and A. B. F. Duncan, *ibid.*, 35, 1389 (1961).
(33) A. E. Douglas, *ibid.*, 45, 1007 (1966).

Table III. Emission Quenching Rate Constants

Azo	Phase	Quencher	τ, μsec	$10^{-9}k_q$, M^{-1} sec^{-1}
DBH	Gas	O_2	0.03 (0.007)	0.70 (3.0)
DBH	Gas	N_2	0.03 (0.007)	0.48 (2.1)
DBH	Gas	*n*-Pentane	0.03 (0.007)	0.63 (2.7)
DBO	Gas	O_2	1.0	2.5
DBO	Gas	N_2	1.0	$<4 \times 10^{-3}$
DBO	Gas	*n*-Pentane	1.0	$<4 \times 10^{-3}$
DBO	Gas	1,3-Cyclohexadiene	1.0	0.47
DBO	Isooctane soln	1,3-Cyclohexadiene	0.33	25.6×10^{-2}
DBO	Isooctane soln	Cyclopentadiene	0.33	5.6×10^{-2}
DBO	Isooctane soln	Piperylene	0.33	3.0×10^{-2}[a]
DBO	Isooctane soln	Cyclopentene	0.33	8.7×10^{-3}
DBO	Isooctane soln	Cyclohexene	0.33	8.4×10^{-3}
DBO	Isooctane soln	*cis*-2-Butene	0.33	1.9×10^{-3}
DBO	Isooctane soln	1-Hexene	0.33	9.8×10^{-4}
DBO	Isooctane soln	1-Octene	0.33	5.5×10^{-4}
DBO	Isooctane soln	Benzene	0.33	$<4 \times 10^{-5}$

[a] A similar value for this constant has recently been reported by S. D. Andrews and A. C. Day, *Chem. Commun.*, 667 (1966).

are accurately known and, again, the observed lifetime is shorter than that calculated on the basis of the Strickler–Berg equation. These deviations are not surprising when one considers recent results for other weak transitions and the breakdown of the mirror-image relationship between absorption and emission in DBO. In other work absence of the mirror-image relation has been observed to result in $\tau > \tau_{\text{calcd}}$,[34,35] just the reverse of what we report here for DBO. All that can be concluded is that, when absorption and emission bands are not mutually symmetrical, there is no longer a simple relationship between integrated absorption and emission probabilities, and the observed lifetime may be either greater or less than the calculated value.

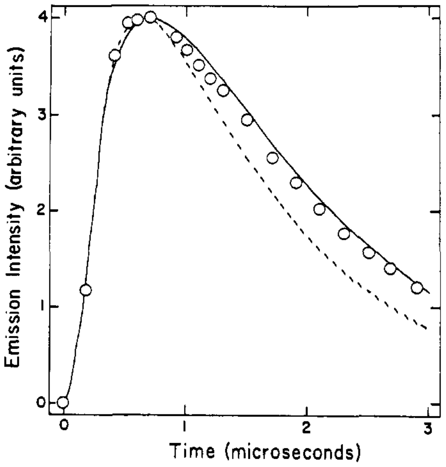

Figure 4. Measurement of emission lifetimes. Experimental points taken from oscilloscope trace (corrected, see text) of emission intensity as a function of time for DBO in the gas phase, pressure 1.16 × 10^{-1} torr. The peak emission signal corresponds to a photomultiplier current of 0.27 mA. Full-line and dashed curves are calculated profiles for τ = 1.00 and 0.75 μsec, respectively.

If, as it appears, the lifetime of the n–π^* excited state of azo compounds can be determined to within an order of magnitude from the Strickler–Berg formula, then the lifetimes of these states for acyclic aliphatic azo compounds must be very short, because in no case has fluorescence been observed. These short lifetimes may be correlated with the structureless nature of the absorptions, since this could indicate a rapid predissociation. In contrast both DBH and DBO which have much longer lifetimes exhibit well-defined vibrational structures.

