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Photochemistry of 2,3-Diazabicyclo[2.2.2]oct-2-ene

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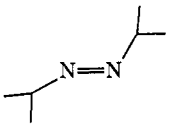
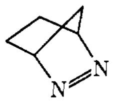
Abstract: The photochemistry of 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) has been investigated in the gas phase and in solution and is compared with that of other azoalkanes. The main fates of DBO in the direct photolysis at low pressures are fluorescence from the n,π^* singlet (S_1^*) and intersystem crossing to the triplet from which decomposition occurs ($\Phi_f = 0.56 \pm 0.10$, $\Phi_{dec}{}^{C_6} = 0.50 \pm 0.05$ at 0.1 Torr). Return of the DBO molecules from the triplet to the ground electronic state (S_0) becomes important at higher gas-phase pressures and particularly in solution. In isooctane $\Phi_{dec}{}^{C_6}$ is only 0.022 and ${}^T\Phi_{dec}{}^{C_6} = 0.014$. Irradiation of DBO in solution results in the buildup of a diffusion-controlled singlet quencher; this quencher is not formed in the triplet-sensitized photolysis. Oxygen quenching of ^{1}DBO* in solution occurs *via* the triplet $DBO(S_1) + O_2 \rightarrow DBO(T_1)$, the rate constant for this process being $6 \times 10^9\ M^{-1}\ sec^{-1}$. From kinetic measurements the triplet energy, E_T, of DBO has been found to be 54.5 kcal mol^{-1} and the lifetimes of the lowest triplet states of DBO and of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) in solution have been estimated as being $<10^{-9}$ sec. The interaction rate constants of triplet benzophenone, naphthyl phenyl ketone, benzil, and biacetyl with a variety of substrates have been determined.

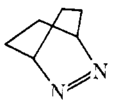
In previous papers we have discussed the photochemistry of azoisopropane (AIP) and 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH).[1,2] In this paper we report on the photochemistry of 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO), give further data for DBH, and draw comparisons between the photochemistry of these three compounds.



AIP



DBH



DBO

Experimental Section

Materials. The preparations of DBH, DBO, and AIP have been described previously.[3-5] All reagents were the best grade commerically available. Benzil was recrystallized from benzene and benzophenone rom ethanol. Benzaldehyde, biacetyl, 1,3-cyclohexadiene, and *trans*-1,3,5-hexatriene were distilled before use. 2-Naphthyl phenyl ketone, *trans*-stilbene, *sec*-butylamine, triethylamine, 1,4-diazabicyclo[2.2.2]octane, and 1,1-dimethylhydrazine were used directly; 1,2-dimethylhydrazine was prepared from the dihydrochloride. The solvents acetonitrile, benzene, and isooctane (2,2,4-trimethylpentane) were distilled once through a good column, the middle fraction being employed. Carbon dioxide was commerical grade (>99.5% CO_2).

Symbolism. In reporting quantum yields, a left superscript T indicates that a triplet-sensitized yield is referred to; in direct photolyses there is no left superscript. The right subscript gives information as to the type of process being monitored; thus f stands for fluorescence, isc for intersystem crossing, and dec for decomposition. The right superscript gives additional information as to the parameter measured; thus, $\Phi_{dec}{}^{\Delta DBO}$ and $\Phi_{dec}{}^{C_6}$ refer to the quantum yield of decomposition of DBO measured in terms of DBO consumption and C_6-hydrocarbon formation, respectively.

In the gas-phase sensitization studies we used benzene and benzaldehyde as donors. They have $S_1 \rightarrow T_1$ intersystem crossing yields (Φ_{isc}) which are significantly less than 1.0.[6,7] This means that

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(1) I. I. Abram, G. S. Milne, B. S. Solomon, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 1220 (1969).

(2) S. Solomon, T. F. Thomas, and C. Steel, *ibid.*, **90**, 2249 (1968).

(3) S. G. Cohen and R. Zand, *ibid.*, **83**, 2895 (1961).

(4) S. G. Cohen and R. Zand, *ibid.*, **84**, 586 (1962).

(5) R. Renaud and L. C. Leitch, *Can. J. Chem.*, **32**, 545 (1954).

(6) P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968).

(7) I. Goldblatt and C. Steel, paper presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

even if the acceptor interacts with all the donor triplets and the probability of decomposition of an acceptor triplet so formed is unity, less than 1 mol of product is formed per einstein of light absorbed by the donor. $\Phi_{dec}^{C_6}$ is therefore defined as the probability of C_6 formation from a triplet DBO molecule which has been formed by triplet sensitization and so takes account of any inefficiency in the intersystem crossing of the donor.

Gas-Phase Photolyses. Photolyses were effected by a high-pressure mercury arc (PEK 100 W) in conjunction with a grating monochromator (Bausch and Lomb) and a quartz lens system to produce a collimated beam. Cylindrical optical cells (100 mm long and 22 mm in diameter, or 200 mm long and 32 mm in diameter) fitted with greaseless high-vaccuum stopcocks were used. Because both the sensitizers and the azo compounds are strongly adsorbed on the glass, the cells had to be seasoned before use.[8] Azo compound in the pressure range 0.09–0.10 Torr was admitted to the cell; then, if required, sensitizer was added by overpressuring. The pressure of the sensitizer (0.4–0.8 Torr) was checked by uv adsorption or by gas chromatographic analysis which was carried out using a 25-ft × 0.125-in. column of 10% SF-96 silicone oil on Chromosorb-W 60–80. Since the decomposition quantum yield of DBO is pressure independent below 1 Torr, relative quantum yields were measured by a matched-cell technique in which both cells were filled with the same pressures of azo and sensitizer but only one was finally overpressured with carbon dioxide. The hydrocarbon products formed in the decomposition were biallyl and bicyclo[2.2.0]hexane; no others in significant amounts could be detected.

Typical light fluxes incident on the cells were 5×10^{-10} einstein sec^{-1} at 254 nm (benzene sensitization), 2×10^{-10} einstein sec^{-1} at 276 nm (benzaldehyde sensitization), and 15×10^{-10} einstein sec^{-1} at 365 nm (direct photolysis). Incident light intensities were measured by ferrioxalate actinometry,[9] and the fraction of light absorbed by the gas was measured by a sensitive balanced photocell circuit (RCA 935 photocell and Hewlett-Packard 425 micro volt ammeter) which was capable of measuring transmission changes of 0.2% with 5% accuracy. The photocells in turn were calibrated against a ferrioxalate actinometer.

In the gas-phase sensitization studies, benzene, benzaldehyde, and biacetyl were used as donors. For the first two materials Φ_{iso} ($S_1 \rightarrow T_1$) is <1.0; moreover, the yields can depend upon the experimental conditions (*viz.*, λ_{irr} and pressure of reagents[7]). Since the probability of triplet DBH decomposition is known to be 1.0, this substance acts as a convenient monitor of the efficiency of donor triplet formation. In the case of benzaldehyde, the concentration of DBH required to trap >95% of the donor triplets can be readily ascertained by observing the quenching of the donor phosphorescence, and for benzene one can add increasing amounts of DBH and observe the pressure at which the rate of C_5 formation "plateaus" ($^3DBH^* \rightarrow C_5 + N_2$). Typically, azo pressures of 0.1 Torr are required to accomplish this. Values of intersystem crossing yields for benzene and benzaldehyde under our experimental conditions were 0.60 ± 0.05 in both cases; the yield so obtained for benzene agrees well with the literature value.[6] The probability of reaction of triplet DBO formed by sensitization ($^3DBO^* \rightarrow C_6 + N_2$) can then be determined by comparing the rates of C_6 and C_5 formation.

