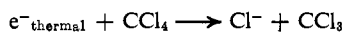Figure 2. Low energy electron inelastic excitation spectrum of carbon disulfide. Ethyl nitrate was used to detect thermal energy electrons by monitoring the NO_2^- ion signal.

Ridge and Beauchamp[19] used CCl_4 as a slow electron detector and monitored the Cl^- signal produced by the reaction

$$e^-_{thermal} + CCl_4 \longrightarrow Cl^- + CCl_3$$

The authors have found that carbon tetrachloride is difficult to work with because of a large Cl^- background signal, presumably produced by surface ionization of CCl_4 absorbed on the filament. The reaction

$$e^-_{thermal} + EtONO_2 \longrightarrow NO_2^- + EtO\cdot$$
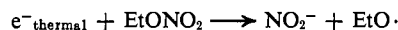
has a cross section of about $240 \times 10^{-16} \, cm^2$ for thermal energy electrons.[4] Figure 2 shows an electron energy excitation spectrum of carbon disulfide obtained using the NO_2^- ion signal from ethyl nitrate to monitor the number of thermal energy electrons produced. The known electronic energy levels are indicated using the designations given by Herzberg.[20] All of the peaks correspond to known spectroscopic states of CS_2 with the exception of the large peak at 7.3 eV. Jacobs and Henglein[18] also saw a large peak at this energy using both SF_6 and CH_3I as electron scavengers. The complete absence of a residual or background signal above an electron energy of 1.5 eV and the large cross section for NO_2^- formation (20 times larger than the most commonly used process, SF_6^- from SF_6) make ethyl nitrate an excellent detector for thermal energy ions.

(20) G. Herzberg, "Electronic Spectra and Electronic Structure of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1966, pp 601–602 and p 594.

Chemiluminescence from Peroxide Decomposition Reactions. The Role of Energy Transfer[1a]

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Contribution from the Department of Chemistry and Laboratory for Nuclear Science, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received August 28, 1969

Abstract: Chemiluminescence from thermal decomposition of dibenzal diperoxide in the presence of aromatic fluorescent compounds was studied. The emitting species was identified as the lowest excited singlet state of the aromatic fluorescer. The excitation step producing this species was shown to involve energy transfer from excited state species produced by the peroxide decomposition, *i.e.*, triplet benzaldehyde and/or singlet oxygen monomers and collisional pairs. Energy transfer from the benzaldehyde triplet was shown to be due to a long-range dipole-dipole interaction in solution. Energy transfer from singlet oxygen monomers, occurring through a two-step mechanism involving the fluorescer triplet as an intermediate, was shown to be more significant than transfer from singlet oxygen collisional pairs.

Addition of dibenzal diperoxide to a paraffin oil solution of dibenzanthrone at 200° was observed by Kurtz to produce red chemiluminescence.[2a] Kurtz proposed a mechanism involving[2a] thermal decomposition of the peroxide, producing oxygen[2b] addition to dibenz-

anthrone,[3] rapid dissociation of the *endo*-peroxide to ground state oxygen, and emission form the dibenzanthrone triplet state.
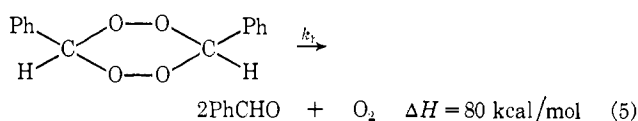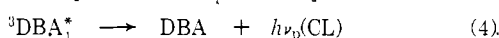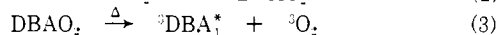
We have identified the emitting species in this system as the lowest excited singlet state of dibenzanthrone by matching the chemiluminescence (CL) and fluorescence spectra. The chemiluminescence spectrum was obtained using a fast image-intensifier spectrograph.[2b]

The question remained as to how the emitting species was produced. Benzaldehyde and oxygen were shown to be the products of peroxide decomposition.

(1) (a) Paper presented at the International Conference on Chemiluminescence, Desert Hot Springs, Calif., March 1969; (b) address all correspondence to this author at the Department of Chemistry, University of Georgia, Athens, Ga. 30601.
(2) (a) R. B. Kurtz, *Ann. N. Y. Acad. Sci.*, 16, 399 (1954); (b) S. Ness and D. M. Hercules, *Anal. Chem.*, 41, 1467 (1969).
(3) M. M. Rauhut, *Accounts Chem. Res.*, 2, 80 (1969).