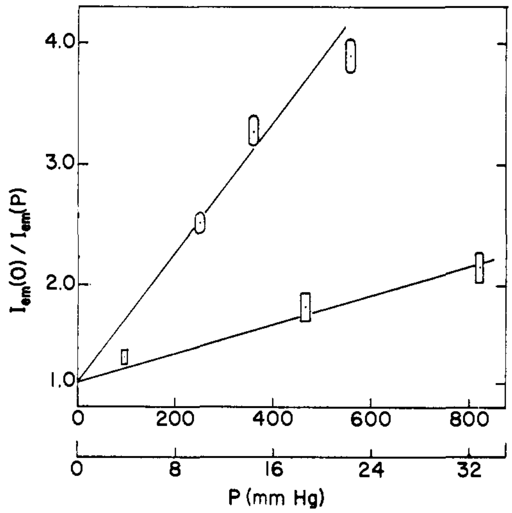

Figure 5. Quenching of emission from DBH and DBO by oxygen. $I_{em}(P)$ is the intensity of emission when P torr of oxygen has been added. The upper abscissa and the rectangles refer to DBH whose pressure was 1.3 torr. The excitation wavelength was 338.6 mμ and the emission was measured at four wavelengths (338.6, 344, 349, and 354 mμ) and averaged. For DBO, lower abscissa and ellipses, the pressure was 0.092 torr, the excitation wavelength 375 mμ, and the emission for two wavelengths 470 and 496 mμ averaged. The temperature was 22° in both cases.

Fluorescence Quenching. The effectiveness of various added gases and solvents at quenching the fluorescence of DBH and DBO is summarized in Table III, in which the quenching rate constants, k_q, have been calculated from the equation

$$\frac{I_{em}(0)}{I_{em}(Q)} = \frac{\varphi_f(0)}{\varphi_f(Q)} = 1 + \tau k_q[Q] \qquad (7)$$

Here $I_{em}(0)$ and $I_{em}(Q)$ are the emission intensities in the absence and presence of the quencher Q, $\varphi_f(0)$ and $\varphi_f(Q)$ are the corresponding quantum yields, τ is the lifetime of the emitting state of the azo compound in the ab-

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(34) J. B. Birks and D. J. Dyson, *Proc. Roy. Soc.* (London), A275, 135 (1963).

(35) W. R. Ware and B. A. Baldwin, *J. Chem. Phys.*, 40, 1703 (1964).

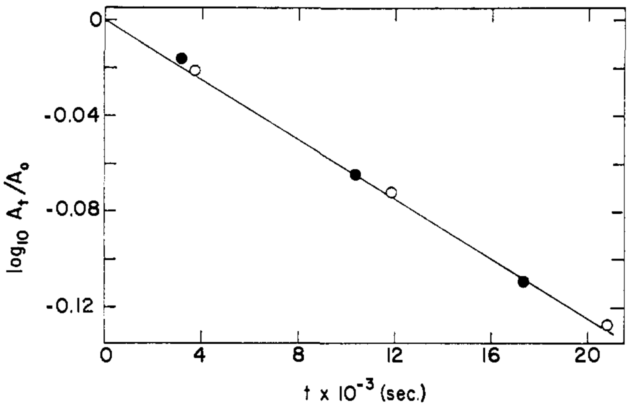

Figure 6. Effect of oxygen on rate of DBH photolysis. The wavelength of photolysis was 334 mμ and the temperature 22°. The DBH concentration at time t was monitored by the absorbance at 338.6 mμ, A_t: ●, DBH pressure 0.803 torr, no added oxygen; ○, DBH pressure 0.803 torr, 857.0 torr added oxygen.

sence of quencher, and $k_q = k_{q,4} + k_{q,5}$ is the sum of the two quenching rate constants defined in eq 4 and 5. Since values of τ had either been determined experimentally (DBO) or could be calculated with fairly good reliability (DBH), absolute values of the k_q's could be obtained.

(a) DBH. Oxygen was found to be effective in quenching the fluorescence of DBH in the gas phase, as shown in Figure 5, but so were other gases such as nitrogen and pentane. This is in agreement with the result that we could observe no emission from DBH in degassed isooctane solution. The pressures of oxygen, nitrogen, and pentane required to reduce the fluorescence to 50% of its quencher-free value were 838, 1210, and 937 torr, respectively. In this case we could not with our present apparatus measure the lifetime of DBH directly but used the value of τ calculated from the Strickler-Berg formula and the quantum yield of fluorescence to obtain the k_q's appearing in the fifth column of Table III.