Some direct photolyses were carried out with 500-ml spherical reaction vessels and a photochemical reactor equipped with "Black-light" lamps; these have a continuous emission in the region 305–425 nm and peak at 352 nm. In this case incident intensities were approximately 1×10^{-8} einstein cm^{-2} sec^{-1}. The results were not significantly different from those carried out using the monochromator and the cylindrical cells.

Solution Photolyses. Solution photolyses were carried out using 1-cm square quartz cells equipped with side degassing bulbs. The progress of the photolysis was followed either optically on a Cary spectrophotometer or by withdrawing 5-μl aliquots for gas chromatographic analysis. Analysis of the dissolved oxygen in the quenching experiments (*vide infra*) was carried out by withdrawing a 50-μl aliquot through a self-sealing silicone rubber septum and by analyzing the solution using 6 ft of 0.25-in. 13× molecular sieve. The sieve effectively removed the solvent (isooctane, acetonitrile) and allowed only the oxygen to pass. Any air leakage could be detected by the presence of nitrogen. Air-saturated solutions of isooctane and acetonitrile at 24° have O_2 concentrations of $3.3 \pm 0.2 \times 10^{-3}$ and $1.9 \pm 0.2 \times 10^{-3}$ M, respectively. Nitrogen, liberated on irradiation of azo solutions, was measured by pumping the gas into a calibrated buret with a Toepler pump. The purity of the sample was checked by gas chromatography.

Emission and Quenching Studies. Steady-state emission spectra and intensities were measured with a Farrand spectrofluorimeter. The singlet lifetimes of DBO[10] and the triplet lifetimes of 2-naphthyl phenyl ketone, benzophenone,[11] benzil, and biacetyl were determined by exciting samples with an air-spark flash (1/*e* time, 0.2×10^{-6} sec) and monitoring the emitted light with a photomultiplier–oscilloscope circuit. A 7-39 Corning filter which passes light in the region 310–410 nm was used in excitation. The following filter systems were used in emission (sample, filter no., wavelength, nm): DBO, 3-73 and 4-96, 400–600; benzophenone, 3-72 and 4-96, 440–600; 2-naphthyl phenyl ketone, 3-70 and 4-96, 490–600; biacetyl, 3-69 and 4-96, 510–600; benzil, 3-68 and 4-96, 520–600. The rate constants of interaction (k_{ir}) of a substrate Q with the excited state were then determined by either direct measurement of the variation of the lifetime of the excited state as Q was added

$$1/\tau_Q = 1/\tau + k_{ir}[Q]$$

or by measuring the steady-state emission intensities in the presence, I_q, and absence, I_0, of Q

$$I_0/I_q = 1 + \tau k_{ir}[Q]$$

Because the emission lifetimes of the triplet donors can vary considerably with the purity of the solvent, it is important that the lifetimes of these compounds be measured directly for the solutions whose emission is being measured. Typical values of τ in various solvents are (triplet, solvent, $\tau \times 10^6$, sec): benzophenone, acetonitrile, 96; benzophenone, benzene, 6.6; benzophenone, isooctane, 2.5; benzil, isooctane, 150; biacetyl, isooctane, 634; 2-naphthyl phenyl ketone, isooctane, 230; 2-naphthyl phenyl ketone, acetonitrile, 215.

Errors. Typical reproducibilities were as follows: quenching constants (*e.g.*, Table I) ±5%, R_0/R_q (Tables II and III) ±5% for C_6, ±5% for N_2, and ±2% for ΔAzo. Quantum yields in solution had a spread of ±5% but this increased to ±10% in the gas phase because I_{abs} was much harder to measure accurately and gas sampling too is subject to greater uncertainties. Solution-phase product ratios, *e.g.*, III/(III + II) in section 4e, had an uncertainty of ±2%.

Table I. Interaction Rate Constants of Ketone Triplets with Various Acceptors

Triplet	Quencher	Solvent	$k_{ir} \times 10^{-9}$, M^{-1} sec^{-1}
Benzophenone	DBO	Isooctane	6.7
Benzophenone	DBO	Acetonitrile	3.8
Benzophenone	DBH	Isooctane	2.6
Benzophenone	DBH	Acetonitrile	3.8
Benzophenone	DBH	Benzene	2.1
Benzophenone	*trans*-Stilbene	Isooctane	6.5
		Acetonitrile	7.5
Benzophenone	1,3,5-Hexatriene	Isooctane	11.2
Benzophenone	1,3,5-Hexatriene	Acetonitrile	11.0
Benzophenone	Oxygen	Isooctane	1.5
Benzophenone	Oxygen	Acetonitrile	1.8
Naphthyl phenyl ketone	*trans*-Stilbene	Isooctane	8.8
Naphthyl phenyl ketone	*trans*-Stilbene	Acetonitrile	10.5
Naphthyl phenyl ketone	1,3,5-Hexatriene	Acetonitrile	12.3
Benzil	1,3,5-Hexatriene	Isooctane	6.9
	DBO	Isooctane	0.26
Biacetyl	DBO	Isooctane	2.0

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

[9] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

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

[11] W. D. K. Clark, A. D. Litt, and C. Steel, *J. Amer. Chem. Soc.*, **91**, 5413 (1969).

Table II. Quenching of Azo Triplets in Solution by Hexatriene and Stilbene

Benzophenone,[a] $M \times 10^2$	Azo, $M \times 10^2$	Quencher, $M \times 10^3$	Solvent	R_0/R_q[b]	F	$F(R_0/R_q) - 1$
8.0	1.3 DBH	0.96 *trans*-Stilbene	Isooctane	1.34	0.84	0.13
2.0	0.9 DBH	0.90 *trans*-Stilbene	Acetonitrile	1.42	0.84	0.19
2.0	1.5 DBH	3.0 Hexatriene	Acetonitrile	1.98	0.63	0.25
1.0	1.9 DBH	2.3 Hexatriene	Benzene	1.39	0.67	−0.07
1.0	1.7 DBH	9.1 Hexatriene	Benzene	2.29	0.34	−0.22
1.0	0.35 DBH	36.0 Hexatriene	Isooctane	1.60	0.69	0.10
2.0	0.90 DBO	1.7 Hexatriene	Isooctane	1.23	0.75	−0.07
2.0	1.6 DBO	9.0 Hexatriene	Isooctane	2.00	0.52	+0.04

[a] λ_{irr} 365 nm for sensitization of DBH and 303 nm for sensitization of DBO. [b] R_0/R_q measured by rates of either C_5 or C_6 production.

Table III. Oxygen Quenching of Sensitized Azo Photolyses[a]

Azo, $M \times 10^2$	O_2, $M \times 10^3$	R_0/R_q	F	$F(R_0/R_q) - 1$	Analytical method	Solvent
0.73 DBH	7.4	2.8	0.68	0.9	ΔDBH	Acetonitrile
		3.2		1.2	N_2	
		31.8		20.6	C_5	
1.3 DBH	1.9	1.5	0.93	0.4	ΔDBH	Acetonitrile
		5.7		4.3	C_5	
4.9 DBH	1.2	5.8	0.99	4.7	C_5	Isooctane
4.9 DBH	2.3	8.0	0.98	6.8	C_5	Isooctane
4.9 DBH	3.0	9.3	0.98	8.1	C_5	Isooctane
1.0 DBO	7.4	2.3	0.74	0.7	ΔDBO	Acetonitrile
		3.2		1.4	N_2	
		3.8		1.7	C_6	
0.8 DBO	1.9	1.4	0.89	0.2	ΔDBO	Acetonitrile
		1.8		0.6	C_6	
0.45 DBO	1.9	1.3	0.84	0.1	ΔDBO	Acetonitrile
		1.7		0.4	C_6	

[a] Benzophenone as sensitizer. λ_{irr} 365 nm (DBH) and 303 nm (DBO). Benzophenone concentration is chosen so that the absorbance is 1.0 in a 1-cm cell at λ_{irr}.