dibenzaldiperoxide (P)

dibenzanthrone (DBA)

dibenzanthrone *endo*-peroxide (DBAO$_2$)

$$P \xrightarrow{\Delta} O_2 + products \tag{1}$$

$$DBA + O_2 \longrightarrow DBAO_2 \tag{2}$$

$$DBAO_2 \xrightarrow{\Delta} {}^3DBA_1^* + {}^3O_2 \tag{3}$$

$$^3DBA_1^* \longrightarrow DBA + h\nu_p(CL) \tag{4}$$

$$2PhCHO + O_2 \quad \Delta H = 80 \ kcal/mol \tag{5}$$
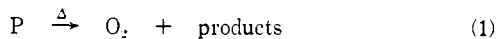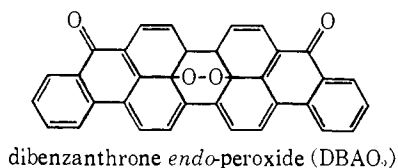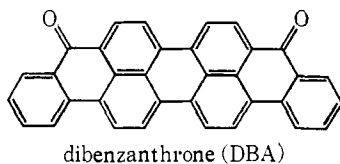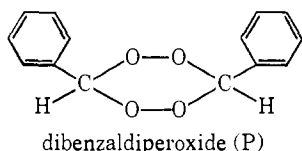
The energy is sufficient to produce either the benzaldehyde triplet (70 kcal/mol) or a singlet oxygen state ($^1\Delta_g$ at 22.5 kcal/mol, $^1\Sigma_g^+$ at 37.5 kcal/mol). Spin considerations allow formation of either species from one peroxide molecule, but not both.

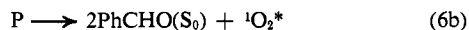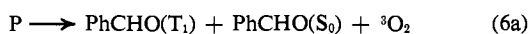$$P \longrightarrow PhCHO(T_1) + PhCHO(S_0) + {}^3O_2 \tag{6a}$$

$$P \longrightarrow 2PhCHO(S_0) + {}^1O_2^* \tag{6b}$$

Five chemiluminescent mechanisms were considered on the basis of the above, and are listed in Table I.

Table I. CL Mechanisms

A. *endo*-Peroxide mechanism[a]

(1) $P \xrightarrow{\Delta} O_2 + products$
(2) $^1A_0 + O_2 \rightarrow {}^1(AO_2)_0$
(3) $(^1AO_2)_0 \xrightarrow{\Delta} {}^3A_1^* + {}^3O_2$
(4) $^3A_1 + {}^3A_1 \rightarrow {}^1A_1^* + {}^1A_0$
(5) $^1A_1^* \rightarrow {}^1A_0 + h\nu_F$ (CL)

B. Charge-transfer complex mechanism

(1) $P + A \rightarrow [P \cdots A]$
(2) $[P \cdots A] \rightarrow products + {}^1A_1^*$
(3) $^1A_1^* \rightarrow {}^1A_0 + h\nu_F$ (CL)

C. Energy transfer from benzaldehyde triplet state

(1) $P \xrightarrow{\Delta} PhCHO(T_1) + PhCHO(S_0) + {}^3O_2$
(2) $PhCHO(T_1) + {}^1A_0 \rightarrow {}^1A_1^* + PhCHO(S_0)$
(3) $^1A_1^* \rightarrow {}^1A_0 + h\nu_F$ (CL)

D. Consecutive energy transfer from $^1O_2$ monomers

(1) $P \xrightarrow{\Delta} 2PhCHO(S_0) + {}^1O_2^*$
(2) $^1A_0 + {}^1O_2^* \rightarrow {}^3A_1 + {}^3O_2$
(3) $^3A_1 + {}^1O_2^* \rightarrow {}^1A_1^* + {}^3O_2$
(4) $^1A_1^* \rightarrow {}^1A_0 + h\nu_F$ (CL)

E. Energy transfer from singlet oxygen collisional pair

(1) $P \xrightarrow{\Delta} 2PhCHO(S_0) + {}^1O_2^*$
(2) $^1O_2^* + {}^1O_2^* \rightarrow ({}^1O_2^*)_2$
(3) $(^1O_2^*)_2 + {}^1A_0 \rightarrow {}^1A_1^* + 2{}^3O_2$
(4) $^1A_1^* \rightarrow {}^1A_0 + h\nu_F$ (CL)

[a] Where $^1A_0$ = ground singlet state of an aromatic compound (*i.e.*, dibenzanthrone).

Chemiluminescence with an excitation step involving formation of a charge-transfer complex between an intermediate species and a fluorescent aromatic compound has recently been proposed by Rauhut in his studies of the peroxyoxalate system.[3] The aromatic compound is thought to catalyze decomposition of the intermediate by providing an acceptor for the energy liberated by decomposition.

Chemiluminescence due to energy transfer from excited singlet oxygen collisional pairs to aromatic singlets in systems evolving molecular oxygen was proposed by Khan and Kasha.[4] The possibility of consecutive energy-transfer steps involving singlet oxygen with an acceptor triplet as intermediate was suggested by Ogryzlo and Pearson.[5]

Triplet–singlet energy transfer has been studied by Ermolaev and Sveshnikova[6] and Bennett.[7] Participation of such a process in solution CL was suggested by Vassil'ev[8] and by Hercules and Abbott.[9]

Nonradiative resonance energy transfer between unlike molecules in solution can be induced by coulombic or exchange interactions. The coulombic interaction can be expanded into a series of terms for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions. Only the dipole–dipole interaction has been identified experimentally.[6,7,10] The dipole–dipole interaction was treated theoretically by Förster.[11] It can occur at distances greater than collisional (20–100 Å) and is dependent on the oscillator strength of the acceptor transition. Exchange transfer has been treated by Dexter[12a] and by Inokuti and Hirayama.[12b] It is collisional and thus requires the donor–acceptor pair to be a $\leq$10–15-Å separation. It is subject to the usual spin selection rules.