The k_q for oxygen corresponds to a collision probability of 4.0 × 10^{-3}, a rather low efficiency for phase quenching of a singlet excited state. For instance, Ware and Cunningham[36] obtained an efficiency of 3 × 10^{-1} for oxygen quenching of anthracene fluorescence, while for benzene and oxygen Ishikawa and Noyes[16] found a probability of 4.9 × 10^{-2}. Values of k_q given in parentheses were obtained using τ's calculated from

$$\frac{\tau_{\mathrm{DBH}}}{\tau_{\mathrm{DBO}}} = \frac{\varphi_f(\mathrm{DBH})\,\tau_0(\mathrm{DBH})}{\varphi_f(\mathrm{DBO})\,\tau_0(\mathrm{DBO})}$$

where the τ_0's were calculated from the absorption spectra, and τ_{DBO} was the observed lifetime of gaseous DBO. The result, $\tau_{\mathrm{DBH}} = 7.0 \times 10^{-9}$ sec, assumes that the actual lifetimes of both DBH and DBO will both differ from their calculated values by the same factor. Collision probability of oxygen quenching of DBH calculated in this way is increased to 1.7 × 10^{-2}.

Both the lack of selectivity among quenchers and the inefficiency of the quenching suggested that a collision-induced dissociation (step 5) prevails over the more familiar "physical" quenching (step 4) in the case of DBH. This supposition was confirmed by an investigation into the effect of the quenchers on the rate of photodissociation. Figure 6 shows the results of a typical set of photolyses in the presence and absence of oxygen. Since $-\mathrm{d}[\mathrm{Azo}]/\mathrm{d}t = 2.303\varphi_d I_0 \bar{A}$, where I_0 is the incident light intensity and $\bar{A}$ the appropriately averaged absorbance, is a good approximation when $\bar{A} \sim 0.05$ or less, we can relate quantum yields of decomposition to rates of photolysis by means of

$$\log\,[\mathrm{Azo}]_0/[\mathrm{Azo}]_t = 2.303\varphi_d \bar{\epsilon} l I_0 t \qquad (8)$$

Here l is the path length of the photolysis cell and $\bar{\epsilon}$ is the averaged extinction coefficient corresponding to $\bar{A}$. Since the weighted average absorbance in the irradiation band was less than 0.07, we could with little error employ eq 8, and in this case we used the absorbance at 29,540 cm^{-1} to follow the azo concentration as a function of time. Within experimental error the two slopes, and hence the quantum yields of decomposition, are the same (see eq 8). This is notwithstanding the fact that the pressure of added oxygen was sufficient to reduce the emission intensity by a factor of 2. Not only were the rates of photolysis in terms of azo consumption the same, but also the rate of production of the usual photolysis products was unaltered by the presence of oxygen, and photolysis to completion gave C_5 hydrocarbons in 100 ± 3% yield. Quenching by reaction 4 would have decreased both the rate of azo consumption and the rate of product formation. On the other hand, reaction 5 predicts the observed decrease in emission together with no essential increase in the rate of product formation since the quantum yield of decomposition would only be changed from 0.85 to 0.92. These results agree with solution phase studies where it was found that although no emission could be detected $\varphi_d = 1.0$ within experimental error and that for every mole of N_2 liberated an equivalent amount of C_5 hydrocarbon was also formed.

Collision-induced dissociations from electronically excited states are well known for diatomic molecules[37,38] and are thought to be an important mechanism of internal energy transfer in the photochemistry of polyatomic molecules.[39,40] In the case of DBH both the absorption and the fluorescence excitation spectrum suggest that spontaneous predissociation may be occurring with significant probability in molecules excited roughly 1500 cm^{-1} above the $v' = 0$ level. The fraction of collisions at 300°K involving energies in excess of 1500 cm^{-1} (4.3 kcal mole^{-1}) is 0.17, which allows one to propose that induced dissociation occurs when a collision supplies the energy necessary to raise DBH* to the vicinity of the crossing point with a repulsive electronic level. It is equally possible, however, that the perturbation of a collision is necessary simply to promote a forbidden radiationless transition to the dissociative state. Whatever the mechanism of transition, step 5 probably is possible because of the location of a dissociative potential energy surface near the $v' = 0$ surface of DBH*.

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(36) W. R. Ware and P. T. Cunningham, *J. Chem. Phys.*, 43, 3826 (1965).