Results and Discussion

(1) Direct and Sensitized Photolysis of DBO in the Gas Phase. Unless specifically mentioned, all data in this paper refer to 24 ± 2°. Figure 1 shows the relative quantum yields of emission and decomposition, as measured by the formation of C_6 hydrocarbons, for the direct photolysis of DBO as a function of pressure. Although the emission yield is insensitive to pressure, the decomposition yield varies markedly, indicating that decomposition does not occur from the emitting state. We have previously reported[2] on data that lead us to identify the emission with fluorescence from $S_1(^1n,\pi^*)$. Further evidence that the emission comes from S_1 is that although DBO effectively quenches the fluorescence of naphthalene[12] and the phosphorescence of benzaldehyde and benzophenone, it is only in the case of naphthalene that sensitized emission can be observed.

$$^1\text{Nap}^* + {}^1\text{DBO} \longrightarrow {}^1\text{Nap} + {}^1\text{DBO}^*$$

$$k_1 = 1.5 \times 10^{10}\ M^{-1}\ \text{sec}^{-1} \quad \text{(isooctane)} \tag{1}$$

$$^3\text{PhCOPh}^* + {}^1\text{DBO} \longrightarrow {}^1\text{PhCOPh} + {}^3\text{DBO}^*$$

$$k_2 = 6.7 \times 10^{9}\ M^{-1}\ \text{sec}^{-1} \quad \text{(isooctane)} \tag{2}$$

$$^3\text{PhCOH}^* + {}^1\text{DBO} \longrightarrow {}^1\text{PhCOH} + {}^3\text{DBO}^*$$

$$k_3 = 5.4 \times 10^{10}\ M^{-1}\ \text{sec}^{-1} \quad \text{(gas)} \tag{3}$$

$$^1\text{DBO}^* \longrightarrow {}^1\text{DBO} + h\nu_f \qquad k_4 = 6.1 \times 10^{6}\ \text{sec}^{-1} \quad \text{(isooctane)} \tag{4}$$

It is therefore likely that decomposition originates either directly or indirectly from the triplet manifold. Evidence in favor of this is to be found in the data given in Figure 2 where we compare the probability of decomposition of triplet DBO as a function of pressure using various donors. We shall discuss these results in detail later in a paper dealing with the pressure dependence of the product yields in the gas-phase photolysis, but it may be noted that the pressure dependence of the C_6 yield from DBO sensitized by the higher energy donors benzene (E_T = 84.7 kcal mol^{-1}) and benzaldehyde (E_T =

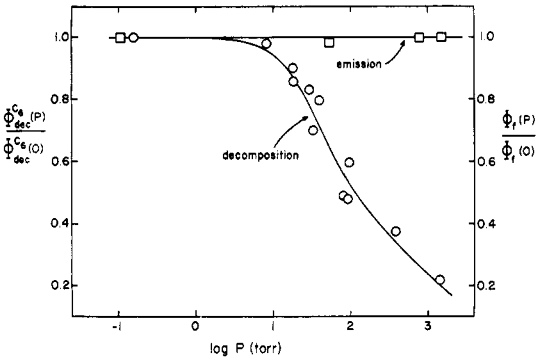

Figure 1. Relative quantum yields of fluorescence and decomposition as a function of total pressure in the direct photolysis of DBO. $P = P_{DBO} + P_{CO_2}$. The range of P_{DBO} was 0.07–0.11 Torr. The circles refer to the left-hand ordinate, the squares to the right-hand ordinate. λ_{irr} 365 nm, dispersion 6.6 nm, $\Phi_{dec}^{C_6}(0)$ = 0.50 ± 0.05, and $\Phi_f(0)$ = 0.56 ± 0.10.

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(12) K. R. Naqvi and C. Steel, *Chem. Phys. Lett.*, 6, 29 (1970).

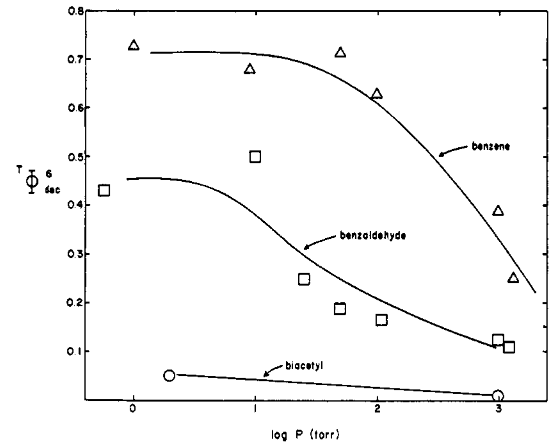

Figure 2. Probability of C_6 formation from triplet DBO as a function of pressure. $P = P_{DBO} + P_{sens} + P_{CO_2}$. The ranges of P_{DBO} and P_{sens} were 0.09–0.20 and 0.40–0.60 Torr, respectively: (□) sensitizer benzaldehyde, λ_{irr} 276 nm; (△) sensitizer benzene, λ_{irr} 254 nm; (○) sensitizer biacetyl, λ_{irr} 436 nm. Dispersion 6.6 nm.

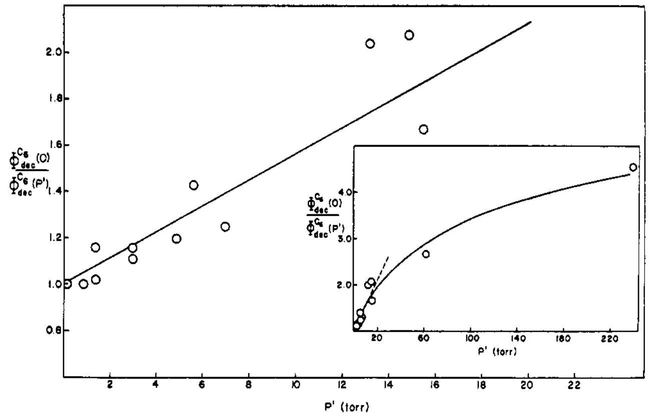

Figure 3. Relative quantum yield of hydrocarbon formation in the direct photolysis of DBO as a function of effective pressure P'. DBO + $h\nu \rightarrow C_6 + N_2$. The collision efficiency of DBO was taken as unity and that of CO_2 as 0.16. Thus $P' = P_{DBO} + 0.16P_{CO_2}$. The lifetime of the state from which dissociation originates, τ, is given by $\tau = (\Phi_{dec}{}^{C_6}(0)/\Phi_{dec}{}^{C_6}(P') - 1)/k_{deact}(P')$. λ_{irr} 365 nm, dispersion 6.6 nm.