Transfer from the benzaldehyde triplet to an acceptor singlet and from a singlet oxygen collisional pair to an acceptor singlet are exchange forbidden and dipole–dipole allowed. Step 1 of the singlet oxygen monomer process is forbidden by both considerations, whereas step 2 is dipole–dipole forbidden and exchange allowed. These considerations are outlined in Table II.

Experimental Section

Reagents. Dibenzanthrone was obtained from General Aniline and Film and purified by extraction into a water–xylene system. The xylene fraction was kept and the xylene removed using a rotary evaporator. The residue was recrystallized three times from methanol. The product gave absorption, fluorescence, and excitation spectra identical with that obtained using purification by column chromatography. Tetrachlorodibenzanthrone was obtained from Badische Aniline and Soda-Fabrik and purified in the same way as dibenzanthrone. Perylene was obtained from Aldrich Chemical Co., Puriss grade, and vacuum-sublimed prior to use. Scintillation grade anthracene was obtained from Pilot Chemicals, Inc., and used without further purification. 9,10-Diphenylanthracene was ob-

(4) A. U. Khan and M. Kasha, *J. Amer. Chem. Soc.*, 88, 1574 (1966).
(5) E. A. Ogryzlo and A. E. Pearson, *J. Phys. Chem.*, 72, 2913 (1968).
(6) V. L. Ermolaev and E. B. Sveshnikova, *Bull. Acad. Sci. USSR, Phys. Ser.*, 26, 29 (1962).
(7) (a) R. G. Bennett, R. P. Schwenker, and R. E. Kellogg, *J. Chem. Phys.*, 41, 3040 (1964); (b) R. E. Kellogg, *ibid.*, 47, 3403 (1967).
(8) R. F. Vassil'ev in "Progress in Reaction Kinetics," Vol. 4, G. Porter, Ed., Pergamon Press, New York, N. Y., 1967.
(9) D. M. Hercules and S. Abbott, M. I. T. Laboratory for Nuclear Science Progress Report, Dec 1966.
(10) M. N. Zwick and H. Kuhn, *Z. Naturforsch.*, 17A, 411 (1962); K. H. Drexhage, M. M. Zwick, and H. Kuhn, *Ber. Bunsenges Physik. Chem.*, 67, 62 (1963).
(11) T. Förster, *Discuss. Faraday Soc.*, 27, 7 (1959).
(12) (a) D. L. Dexter, *J. Chem. Phys.*, 21, 836 (1953); (b) M. Inokuti and F. Hirayama, *ibid.*, 43, 1978 (1965).

Table II. Spin Considerations of Energy Transfer Mechanisms

Transfer process	Exchange spin[a] requirements	Förster spin requirement (transition dipole of acceptor transitions)
$^3(PhCHO)_1^* + {}^1A_0 \rightarrow {}^1A_1^* + {}^1(PhCHO)_0$	Forbidden[b] $S_D^* \neq S_A^*$	Allowed ($^1A_0 \rightarrow {}^1A_1^*$)
$^1A_0 + ({}^1O_2^*)_2 \rightarrow {}^1A_1^* + 2{}^3O_2$	Forbidden $S_D^0 \neq S_A^0$	Allowed ($^1A_0 \rightarrow {}^1A_1^*$)
$^1A_0 + {}^1O_2^* \rightarrow {}^3A_1^* + {}^3O_2$	Forbidden[b] $S_D^* \neq S_A^*$; $S_D^0 \neq S_A^0$	Forbidden ($^1A_0 \rightarrow {}^3A_1^*$)
$^3A_1^* + {}^1O_2^* \rightarrow {}^1A_1^* + {}^3O_2$	Allowed $S_D^* = S_A^*$; $S_D^0 = S_A^0$	Forbidden ($^3A_1^* \rightarrow {}^1A_1^*$)

[a] S^0 = spin multiplicity of the ground electronic state; S^* = spin multiplicity of the excited electronic state. [b] Forbidden only in the zeroth approximation. The collisional complex formed can have varied multiplet states which fulfill the $\Delta M_s = 0$ requirement; however, the probability of such a process will be lower than for an "allowed" process.

tained from K & K chemicals and vacuum-sublimed prior to use. Rhodamine B was obtained from K & K chemicals and used without further purification. Fluorescein and its tetrabromo and tetraiodo derivatives were obtained in the form of sodium salts from Eastman Organic Chemicals and dried at 100° prior to use. Dibenzal diperoxide, di-p-chlorodibenzal diperoxide, and di-p-nitrodibenzal diperoxide were synthesized according to the method of Baeyer and Villiger[13] and recrystallized twice from benzene.