(37) G. Herzberg, "Spectra of Diatomic Molecules," 2nd ed, D. Van Nostrand Co., New York, N. Y., 1950, p 413 ff.

(38) J. I. Steinfeld, *J. Chem. Phys.*, 44, 2740 (1966).

(39) H. Sponer, *Radiation Res. Suppl.*, 1, 558 (1959).

(40) J. Hagege, S. Leach, and C. Vermeil, *J. Chim. Phys.*, 62, 403 (1965).

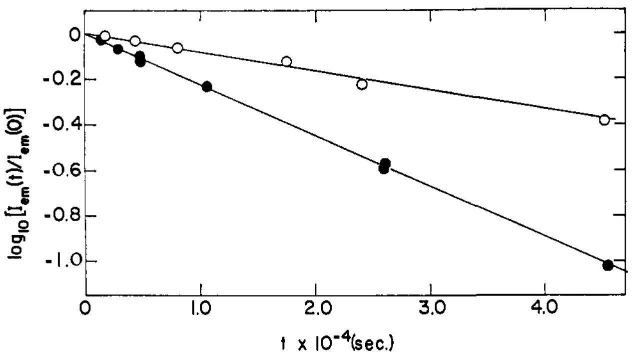

Figure 7. Effect of oxygen on the rate of DBO photolysis. The wavelength of photolysis was 365 mμ and the temperature 22°. The DBO concentration at time t was monitored by measuring the intensity $I_{em}(t)$ at the emission maximum, 446 mμ: ○, DBO pressure 0.039 torr, no added oxygen; ●, DBO pressure 0.039 torr, 16.2 torr added oxygen.

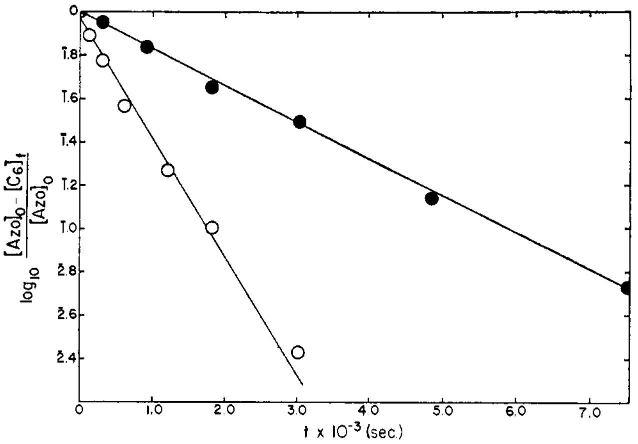

Figure 8. Effect of oxygen on the rate of DBO photolysis. The wavelength of photolysis was 365 mμ and the temperature 22°. $[Azo]_0$ is the azo concentration at t = 0, and $[C_6]_t$ is the total C_6 hydrocarbon concentration at time t: ●, DBO pressure 0.100 torr, no added oxygen; ○, DBO pressure 0.039 torr, 16.9 torr added oxygen.

(b) DBO. Quenching rate constants for DBO were determined from experimentally determined values of τ, removing the uncertainty associated with the same quantities for DBH. As shown by Figure 5, oxygen effectively quenches the emission from DBO*, with a rate constant of 2.5×10^9 M^{-1} sec^{-1}. This corresponds to a collisional efficiency of 1.4×10^{-2}. In contrast the addition of 1540 torr of N_2 had no effect in quenching the emission so that we can say for N_2, $k_q < 4 \times 10^6$ M^{-1} sec^{-1}. These results are in agreement with our solution phase studies. First, DBO fluoresces strongly in both isooctane and in water, a result which would not be expected if collisional deactivation of the fluorescence by "inert" molecules were important at reasonable pressures. Second, outgassing a solution of DBO in isooctane the emission yield increased from 0.027 to 0.20, indicating an effective quenching by O_2 dissolved in the aerated solution.

It should be noted from Tables I and II that the ratio φ_d/φ_f decreases from 0.91 in the gas to 0.43 in isooctane solution. This change may reflect some slight change in the geometry of the excited state and of the potential surfaces involved, but probably implies no basic change in the mechanism of the primary processes.