71.6 kcal mol^{-1}) is similar to that obtained in the direct photolysis, but that for biacetyl (E_T = 54.9 kcal mol^{-1}) the yield is much lower even at low pressure. It should be emphasized that this low yield is not due to inefficient capture of biacetyl triplets by DBO, since by monitoring the biacetyl phosphorescence we were able to establish that 0.070 Torr of DBO, the minimum azo pressure used, captured more than 95% of the biacetyl triplets. However, it may still be asked whether the pressure effect on the decomposition yields results from deactivation in the triplet manifold or in the vibrationally excited ground state ($S_0{}^v$) produced by intersystem crossing from T_1. In section 2 we report the triplet energy of DBO (E_T = 54.5 ± 1.5 kcal mol^{-1}). This energy is the minimum excess vibrational energy associated with $S_0{}^v$. Carrying out an RRMK calculation on the dissociative lifetime of such a molecule, we obtain a value of 10^{-3} sec.[13] Increasing this energy to 76 kcal mol^{-1}, E_S(DBO), decreases the lifetime to 10^{-6} sec. However, if the state from which decomposition originates can be deactivated by collision with gas X at pressure P' with a rate constant k_{deact}, then $\Phi_{dec}{}^{C_6}(0)/\Phi_{dec}{}^{C_6}(P') = 1 + \tau k_{deact}(P')$, where τ is the lifetime of the state from which decomposition originates.[16] Assuming unit deactivation efficiency of the state by DBO and an efficiency of 0.16 for CO_2,[17] we determine τ from the data in Figure 3 as 2.2 ± 10^{-9} sec. The value so obtained is too short for that of a vibrationally excited ground state, so at present we favor the view that the bulk of the decomposition occurs from T_1.

(2) Triplet Energy of DBO. In order to determine the triplet energies of compounds which do not phosphoresce, Hammond[18] has developed a "chemical" method

$$^3D^* + {}^1A \longrightarrow {}^1D + {}^3A^* \qquad (5)$$

$$^3A^* \longrightarrow \text{reaction} \qquad (6)$$

If $E_T(D) > E_T(A)$, $^3A^*$ is formed efficiently and this process is monitored by the subsequent reaction of $^3A^*$. In this way E_T(DBH) has been determined as 60 ± 1 kcal mol^{-1}.[19] If $^3A^*$ does not undergo a well-defined reaction, E_T(A) may still be determined if we can determine k_5 as a function of E_T(D) for different donors. For benzil, biacetyl, and benzophenone, E_T = 53.7, 54.9, and 68.5 kcal mol^{-1}, respectively,[20] and we obtain k_5 = 0.26 × 10^9, 2.0 × 10^9, and 6.7 × 10^9 M^{-1} sec^{-1}. From these data we estimate that E_T(DBO) lies between 53 and 56 kcal mol^{-1}. It is interesting to note that the singlet–triplet splitting for DBO, 76.0–54.5 kcal mol^{-1}, is similar to that for DBH, 84.3–60 kcal mol^{-1}.

(3) Lifetimes of Triplet DBH and DBO in Solution. Although we have been able to detect fluorescence from both DBH and DBO, we have not been able to observe any phosphorescence even at −196°;[2] we therefore had to use an indirect method for estimating their triplet lifetimes (τ_T). The absolute values of the rate constants associated with this section are given in Table I.

The azo triplet ($^3A^*$) is produced by resonance energy transfer from a suitable triplet donor ($^3D^*$). A quencher (Q) whose E_T is less than E_T(A) then interacts with $^3A^*$ in competition with the pseudo-unimolecular decay processes of the latter. Q can of course also interact with $^3D^*$.

In the case of DBH, benzophenone (Bz) was chosen as donor because $E_T(Bz) > E_T(DBH)$ and because benzophenone can be irradiated at a wavelength at which DBH does not absorb (365 nm). The first quencher we used was *trans*-stilbene (St) because (a) $E_T(St) < E_T(DBH)$, (b) its quenching properties have been

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(13) The formula[14] employed for the lifetime is $1/\tau = A\{[(E - E_0) + a^+E_z{}^+]/(E + aE_z)\}^{S-1}$. The values of A, E_0, and S are 10^{14} sec^{-1}, 44.6 kcal mol^{-1}, and 48, respectively. Values of E_z and $E_z{}^+$ were taken as 104 and 101 kcal mol^{-1}; a and a^+ may be estimated by the method of Whitten and Rabinovitch.[15] For example, for E = 54 kcal mol^{-1}, a^+ = 0.708 and a = 0.819; for E = 76 kcal mol^{-1}, a^+ = 0.778 and a = 0.846.

(14) D. W. Setser, B. S. Rabinovitch, and E. G. Spittler, *J. Chem. Phys.*, **35**, 1840 (1961).

(15) G. Z. Whitten and B. S. Rabinovitch, *ibid.*, **38**, 2466 (1963).

(16) E-C. Wu and O. K. Rice, *J. Phys. Chem.*, **72**, 542 (1968).

(17) T. F. Thomas, C. I. Sutin, and C. Steel, *J. Amer. Chem. Soc.*, **89**, 5107 (1967).

(18) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *ibid.*, **86**, 3197 (1964).

(19) P. S. Engel, *ibid.*, **91**, 6903 (1969).

(20) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, pp 298 and 301.

extensively investigated,[6] and (c) at moderate concentrations it does not absorb at 365 nm.

We therefore have

$$^3Bz^* + {}^1A \longrightarrow {}^1Bz + {}^3A^* \quad (7)$$

$$^3Bz^* + {}^1St \longrightarrow {}^1Bz + {}^3St^* \quad (8)$$

$$^3A^* \longrightarrow C_5 + N_2 \quad (9)$$

$$^3A^* + {}^1St \longrightarrow {}^1A + {}^3St^* \quad (10)$$

If R_0 and R_q are the rates of DBH consumption in the absence and presence of Q, then

$$F(R_0/R_q) - 1 = \tau_T k_q[Q] \quad (11)$$

where F is the fraction of benzophenone triplets transferring their energy to A, τ_T is the lifetime of $^3A^*$ in the absence of Q, and k_q is the quenching constant of Q with $^3A^*$. In this case $F = k_7[A]/(k_7[A] + k_8[St])$, $\tau_T = 1/k_9$, and $k_q = k_{10}$. The plot of $F(R_0/R_q) - 1$ *vs.* [Q] should yield a straight line with slope $\tau_T k_q$. We felt that the best estimate of k_q would be obtained by equating it with the interaction rate constant of Q with a donor whose triplet energy lay close to that of DBH, because such a donor and DBH must have similar normalized emission bands.[12] 2-Naphthyl phenyl ketone, $E_T = 59.6$ kcal mol^{-1},[20] is such a molecule. The choice of 2-naphthyl phenyl ketone could be criticized on the grounds that its triplet is $\pi-\pi^*$ in character[21] as compared to the n-π^* character of triplet DBH, and that the sizes of the two molecules are quite different. However, as the interaction rates for these two molecules with stilbene should be close to diffusion controlled, the use of the k_q of the ketone should be a good estimate.

Some representative data are given in Table II; in fact, it turned out that the values of $F(R_0/R_q) - 1$ were sufficiently small that we could obtain no reliable values for the slope and hence for τ_T. We could not go to *trans*-stilbene concentration greater than approximately 5×10^{-3} *M* in isooctane or acetonitrile because of solubility restrictions. Thus *trans*-1,3,5-hexatriene was substituted for stilbene. Practically no quantitative quenching studies have been carried out using this molecule, but it has no absorption at 365 nm and has a low triplet energy, 47.5 kcal mol^{-1}.[22] Again we could observe no significant interaction of the hexatriene with $^3DBH^*$. Putting an upper value of 10 M^{-1} on $\tau_T k_q$ gives a maximum value of the lifetime of $^3DBH^*$ in solution of 10^{-9} sec.