Dibenzophenone diperoxide was synthesized by ozonolysis of tetraphenylethylene according to the method of Marvel and Nichols.[14]

Solvents. Diethylene glycol (Union Carbide Chemicals), isopropylbenzene (Eastman Organic Chemicals, practical grade), n-heptanol (Aldrich Chemical Co., Puriss grade), n-hexanol (Aldrich Chemical Co., Puriss grade), chlorobenzene (Matheson Coleman and Bell, practical grade), and t-butylbenzene (Aldrich Chemical Co., practical grade) were vacuum-distilled prior to use.

Apparatus. Chemiluminescence.—Kinetics were studied using the apparatus of Figure 1. The reaction cell was a cylindrical
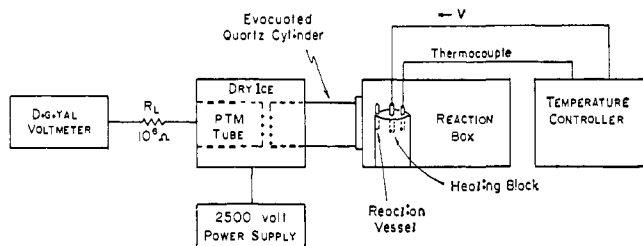
Figure 1. Light kinetics apparatus.

aluminum block into which holes were drilled to accommodate the heating block of an F and M Model 40 temperature controller, a 6 × 50 mm thermocouple tube, and a 6 × 50 mm sealed Pyrex reaction tube. The thermocouple monitored the block temperature with feedback to the temperature controller. Reaction tubes were flame-sealed, with the tube placed in liquid nitrogen. The slot for the reaction tube looked onto the face of an evacuated quartz cylinder, which provided a thermal barrier between the block and the light detector, an RCA 7265 photomultiplier tube (S-20 response). The phototube was housed in a Pacific Photometric Instruments Model 78 housing, featuring magnetic shielding of the tube and Dry Ice cooling to reduce noise. The tube was powered by a Model 2500 M Kepco power supply. The output of the tube was developed across a 10^6-ohm resistor and monitored with a Hewlett-Packard 3440A digital voltmeter with 3443A High Gain/Auto-Range plug-in unit. Chemiluminescence spectra were recorded using a fast image-intensifier spectrograph constructed in this laboratory.[2b] Spectra were recorded on high-speed Type 107 Polaroid film, which produced a positive print. Negatives were then made, suitable for densitometer recording.

Spectroscopic. Phosphorescence spectra were obtained on a system constructed from Aminco building blocks, employing an EMI 9558 QA photomultiplier tube. The spectra were corrected for monochromator-photomultiplier response. Absorption spectra were obtained on a Cary Model 14 spectrophotometer. Phos-

phorescent lifetimes, at 77°K, were determined using a 20-μsec flash lamp to excite phosphorescence and a photomultipler-oscilloscope detection system to follow the decay. Quantum yields of fluorescence were obtained on the Turner Model 210 spectrofluorometer for compounds with negligible fluorescence above 650 nm and on the Aminco–Bowman spectrophotofluorometer for compounds with fluorescence at wavelengths longer than 650 nm.

Procedures

The technique for obtaining quantum yields of fluorescence using the Turner 210 spectrofluorometer has been reported by Turner.[15] Quantum yields of fluorescence were obtained on the Aminco–Bowman spectrophotofluorometer, following the method of Parker and Rees.[16]

Light Kinetics. A sample plot of chemiluminescence intensity vs. time is shown in Figure 2. Part A corre-
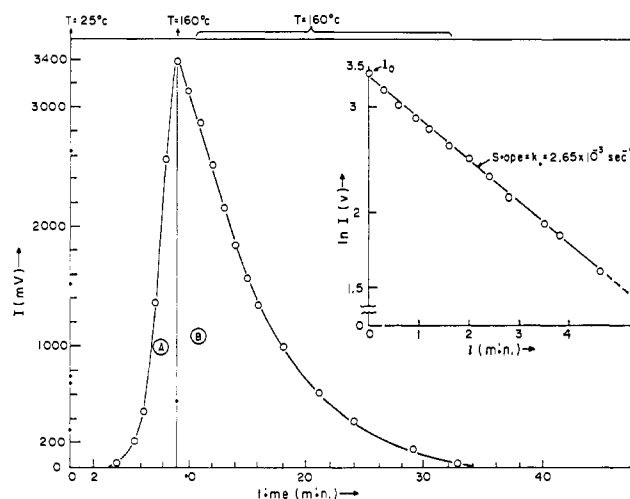
Figure 2. Intensity–time curve for the decomposition of dibenzal diperoxide in a diethylene glycol solution of perylene. Insert: log intensity–time curve for the above system.