The mechanism of oxygen quenching in the gas phase appears to be by reaction 4 rather than by 5. Quenching by the former process would decrease the quantum yields of fluorescence and decomposition by the same extent. This we showed to be true by comparing the rates of DBO photolysis in the presence and absence of oxygen. Because of the low absorbance of the sample ($<6 \times 10^{-4}$ at 26,610 cm^{-1} in a 1-cm cell for DBO at its saturation vapor pressure at room temperature), the most convenient method of following the change of concentration of DBO with time was to follow the emission intensity on the assumption that $[DBO]_t \propto I_{em,t}$. The results are shown in Figure 7, where it appears that the rate of photolysis is reduced 2.7 times by the addition of 16.2 torr of oxygen. Because of the somewhat indirect method of measuring the azo concentration, we also determined the rate of photolysis both in the presence and the absence of oxygen by following the rate of formation of C_6 hydrocarbon (mainly biallyl) gas chromatographically. These results are shown in Figure 8. The ratio of the quantum yields for C_6 formation in the absence and in the presence of 16.9 torr of oxygen is 3.3. Moreover, there is no loss of C_6 on photolysis in oxygen. The values of $\varphi_f(0)/\varphi_f(Q)$ for the same pressure of O_2, as determined from the quenching studies, Figure 5, was 3.0. Thus the addition of oxygen does indeed decrease the quantum yields of fluorescence and decomposition by the same extent.

The inefficient quenching of DBO emission by nitrogen and isooctane may indicate that crossing of the dissociative electronic state with the potential energy surface of DBO* occurs at much higher vibrational levels than in the case of DBH. This proposal is consistent with the markedly different values of the ratio φ_d/φ_f in the two azo compounds, 65:1 for gaseous DBH and 0.91:1 for gaseous DBO. If a significant potential energy barrier has to be crossed or a large change in geometry of the excited state has to be effected in order for DBO to reach a dissociative electronic state, then a smaller value of k_3 would be expected for DBO.

While we were engaged in these quenching studies, there appeared a report by Stephenson, *et al.*,[41] on the singlet quenching of aromatic hydrocarbons by conjugated dienes. We wished to see if singlet DBO could also be quenched by dienes and other olefins. Some preliminary results are given in Table III. Because of the low efficiency of the quenching by these compounds, it is important to ensure the absence of impurity quenching. The hydrocarbons were therefore subjected to three stages of purification: (i) column chromatography using basic alumina, (ii) gas chromatography using a silicone oil column; (iii) fractional trap-to-trap distillation on a vacuum line. Similar quenching constants were obtained from samples which had been subjected to one or to three stages of purification increasing our confidence in the absence of impurity quenchers. The quenching constants were determined from eq 7 using at least three different concentrations. In each case a good Stern–Volmer plot was obtained. Several conclusions may be drawn from the results.

(i) The solution phase quenching constants for both piperylene and 1,3-cyclohexadiene are similar to those found by Stephenson, *et al.*, for the quenching of

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

naphthalene and 1-methylnaphthalene by these dienes. This suggests that a common quenching mechanism may be operative in all three cases.

(ii) Just as with oxygen, the quenching by olefins is physical in nature in that there is no direct chemical reaction between DBO and olefin. This was demonstrated by photolyzing the DBO in the presence and the absence of 1,3-cyclohexadiene and showing that, as for oxygen, the two rates of photolysis were proportional to the fluorescence intensities, and that there was no net loss of C_6 hydrocarbons.

At present there is no simple and obvious mechanism for the fluorescence quenching by olefins. The triplet energies of the monoolefins[42] are very close to that of the $(n-\pi^*)$ singlet state of DBO, so that electronic energy transfer involving coupled electronic transitions is possible although spin forbidden. It is also interesting to note that k_q(diene) > k_q(monoolefin) > k_q(aromatic) which is also the order of electron localization energies.[43] However, it should also be observed that cyclic olefins appear to be significantly better quenchers than acyclic olefins. The reason for this is not at all obvious but may relate to certain steric requirements of the quenching complex or a slight lowering of the triplet level. Hopefully our current studies which embrace a much wider range of conditions and quenchers will throw more light on this problem.