As the quantum yield of decomposition for $^3DBO^*$ is over 50 times less than that of ^3DBH, it was felt that the lifetime of the former might be considerably longer than the lifetime of $^3DBH^*$, and thus measurable.

To produce $^3DBO^*$, benzophenone was again used as sensitizer. However, owing to the strong absorption of DBO at 365 nm, the benzophenone must be irradiated at 303 nm where DBO absorption is minimal, but this still put an upper bound on the DBO concentration that can be conveniently employed. Moreover, at this wavelength *trans*-stilbene becomes unacceptable as a quencher because of its large extinction coefficient, so only *trans*-1,3,5-hexatriene was employed. Once again we could observe no significant interaction of the hexatriene with $^3DBO^*$ and consequently put an upper bound to the lifetime of $^3DBO^*$ in solution of 10^{-9} sec.

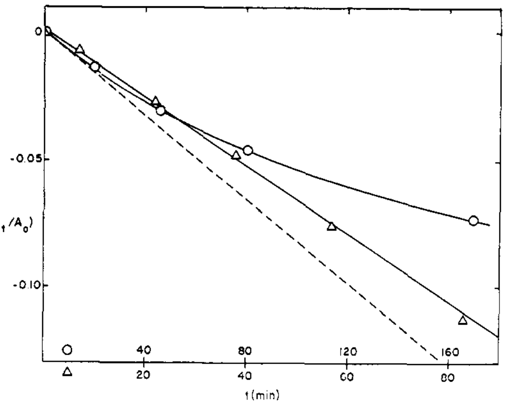

Figure 4. Absorbance *vs.* time plot for photodecomposition of DBO (8×10^{-3} *M*) at 24°: (○) direct photolysis in isooctane, (△) biacetyl-sensitized (5.7×10^{-2} *M*) photolysis in isooctane. A_0 and A_t are the absorbances at times 0′ and *t*. The dashed line refers to the curve that would be obtained in the direct photolysis if the quantum yield remained invariant.

In section 4c we describe experiments which were carried out at even higher concentrations of Q and which support this upper limit for the triplet lifetime.

(4) Solution-Phase Photolysis of DBO. (a) Emission Yields and Singlet Lifetimes. In isooctane the measured lifetime of $^1DBO^*$ is 0.33×10^{-6} sec and the fluorescence yield (Φ_f) is 0.20. In acetonitrile the measured lifetime increases to 1.0×10^{-6} sec and Φ_f is 0.37. Therefore, the radiative lifetimes in isooctane and acetonitrile are respectively 1.65×10^{-6} and 2.7×10^{-6} sec. A Strickler–Berg calculation[23] using the absorption spectra of DBO in these two solvents yields the values 2.9×10^{-6} and 4.8×10^{-6} sec [ϵ_{max}(isooctane) 193 M^{-1} cm^{-1} and ϵ_{max}(acetonitrile) 116 M^{-1} sec^{-1}]. Although the absolute values of the measured and calculated lifetimes differ somewhat, the ratios are in excellent agreement.

(b) Quencher Formation. In the direct photolysis of DBO in isooctane a singlet quencher is produced as the reaction proceeds. This can be seen by monitoring both the absorbance and the emission as a function of photolysis time. In Figure 4 we show an absorbance *vs.* time plot. The circles are the experimental values, while the dashed line refers to the values that would be obtained if $\Phi_{dec}{}^{\Delta DBO}$ remained constant at its initial value; in fact, as the reaction proceeds the quantum yield of decomposition decreases. At the beginning of the reaction the yield is 0.068, while after 15% decomposition (170 min) it drops to 0.016, a fourfold change; at the same time Φ_f changes by fourfold from 0.20 to 0.049. There is a similar state of affairs when acetonitrile is used as the solvent.

Because of the known ability of quadricyclene (I) to act as a singlet quencher,[24,25] we initially suspected that bicyclo[2.2.0]hexane (II) was the quencher being formed. However, this is not so because the quenching constant of II with $^1DBO^*$ is $\ll 5 \times 10^8$ M^{-1} sec^{-1}. In fact, quadricyclene was found to be a very poor quencher of $^1DBO^*$, the quenching constant being $\ll 2 \times 10^6$ M^{-1} sec^{-1}. We also know the biallyl (III) is not the

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

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[25] B. S. Solomon, C. Steel, and A. Weller, *Chem. Commun.*, 927 (1969).


I


II


III

quencher, since the decomposition yield is not altered when DBO is irradiated in the presence of 10^{-2} *M* biallyl.

During the photolysis in isooctane there is a discrepancy between the amount of DBO consumed (ΔDBO) and the amount of C_6 and N_2 formed. Thus in a typical experiment we found $DBO_0 = 8.0 \times 10^{-3}$, $\Delta DBO = 12.3 \times 10^{-4}$, $C_6 = 4.2 \times 10^{-4}$, and $N_2 = 4.0 \times 10^{-4}$ *M*, isooctane solvent. The state of affairs in acetonitrile was not greatly different, $DBO_0 = 7.1 \times 10^{-3}$, $\Delta DBO = 15.2 \times 10^{-4}$, $C_6 = 9.2 \times 10^{-4}$, and $N_2 = 9.4 \times 10^{-4}$ *M*. Constructing a Stern–Volmer plot of the fluorescence intensity of DBO *vs.* the concentration of missing material, we obtained quenching constants for the latter of 1.1×10^{10} and 0.3×10^{10} M^{-1} sec^{-1} in isooctane and acetonitrile.

Because the nitrogen yield equals the C_6 yield, it would appear that the quencher is a nitrogen-containing compound. Amines such as triethylamine, *sec*-butylamine, and 1,4-diazabicyclo[2.2.2]octane were found to be quite inefficient quenchers of ^{1}DBO*, but 1,2-dimethylhydrazine and 1,1-dimethylhydrazine quenched the DBO fluorescence strongly. The quenching constants for the latter two compounds in acetonitrile were 0.34×10^{10} and 0.10×10^{10} M^{-1} sec^{-1}, respectively. It would seem therefore that a compound with the reduced form of the azo linkage is quenching the DBO emission in the direct photolysis. Furthermore, as the photolysis proceeds, a structureless absorption starting at approximately 300 nm builds up. The hydrazines also show such an absorption. We have not isolated the quencher formed in the DBO photolysis, but are now commencing a more systematic study of singlet quenching by hydrazines and hope to say more later on the mechanism of quencher formation in DBO. In contrast, in the case of triplet sensitization (biacetyl and benzophenone used), there was no missing product and the quantum yield did not change with extent of photolysis (see Figure 4). A typical analysis was $Biac_0 = 0.057$, $DBO_0 = 6.0 \times 10^{-3}$, $\Delta DBO = 5.9 \times 10^{-4}$, and $\Delta C_6 = 5.8 \times 10^{-4}$ *M*. Therefore, the quencher seems to be formed by reaction solely from the singlet manifold.

In summary, although there is photochemical reaction, the major fates of excited singlet DBO molecules are fluorescence (see section 4a) and eventual return to the ground state; the amount of reaction is quite small. We shall present evidence below which suggests that this return to the ground state proceeds *via* intersystem crossing to T_1 and that a considerable fraction of the C_6 formation also originates from T_1.