sponds to the period before the block reaches the preset temperature T (i.e., 160°). Part B shows the decay of the CL at temperature T. The area under the I–t curve corresponds to the total quanta emitted. The time at which T is reached (peak I), where decay of I begins, is defined as zero time. To calculate the peroxide concentration at this point (P_0), the initial concentration of peroxide in the tube prior to heating is multiplied by the ratio of the area of B to the total area under the curve. Areas were determined with a planimeter. Values of Q (total quanta emitted) given in

(13) A. Baeyer and V. Villiger, *Chem. Ber.*, **33**, 2484 (1900).
(14) C. S. Marvel and V. Nichols, *J. Org. Chem.*, **6**, 296 (1941).
(15) G. K. Turner, *Science*, **146**, 183 (1964).
(16) C. A. Parker and W. T. Rees, *Analyst* (London), **85**, 587 (1960).

Table III. CL from Decomposition of Dibenzal Diperoxide (P) in Diethylene Glycol[a]

[P_0], M	k_1, sec^{-1}	Filter[b]	I_0[c]	Q[e]	ϕ_{CL}
1.47×10^{-2}	1.46×10^{-2}	None	117 ($\sim$84.5 + 18.4)		
1.40×10^{-2}	1.58×10^{-2}	485 nm	84.5	4.09×10^9	9.71×10^{-10}
			6.46×10^7 [d]		
1.38×10^{-2}	1.38×10^{-2}	600 nm	18.4	2.68×10^9	6.46×10^{-10}
			3.70×10^7 [d]		

[a] Temperature = 180°. [b] The 485 nm filter is a broad band isolation filter (half-width 140 nm) and the 600 nm filter is a sharp cutoff filter. [c] I_0 in mV, corrected for absorption by filter. [d] I_0 in quanta/sec, corrected for apparatus geometry and spectral response of photomultiplier, as discussed in the Experimental Section. [e] Q, the total chemiluminescence yield, in quanta is evaluated by: $Q = I_0 \int_0^\infty e^{-k_1 t} \, dt = I_0/k_1$.

later discussions refer to the quanta emitted in part B. A plot of ln I vs. time, at constant T, was linear as shown, indicating the decomposition to be first order.

The absolute value of a CL intensity, I (recorded in mV on the digital voltmeter), in units of quanta/sec was obtained by comparison with an equal volume of standard solution of tritiated hexadecane-^{14}C in monoisopropylbiphenyl with a scintillator mixture of PPO and POPOP.[17] As the spectral distribution of the light emitted in these experiments was somewhat different from that of the scintillator mixture, a correction factor taking into account the sensitivity of the S-20 photocathode of the photomultiplier tube was included.

Results and Discussion

CL with No Fluorescent Compound Present. Weak CL was detected from decomposition of dibenzal diperoxide in diethylene glycol, in the absence of a fluorescer. The emission was too weak to obtain a spectrum on the image-intensifier spectrograph. Utilization of
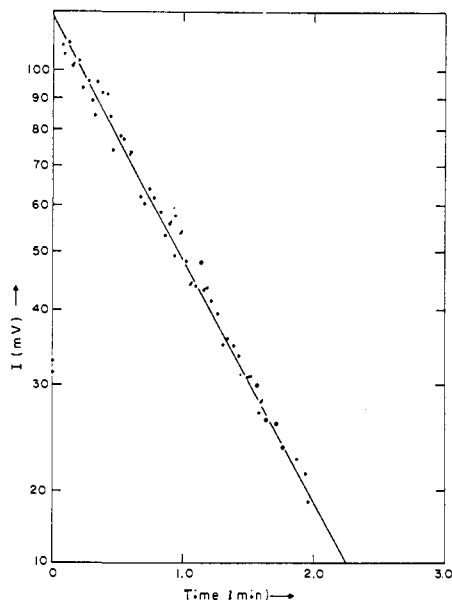

Figure 3. Decay of chemiluminescence from the decomposition of dibenzal diperoxide in a diethylene glycol, 180°, no filter present, intensity-time curve.

filters isolated two emissions: an emission appearing in the 400–540-nm region and an emission appearing to the red of 600 nm. The decay of the filtered and unfiltered emission studied at 180° was first order with a

(17) J. W. Hastings and G. Weber, *J. Opt. Soc. Amer.*, **53**, 1410 (1963).

decay constant $k_1 = 1.46 \times 10^{-2}$ sec^{-1}. A plot of ln I vs. t, where I is the intensity of emission (in mV) at time t for the unfiltered CL, is shown in Figure 3. The total quanta emitted, Q, and the quantum yield of chemiluminescence, $\phi_{CL} = Q/P_0$ (where P_0 = initial peroxide concentration), are listed in Table III.