Mechanisms of Aliphatic Azo Photodecomposition. Various mechanisms for the photochemical decomposition of azo compounds may be considered. (i) The internal conversion of electronic into vibrational energy is attractive in that it allows compounds to decompose by identical routes both thermally and photochemically, and there is evidence that some reacactions go by this path.[44-46] However, processes which involve the conversion of electronic into vibrational energy are generally considered unfavorable because of Franck-Condon restrictions. In the case of aliphatic azo compounds, even if all the electronic energy is converted into vibrational energy, then the lifetime of the resultant vibrationally excited molecule as calculated by RRK theory is still sufficiently long that at high pressures such as exist in solution the probability of collisional deactivation should be so great that no photochemical decomposition should occur—while it does. Therefore, if we insist on such a mechanism for low pressures, then for high pressures in the gas phase or in solution we have to postulate the existence of another route. This could be a pressure-induced dissociation. In the case of DBH, an internal conversion mechanism cannot be operative because the RRK lifetime of vibrationally excited DBH formed by 338-mμ irradiation is calculated to be 2×10^{-8} sec, and there is no dependence of the rate of photolysis up to pressures as high as 1 atm of added gas.

(ii) Recently Worsham and Rice[47] have considered the possibility that azoethane decomposes by a direct dissociation in which the controlling step is the rate at which vibrational energy in the electronically excited state is accumulated in some (unspecified) vibration; this corresponds to type II predissociation.[37] However, they have to assign what would appear to be unreasonably large fractions of the total energy associated with the vibronic transition to the vibrational energy of the excited state, 50–100% depending on their choice of parameters, in order to get agreement between their model and the experimental results. This certainly cannot be the mechanism for DBH and DBO where photodecomposition occurs even when the irradiation is in the $(0' \leftarrow 0'')$ band.

(iii) Aliphatic azo compounds which have been excited to their triplet state by triplet transfer are also known to dissociate,[48] so we may ask if under direct photolysis azo compounds photodissociate by first undergoing intersystem crossing to the triplet state. In the case of DBH, for which we have done the most work, there is no evidence for the intermediacy of a triplet state. Even in the presence of 1000 torr of O_2 the rate of photolysis is not affected so that if a triplet state is involved it must have a very short lifetime.

Also, we have found that the product distribution which we obtain when DBH is induced to decompose by triplet transfer from benzaldehyde is very different from that found for direct photolysis. We shall report later in greater detail on these studies.

The Production of Radicals. Acyclic aliphatic azo compounds on photolysis yield free radicals; however, we have no evidence that DBH or DBO on photolysis yields 1,3-cyclopentadiyl or 1,4-cyclohexadiyl biradicals, respectively. For example, pressures up to 1000 torr of oxygen and photolysis in furan solution had no effect on the ratio of C_5 hydrocarbons produced to DBH consumed, which remained at 1.0. In a previous paper we mentioned[9] some inconsistent results on the photolysis of DBH in the presence of 1 torr of nitric oxide at 100° where the yield of C_5 hydrocarbons was less than 100%. We have since repeated this work and have shown that even in the presence of 10 torr of NO, where the NO is in tenfold excess over the DBH, we can still recover $100 \pm 2\%$ C_5 hydrocarbon provided the commercial NO is very carefully purified.[49] These results all indicate that if, in fact, 1,3-cyclopentadiyl is formed it must have a very short lifetime, certainly less than 10^{-10} sec.

Acknowledgments. One of us (B. S. S.) acknowledges support from the National Science Foundation under College Faculty Summer Participation Grant GY-2373, and we thank Professor Robin H. Hochstrasser and Mr. Charles I. Marzzallo (University of Pennsylvania) for carrying out the low-temperature emission spectrum of DBO. Dr. A. C. Day (Oxford) communicated his results on piperylene quenching to us prior to their publication.

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[42] D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

[43] M. Szwarc and J. H. Binks, "Theoretical Organic Chemistry," paper presented to Kekulé Symposium, Butterworth & Co., Ltd., London, 1959, p 262.

[44] R. Srinivasan, *J. Am. Chem. Soc.*, 84, 3982 (1962).

[45] C. S. Parmenter, *J. Chem. Phys.*, 41, 658 (1964).

[46] J. P. Chesick, *ibid.*, **45**, 3934 (1966).

[47] C. Worsham and O. K. Rice, *ibid.*, **46**, 2021 (1967).

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

[49] E. E. Hughes, *J. Chem. Phys.*, **35**, 1531 (1961).