(c) Oxygen Quenching of Singlet DBO. Oxygen markedly quenches the fluorescence of DBO in both isooctane and acetonitrile. Thus 3.3×10^{-3} *M* oxygen in isooctane (air-saturated solution at 23°) reduces the emission by a factor of 7.4 and in acetonitrile 1.85×10^{-3} *M* oxygen (air-saturated solution) reduces the emission by a factor of 13.0. These correspond to oxygen quenching constants of 5.9×10^9 and 6.5×10^9 M^{-1} sec^{-1}, respectively. In both cases the hydrocarbon yields in the direct photolyses are affected much less. In acetonitrile, for example, the quantum yield of biallyl fell from 0.023 to 0.019 while the yield of bicyclohexane decreased from 0.013 to 0.006 on the addition of 1.85×10^{-3} *M* oxygen. Obviously O_2 cannot be physically quenching the first singlet (S_1) directly to the ground state (S_0); otherwise the hydrocarbon yield would have to decrease by at least the same extent as the emission. In fact the data are consistent with there being an exchange induced intersystem crossing,[26] and it is interesting to note that Hoytink has concluded that such processes should be close to being diffusion controlled. The following are allowed by the spin conservation rules.

$$^1\text{DBO}^* + O_2(^3\Sigma_g^-) \longrightarrow {}^3\text{DBO}^* + O_2(^1\Delta_g) \qquad (12)$$

$$^1\text{DBO}^* + O_2(^3\Sigma_g^-) \longrightarrow {}^3\text{DBO}^* + O_2(^3\Sigma_g^-) \qquad (13)$$

The energy difference between the $^1\Delta$ and $^3\Sigma$ states of oxygen is 22.6 kcal mol^{-1}, while we estimate that the singlet–triplet splitting of DBO is 21.5 ± 1.5 kcal mol^{-1}, so the first process is probably just energetically feasible. In earlier studies with DBO in the gas phase,[2] no evidence was obtained for oxygen inducing intersystem crossing which could possibly indicate the involvement of charge-transfer states in solution.[26,27] The ability to observe the formation of the triplet from the singlet under the action of oxygen rests on the very short lifetime of triplet DBO as compared to singlet DBO. This is not a general situation, so this system holds considerable promise for more detailed studies on exchange induced crossings.

If oxygen does so induce the intersystem crossing of DBO, then we can calculate $\Phi_{dec}{}^{III}(O_2)$, the quantum yield of biallyl formation in the direct photolysis of DBO in the presence of oxygen, from $^T\Phi_{dec}{}^{III}(O_2)$, the yield of biallyl formed from ^{3}DBO* in a solution of the same O_2 concentration, and from $\Phi_f(O_2)$, the DBO fluorescence yield, again at the same oxygen concentration.

$$\Phi_{dec}{}^{III}(O_2) \approx {}^T\Phi_{dec}{}^{III}(O_2)\{1 - \Phi_f(O_2)\} =$$
$$0.019(1 - 0.0276) = 0.0184 \quad \text{(isooctane solvent)}$$

The directly determined value of $\Phi_{dec}{}^{III}(O_2)$ is 0.019. For bicyclohexane we find $\Phi_{dec}{}^{II}(O_2) = 0.006$ and $^T\Phi_{dec}{}^{II}(O_2) = 0.007$. The good agreement is further evidence that, in the direct photolysis in the presence of oxygen, the small amount of photolysis that is observed originates from the triplet rather than from the singlet manifold.

The presence of oxygen effectively allows one to produce ^{3}DBO* quantitatively in the direct photolysis of DBO. We therefore photolyzed undegassed solutions in the presence and absence of large concentrations of *trans*-1,3,5-hexatriene. Under these conditions we should have $R_0/R_q = 1 + \tau_T k_q[Q]$. After allowance was made for the small amount of singlet quenching by hexatriene, we found that even for 0.2 *M* hexatriene in isooctane $(R_0/R_q) - 1 \leq 0.2$. This puts a maximum value of 0.2×10^{-9} sec on τ_T(DBO), in agreement with the sensitization studies (section 3).

(d) Effect of Oxygen on Sensitized Photolyses of DBH and DBO. Because oxygen is a well-known triplet quencher and has been used to seek for evidence of the presence of azo triplets,[2,28] we wondered if in

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[26] G. J. Hoytink, *Accounts Chem. Res.*, **2**, 114 (1969).

[27] I. B. Berlman, C. R. Goldschmidt, G. Stein, Y. Tomkiewicz, and A. Weinreb, *Chem. Phys. Lett.*, **4**, 338 (1969).

[28] E. L. Allred and R. L. Smith, *J. Amer. Chem. Soc.*, **91**, 6766 (1969).

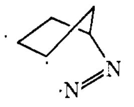
light of the short azo triplet lifetimes determined in section 3 the use of O_2 would have any validity. Obviously, oxygen has potential problems in that it could also react with radical intermediates. We first measured the rate constants of quenching triplet benzophenone by oxygen in isooctane and acetonitrile (Table I). It is interesting to observe that these constants are significantly smaller than the constants for oxygen quenching of aromatic hydrocarbon singlets ($k \sim 3 \times 10^{10}$ M^{-1} sec^{-1})[29] but are similar to the oxygen quenching constant of anthracene triplets ($k \sim 3 \times 10^{9}$ M^{-1} sec^{-1}).[30]

Irradiating benzophenone in a solution containing Azo and O_2 produces ^{3}Azo* in an oxygen environment. Equation 11 now is

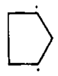
$$F(R_0/R_q) - 1 = \tau_T k_q[O_2] \qquad (11)$$

where k_q is the quenching constant of ^{3}Azo* by O_2, which we assume to be equal to the corresponding constant for triplet benzophenone (Table I). Using the data in Table III for R_0/R_q in terms of azo consumption we obtain $\tau_T k_q = 126$ M^{-1} for DBH and 98 M^{-1} for DBO. Thus in both cases τ_T should be about 50×10^{-9} sec, which is about two orders of magnitude greater than the lifetime estimated by *trans*-stilbene and hexatriene quenching.

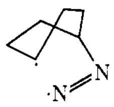
When E_T(donor) > E_T(acceptor), the mechanism of *trans*-stilbene and 1,3,5-hexatriene triplet quenching is believed to occur *via* exchange-induced resonance energy transfer,[31] and we have as yet no theoretical reasons for believing azo compounds would be in any sense anomalous donors.[12] Therefore, a certain degree of confidence is attached to the upper limits placed on triplet lifetimes of DBH and DBO in section 3. Possibly then, oxygen interacts with some longer lived intermediate. In this latter case, a possibility is that the dissociations occur *via* IV and VI and that oxygen interacts with these species. Although such species have been postulated in the photochemistry of azo compounds,[32] there is no convincing direct evidence as yet for their existence.



IV



V



VI

The most dramatic effect of oxygen on the sensitized DBH photolysis, however, is manifested in the large discrepancy between R_0/R_q values as measured in terms of either nitrogen production or DBH consumption, and R_0/R_q values measured in terms of C_5 formation (Table III). This strong oxygen inhibition of C_5 formation is a chemical rather than a physical effect, as one can observe a decrease in oxygen concentration as the photolysis proceeds. A simple explanation of the result is that oxygen is attacking V and so removing the source of C_5. The maximum rate constant at which this attack could occur is $\sim 10^{10}$ M^{-1} sec^{-1} and therefore a minimum lifetime of 10^{-7} sec can be assigned to V.