The 400–540-nm emission lies in the region of benzaldehyde phosphorescence. The emission to the red of 600 nm is thought to correspond to phosphorescence of the excited singlet oxygen collisional pair $(^1\Delta_g)_2$, which peaks at 633.5 nm. The unfiltered emission signal, the bulk of which (80%) is due to the emission in the 400–540-nm region, due to the relatively weak spectral response of the photomultiplier at 633.5 nm, is approximately proportional in intensity to the initial peroxide concentration, as expected for benzaldehyde phosphorescence. Singlet oxygen collisional pair phosphorescence would be dependent on the square of the initial peroxide concentration, but the emission observed was too weak to allow a study of intensity vs. initial peroxide concentration.

CL in the Presence of Fluorescent Compounds. Decomposition of dibenzal diperoxide in diethylene glycol solutions of a series of fluorescent aromatic compounds at 160° produced CL of sufficient intensity to be photographed on the image-intensifier spectrograph. The CL spectrum matched the fluorescence spectrum of the aromatic compound in each case. A typical example is shown in Figure 4. For comparison of the CL yields,
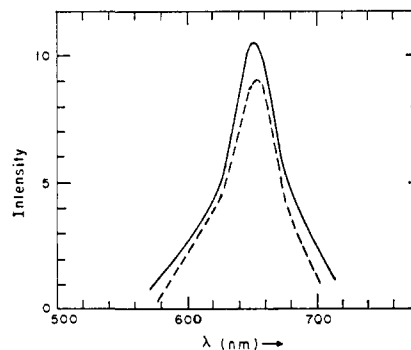
Figure 4. Chemiluminescence spectrum from the decomposition of dibenzal diperoxide in a diethylene glycol solution of dibenzanthrone (—); fluorescence spectrum of dibenzanthrone (---).

the term ϕ_e, the yield of excited state formation, was defined as the ratio of the chemiluminescence yield to the fluorescence quantum yield of the aromatic compound, normalized to a concentration of the aromatic compound of 2.55×10^{-5} M as unity.

$$\phi_e = (\phi_{CL}/\phi_F^A)(F_c) \qquad (7)$$

F_c = concentration factor = $2.55 \times 10^{-5} M/[A]$ and $\phi_{CL} = Q/P_0$.

Table IV. CL from Decomposition of Dibenzal Diperoxide in Diethylene Glycol Solution of Aromatic Compounds at 160°

Aromatic compound[a]	ϕ_F^A [b]	k_1, sec^{-1}	ϕ_e
Perylene	0.85	2.65×10^{-3}	7.74×10^{-8}
Rhodamine B	0.60	2.75×10^{-3}	3.47×10^{-8}
9,10-Diphenylanthracene	0.88	2.75×10^{-3}	1.93×10^{-8}
Anthracene	0.24	2.90×10^{-3}	1.19×10^{-8}
Fluorescein	0.79	2.65×10^{-3c}	1.76×10^{-7}
Tetrabromofluorescein	0.55	2.65×10^{-3}	1.61×10^{-7}
Tetraiodofluorescein	0.07	2.65×10^{-3}	7.40×10^{-7}
Tetrachlorodibenzanthrone	0.38	2.45×10^{-3}	6.30×10^{-6}
Dibenzanthrone	0.12	2.50×10^{-3}	8.76×10^{-5}

[a] Concentrations used were ~ 1–$3 \times 10^{-5} M$ aromatic compound, $3 \times 10^{-2} M$ peroxide. The solutions were bubbled with nitrogen prior to experiment. [b] ϕ_F^A was determined at room temperature and corrected to ϕ_F at 160° by using the approximation $\phi_F^T = \phi_F^{25°} - (1 \times 10^{-3}\Delta T)(\phi_F^{25°})$. The aromatic compounds used are fairly rigid molecules and their fluorescence yields are not expected to be greatly affected by temperature. The above approximation agrees fairly well with data on tetrabromofluorescein[18] and is assumed to hold for other rigid molecules. [c] Decomposition of fluorescein appeared to occur at ca. zero time. The reaction was run to t_0 and I_0 was recorded. The system was quenched in ice and the fluorescence measured to determine A ($t=0$). An average k_1 was assumed, and from these values, ϕ_{CL} and ϕ_e were estimated.

The observed light yields are inconsistent with those expected from an *endo*-peroxide mechanism. The tendency to form an *endo*-peroxide has been related to the reactivity of the 1,4 positions of a phenyl ring in a fused ring system.[19,20] Anthracene and 9,10-diphenylanthracene, with relatively active *meso* positions, have a strong tendency to form *endo*-peroxides.[21] Perylene, fluorescein, dibenzanthrone, and the other compounds studied should exhibit less tendency to form *endo*-peroxides. However, the light yields of the latter compounds exceed those for the anthracene compounds.

The first-order decay constant of chemiluminescence (see Figure 2 and Table IV) was independent of the particular aromatic compound present. This is inconsistent with the charge-transfer complex mechanism (mechanism B), in which the aromatic compound catalyzes peroxide decomposition. There was no obvious correlation between ionization potential and the chemiluminescence yields, as expected on the basis of Rauhut's considerations.