These data for oxygen may be contrasted with results observed in the direct photolysis of DBH, where there was no difference in the rate of photolysis in the presence (7.4×10^{-3} M) and absence of oxygen. This noneffect of oxygen indicates that the direct photolysis does not proceed *via* the triplet for DBH.

The absence of trapping by oxygen in the direct photolysis indicates that different intermediates are involved in the direct and triplet sensitized irradiations. If the decomposition in the direct photolysis occurs in a concerted fashion, then there can be no trapping of a radical entity by oxygen and the interaction of oxygen in the triplet-sensitized photolysis could be with V, the spins of the free electrons being either parallel or antiparallel. If, however, the direct (singlet) photolysis proceeds *via* a biradical, the latter must have the spins antiparallel, and thus oxygen would be interacting with the spin-aligned form of V in the triplet-sensitized photolysis. A concerted decomposition of ^{3}DBH* is not possible because of the high triplet energies of both nitrogen and bicyclo[2.1.0]pentane.

In the case of DBO, the difference between the R_0/R_q values, measured in terms of DBO consumption and C_6 formation, is less dramatic but is still consistent with oxygen intercepting a hydrocarbon radical.

Because of these complexities the use of oxygen as a test for triplets and the measurement of their lifetimes has to be treated with some caution.

(e) Quantum Yields in Sensitized and Direct Photolyses in Solution. In the sensitized photolysis with biacetyl or benzophenone as sensitizer, $^{T}\Phi_{dec}{}^{C_6} = 0.014$ (isooctane) and 0.033 (acetonitrile) and the yield of C_6 formation equals the yield of DBO disappearance ($^{T}\Phi_{dec}{}^{\Delta DBO}$). Therefore, the predominant fate of ^{3}DBO* is ultimate return to the ground state, since we have also been unable to detect any phosphorescence.[2] In these sensitized photolyses 73% of the C_6 yield is III, the remaining 27% being II; no other hydrocarbon in significant yield could be detected.

In the direct photolysis $\Phi_{dec}{}^{\Delta DBO} = 0.068$ (isooctane) and 0.065 (acetonitrile), so that the predominate fate of excited molecules is either fluorescence or ultimate return to the ground state. The small amount of reaction that does occur in solution appears to take place from both the triplet and the singlet manifold. In section 4b we mentioned the discrepancy between the ΔDBO and the C_6 yields and showed how this was due to a singlet reaction forming a quencher. The C_6 products (58% III and 42% II) would appear to originate from both singlet and triplet manifolds. In the gas phase we have observed that the major fates of molecules in S_1 are fluorescence and intersystem crossing to the triplet. It would seem likely that the same holds true in solution so that $\Phi_{isc} + \Phi_f \approx 1$. Thus the quantum yield of C_6 hydrocarbon originating from the triplet manifold in the direct photolysis should be $(1 - \Phi_f)^{T}\Phi_{dec}{}^{C_6} = (1 - 0.2)0.014 = 0.011$ (isooctane) and $= (1 - 0.37)0.033 = 0.021$ (acetonitrile). These are to be compared with the experimental yields of 0.022 and 0.036, which indicate that only 50–60% of the C_6 yield in the direct photolysis originates from T_1. So it is not surprising that the hydrocarbon ratios in the direct and sensitized photolyses differ somewhat.

(5) General Discussion. In Table IV we have gathered together some of the parameters associated

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(32) W. R. Roth and M. Martin, *Tetrahedron Lett.*, 4695 (1967).

Table IV. Parameters in the Photolyses of Azoalkanes[a]

Parameter	Phase	DBH	DBO	AIP
E_S, kcal mol^{-1}	Solution	84.3	76.0	<68[b]
E_T, kcal mol^{-1}	Solution	60[33]	54.5[c]	<55[b]
τ_S, sec	Gas	7×10^{-9}	1.0×10^{-6}	$<10^{-10}$
	Solution	$<10^{-10}$	3.3×10^{-7}	$<10^{-10}$
τ_T, sec	Gas		2×10^{-9}	$>0.5 \times 10^{-9}$
	Solution	$<10^{-9}$	$<10^{-9}$	
Φ_f	Gas	1.4×10^{-2}	0.56	$<5 \times 10^{-6}$
	Solution	$<10^{-4}$	0.20	$<5 \times 10^{-6}$
Φ_{dec}[g]	Gas	1.0	0.50	1.0
	Solution	1.0	0.022[c]	0.025[d]
$^T\Phi_{dec}$	Gas	1.0[e]	0.78[c]	0.10[b]
	Solution	1.0[c,f]	0.014	< 0.10

[a] The values in this table are compiled from ref 1 and 2 unless otherwise indicated. [b] Unpublished results from this laboratory. [c] This work. [d] Isomerization quantum yields are high. [e] Reference 7. [f] Reference 33. [g] Φ_{dec} and $^T\Phi_{dec}$ are in terms of hydrocarbon formation; all gas-phase data are limiting values at low pressures and solution data are for isooctane as solvent.

with both the direct and the triplet-sensitized photolyses of DBH, DBO, and AIP. It is apparent that there are very marked differences in their photochemistries.

In solution the lifetime of ^{1}DBH* is $<10^{-9}$ sec ($\Phi_f < 10^{-3}$, $\tau_{rad} = 2.1 \pm 10^{-6}$ sec), and comparison of the rates of C_5 formation in the presence and absence of oxygen for both the direct and the triplet-sensitized photolyses shows that certainly $<10\%$ of the direct photolysis proceeds *via* the triplet. If dissociation occurred *via* internal conversion to S_0^{vib}, one would expect essentially complete collisional deactivation in solution. Therefore, the result that the dissociation yield is unity in solution strongly supports direct dissociation from S_1. This result is in agreement with previous findings.[2,28] The probability of dissociation of ^{3}DBH* in solution is also close to unity and this likewise suggests direct dissociation from T_1.

In an earlier paper[2] we pointed out that although DBH does fluoresce weakly in the gas phase, there is a collision-induced process which removes molecules from S_1 so that fluorescence decreases dramatically at high pressures or in solution. At that time we were unable to distinguish between the possibilities of collision-induced dissociation from S_1 or induced intersystem crossing to the triplet followed by dissociation. In that oxygen has a very different effect on the direct and sensitized photolyses of DBH in solution, we may now eliminate the possibility of induced intersystem crossing. The pressure-induced dissociation of ^{1}DBH* is reflected in the short singlet lifetime in solution.

In contrast, ^{1}DBO* has a much longer lifetime both in the gas phase and solution, so that a significant fraction of the molecules fluoresce. If the remainder all cross to the triplet manifold we obtain an upper limit to the rate constant of intersystem crossing of 2.4×10^6 sec^{-1} in isooctane ($= 1 - \Phi_f/\tau_s$). Since the singlet–triplet splittings for DBH and DBO are comparable, it is likely that k_{isc} for DBH is also of the order 10^6 sec^{-1}, so we see that in this case intersystem crossing cannot compete with dissociation from S_1. In the case of DBO, however, most of the dissociation which is observed in the gas phase does originate from the triplet.

The triplet lifetimes of DBH and DBO in solution are very short. Even if it ultimately turns out that the interaction rate constants of *trans*-stilbene and *trans*-1,3,5-hexatriene with the azo triplets do not in fact have their expected diffusion-controlled values, thus invalidating our limits on the triplet lifetimes, the oxygen quenching data also put an upper limit on the lifetime of $\sim 0.5 \times 10^{-7}$ sec. The value for DBH may not be surprising in that the yield of sensitized decomposition is unity within experimental error, so the short lifetimes reflect a high rate constant for dissociation. But in the case of DBO only 1.4% of the triplet molecules dissociate to C_6 hydrocarbons and nitrogen. Since the consumption of DBO equals the C_6 production, the rest must ultimately return to the ground state. The question then arises as to why the lifetime of ^{3}DBO* is so short.

The rate constants for radiationless intersystem crossings ($T_1 \rightarrow S_0$) for aromatic hydrocarbons are extremely low (10^2–10^{-2} sec^{-1}), and the same is true for the corresponding constants for aromatic n,π* triplets ($\sim 10^2$ sec^{-1}).[34] Although these constants are determined in low-temperature glasses, it is generally assumed that the rates are insensitive to temperature and the nature of the medium.[35] Apparently these rate constants increase dramatically to values in excess of 10^7 sec^{-1} when the triplet geometry differs significantly from that of the ground state,[36] presumably because the Franck–Condon factor in the matrix element of the perturbation Hamiltonian becomes particularly favorable.[35] Similar factors might be operative in the case of DBO. DBO, for example, is a far less rigid compound than DBH, as is indicated from their absorption spectra. Nevertheless, we feel that the lifetime of triplet DBO is probably too short to be explained solely on such physical grounds and that chemical processes should be considered. For example, ^{3}DBO* could decompose to give VI, which would be capable of either eliminating nitrogen or ultimately returning to ground-state DBO.

Because of the relatively rigid nature of DBO and DBH, their ^{3}(n,π*) states probably lie considerably below the ^{3}(π,π*) states, which in turn are above the ^{1}(n,π*) states.[37] In contrast, acyclic azo compounds such as AIP most likely have the ^{3}(π,π*) state lying below the ^{1}(n,π*) state, so their intersystem crossing can now

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(33) P. S. Engel, *J. Amer. Chem. Soc.*, **89**, 5031 (1967).

(34) D. A. Anthenius, J. Schmidt, and J. H. van der Waals, *Chem. Phys. Lett.*, **6**, 255 (1970); W. Siebrand, "The Triplet State, Beirut Symposium (1967)," A. B. Zahlan, Ed., Cambridge University Press, New York, N. Y., 1967, p 31.

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(36) E. F. Ullman and W. A. Henderson, Jr., *J. Amer. Chem. Soc.*, **89**, 4380 (1967).

(37) C. Steel and G. S. Milne, paper presented at the Symposium on Organic and Physical Aspects of Photochemistry, Annual Meeting of the Chemical Society, April 1969.

occur to the ${}^3(\pi,\pi^*)$ state with resulting cis–trans isomerization. It is therefore not surprising that the intersystem crossing rate constant for AIP is greater than the corresponding constants for DBO and DBH, being in excess of 10^{10} sec^{-1}.[1] For bicyclic azo compounds, the lower intersystem rate constants may be understood in terms of a crossing to a (n,π^*) rather than a (π,π^*) manifold[38] and less marked differences between the equilibrium geometries of the states, resulting in less favorable Franck–Condon factors.[35]

In this previous work we have used sensitization extensively as a source of triplet molecules.[1,7] In Table I the interaction rate constante (k_{ir}) of a variety of substrates, including azo compounds, with several triplet donors are recorded. However, these constants are specifically values required for the estimation of triplet lifetimes and are neither for a systematic group of acceptors nor designed to study the variations in k_{ir} *per se*. One of us has recently reported on the factors influencing the rates of singlet–singlet energy transfer involving aliphatic azo compounds,[12] and we are now in the process of expanding the number and type of triplet donors and quenchers listed in Table I in order to establish patterns of triplet quenching. It is hoped in this way to obtain a better understanding of the factors involved in triplet–triplet energy transfer.

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

Photolysis of *n*-Pentylazomethane Vapor. Reactions of the *n*-Pentyl Radical[1]

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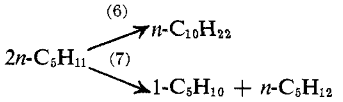
Abstract: The vapor-phase photolysis of *n*-pentylazomethane was studied in the temperature range 24–162°. The product rate data fit well the proposed reaction scheme involving methyl and *n*-pentyl radicals. Evidence for the generation of photochemically activated *n*-pentyl radicals was found. The implications of this evidence to previous work on the photolysis of azoalkanes are discussed. When the concentration of photochemically activated radicals was minimized, the thermal rate constants for the isomerization and H-atom abstraction reactions of the *n*-pentyl radical were determined: $n\text{-C}_5\text{H}_{11} \rightarrow sec\text{-C}_5\text{H}_{11}$ (17), $k_{17} = 3.3 \times 10^8 \exp(-15.1 \times 10^3/RT)$ sec^{-1}; $n\text{-C}_5\text{H}_{11} + n\text{-C}_5\text{H}_{11}\text{N}_2\text{CH}_3 \rightarrow n\text{-C}_5\text{H}_{12} + \text{C}_5\text{H}_{10}\text{N}_2\text{CH}_3$ (20), $k_{20} = 4.2 \times 10^{11} \exp(-7.8 \times 10^3/RT)$ mol^{-1} cm^3 sec^{-1}. The disproportionation to combination ratio at 25° for *n*-pentyl radicals was estimated to be 0.14, and $\Delta(\text{Me}, n\text{-Pe}) = 0.033$.

There is almost no quantitative information in the literature on the reactions of the *n*-pentyl free radical. Only one estimate of the disproportionation to combination ratio has been reported.[2] The data obtained by Wijnen from his study of the photolysis of 2-heptanone vapor gave a value of ~0.2 for k_7/k_6 at 63°.



$$2n\text{-C}_5\text{H}_{11} \begin{cases} \xrightarrow{(6)} n\text{-C}_{10}\text{H}_{22} \\ \xrightarrow{(7)} 1\text{-C}_5\text{H}_{10} + n\text{-C}_5\text{H}_{12} \end{cases}$$

Of special interest is the isomerization of *n*-pentyl radicals *via* a 1,4 hydrogen-atom transfer. Wijnen observed products from the *sec*-pentyl radical and suggested that they resulted from isomerization of *n*-pentyl. He did not measure a rate constant. Isomerization of C_5, C_6, and C_7 alkyl radicals is well documented,[3] but the activation energies and *A* factors are only known as estimates. Recently the Arrhenius parameters of the only two reported rate constants[4,5] for isomerization of alkyl radicals have been shown to be uncertain.[6]

Rabinovitch and coworkers[7] have studied the unimolecular isomerization of ten different vibrationally excited alkyl radicals. While no activation energy was measured, their theoretical RRKM calculations for 5_{ss} isomerization rates fitted the experimental rate constant best when the threshold energy for isomerization was ~15 kcal mol^{-1}. According to the notation of Rabinovitch,[7] the 1,4 H-atom transfer for *n*-pentyl would be a 5_{sp} process, indicating a five-membered ring activated complex in which a secondary C–H bond is broken and a primary C–H bond is formed.

The present work was initiated to obtain more reliable kinetic data on *n*-pentyl radical reactions. A clean source of *n*-pentyl radicals was needed. In view of the extensive work of Calvert and coworkers[8] who used the photolysis of azoalkanes as clean alkyl radical sources, the photolysis of 1,1′-azo-*n*-pentane was expected to be

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(1) Presented at the Midwest Regional Meeting of the American Chemical Society, Lincoln, Neb., 1970, No. 622.

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