Confirmation of Triplet–Singlet Energy Transfer. The data of Table IV are consistent with energy transfer to the excited singlet state of the aromatic compound A from donors produced by peroxide decomposition. Possible donors are benzaldehyde triplet, singlet oxygen monomer, and singlet oxygen collisional pairs. The mechanisms are C, D, and E, respectively, of Table II. The case of triplet–singlet energy transfer (mechanism C) will now be considered.

For the case of dipole–dipole energy transfer, Förster derived an expression for R_0, the "critical" intermolec-

(18) C. A. Parker and C. G. Hatchard, *Trans. Faraday Soc.*, **57**, 1894 (1969).
(19) W. Bergman and M. J. McLean, *Chem. Rev.*, **28**, 367 (1941).
(20) Y. A. Arbuzov, *Russ. Chem. Rev.*, **34**, 558 (1965).
(21) C. Dufraisse and M. Gerard, *Bull. Soc. Chim. Fr.*, [3] **4**, 2052 (1937); *C. R. Acad. Sci., Paris*, **202**, 1859 (1936).

lar distance between donor and acceptor molecules, at which the probability of energy transfer equals the sum of the probabilities for all other deexcitation processes of the donor excited state.

$$R_0^6 = \frac{9000 \ln 10 K^2 \phi_D}{128\pi^5\eta^4 N} \int_0^\infty f_D(\bar{\nu})\epsilon_A(\bar{\nu}) \, d\bar{\nu}/\bar{\nu}^4 \qquad (8)$$

ϕ_D is the quantum yield of donor emission in the absence of acceptor, K is a geometric factor, η is the solvent refractive index, N is Avogadro's number, $f_D(\bar{\nu})$ is the donor emission distribution in quanta and normalized to unity on a wave-number scale, $\epsilon_A(\bar{\nu})$ is the molar decadic extinction coefficient of the acceptor, and $\bar{\nu}$ is the frequency wave number. The integral in the expression is termed the Förster overlap integral, $J(\bar{\nu})$. At R_0

$$k_{et}[D][A_0] = k_p[D] + k_{ic}[D][S] + k_Q[D][Q] + \ldots \qquad (9)$$

where [D] is the donor concentration, [A_0] is the "critical" acceptor concentration, and k_p, k_{ic}, and k_Q are the rate constants for phosphorescence, internal conversion, and quenching by other species. Thus

$$k_{et} = (a/\tau_D)[\phi_D J(\bar{\nu})]^{1/2} \qquad (10)$$

where

$$a = \left(\frac{4\pi N}{3000}\right)\left(\frac{9000 \ln 10 K^2}{128\pi^5\eta^4 N}\right)^{1/2}$$

and τ_D is the donor lifetime. For energy transfer from a particular donor species to different acceptors, the second-order rate constant for energy transfer, k_{et}, will be directly proportional to $[J(\bar{\nu})]^{1/2}$, and a plot of k_{et} vs. $[J(\bar{\nu})]^{1/2}$ should be linear. The chemiluminescent intensity I at time t can be expressed as

$$I = q(d[PhCHO]/dt) \qquad (11)$$

where q = CL quanta emitted/molecule of PhCHO produced. Substitution of the rate expression for eq 5 into eq 10 yields
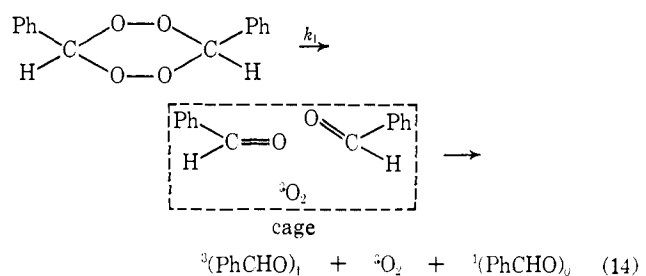
$$\ln I = \ln 2k_1 q P_0 - k_1 t \qquad (12)$$

The slope of a plot of $\ln I$ vs. time is equal to k_1. The y intercept, I_0, is equal to $2k_1 q P_0$, and thus q can be evaluated.

To determine q', defined as the number of $^1A_1{}^*$ molecules produced per molecule of PhCHO produced, one writes

$$q' = q/\phi_F^A \qquad (13)$$

where ϕ_F^A is the acceptor quantum yield of fluorescence.

For each benzaldehyde triplet molecule produced, a triplet oxygen molecule and a ground singlet benzaldehyde will be produced in its decomposition cage.

$$^3(PhCHO)_1 + {}^3O_2 + {}^1(PhCHO)_0 \qquad (14)$$

Extensive cage quenching of the benzaldehyde triplet is expected to occur and will greatly reduce the number

of triplets reaching solution. Once the triplet T_1 leaves the cage, it may be deactivated by a number of processes in solution.

Energy transfer

$$T_1 + {}^1A_0 \xrightarrow{k_{et}} {}^1A_1^* + {}^1S_0 \qquad (15)$$

Bimolecular quenching by O_2

$$T_1 + O_2 \xrightarrow{k_Q} O_2 + {}^1S_0 \qquad (16)$$

Internal conversion through solvent medium

$$T_1 + \text{solvent} \xrightarrow{k_{ic}} \text{solvent}^X + {}^1S_0 \qquad (17)$$

Phosphorescence

$$T_1 \xrightarrow{k_p} {}^1S_0 + h\nu_p \qquad (18)$$

Triplet–triplet annihilation

$$T_1 + T_1 \xrightarrow{k_{TT}} {}^1S_0 + {}^1S_1^* \qquad (19)$$

A is the acceptor, ${}^1S_0$ is the benzaldehyde ground singlet state, and ${}^1S^*$ is the benzaldehyde first excited singlet state. Applying a steady-state assumption for T_1

$$q' = \phi_T \phi_C \frac{k_{et}(A)}{k_{et}(A) + k_p + k_{ic}(\text{solv}) + k_{TT}(T_1) + k_Q(Q)} \qquad (20)$$

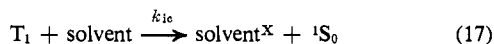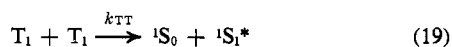where ϕ_T is the number of triplet molecules formed per total benzaldehyde molecules formed and ϕ_C is the proportion of triplets surviving cage quenching. Both k_p and k_{TT} will be much smaller than $k_{ic}(\text{solv})$ or $k_Q(Q)$, and since $k_{et}(A)$ will be small relative to $[k_{ic}(\text{solv}) + k_Q(Q)]$,[22] then

$$q' = \phi_T \phi_C \frac{k_{et}(A)}{k_{ic}(S) + k_Q(Q)} \qquad (21)$$

For the case of transfer from a particular donor species to different acceptors, in the same solvent and at the same temperature, the term $[k_{ic}(S) + k_Q(Q)]$ is a constant (K') and

$$Ck_{et} = q'/(A) \qquad (22)$$

where $C = \phi_C \phi_T/K'$. Thus, Ck_{et} can be evaluated, and since C is a constant, from eq 9, $Ck_{et} = [J(\bar{\nu})]^{1/2}$.

Values of Ck_{et} were thus determined from the chemiluminescence data. The Förster overlap integral $J(\bar{\nu})$ was evaluated graphically from the benzaldehyde phosphorescence spectrum and the absorption spectrum of each aromatic compound. The data are presented in Table V. The plot of Ck_{et} vs. $[J(\bar{\nu})]^{1/2}$, shown in Figure 5, was linear for the cases of perylene, rhodamine B, anthracene, and 9,10-diphenylanthracene. These compounds were not expected to undergo significant energy transfer by the singlet oxygen mechanisms (to be discussed later). The remaining compounds gave higher values than expected assuming triplet–singlet energy transfer from benzaldehyde to be the only mechanism operative.

Treating the dibenzal diperoxide-perylene system as a case of pure triplet–singlet energy transfer chemiluminescence, one expects the chemiluminescence yield in total quanta, Q, to be directly proportional to the initial

(22) It is expected that $k_{et} = 10^9$, and for (A) $= 10^{-5}$ M, $k_{et}(A) = 10^4$; $k_{ic}(\text{solv})$ for the triplet expected to be 10^{-6} × the spin-forbiddenness of the T–S interaction × $k_{diffusional}$ × (solv) × 10^5, and $k_Q(O_2) = 10^{5-6}$.
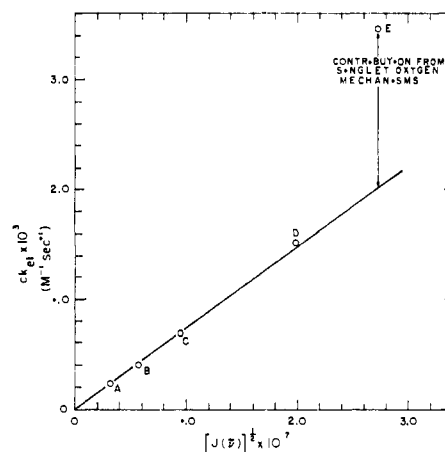

Figure 5. Plot of Ck_{et} vs. $[J(\bar{\nu})]^{1/2}$ for triplet → singlet energy-transfer chemiluminescence from the benzaldehyde triplet to aromatic acceptors: (A) anthracene, (B) 9,10-diphenylanthracene, (C) rhodamine B, (D) perylene, (E) fluorescein.

peroxide concentration P_0. The system was studied with different P_0 values in the range of 3×10^{-3}–3×10^{-2} M, and a plot of Q vs. P_0 was linear.

Table V. Chemiluminescence from Decomposition of Dibenzal Diperoxide in Diethylene Glycol Solutions of Aromatic Compounds at 160° [a]

Acceptor	Ck_{et}	$[J(\bar{\nu})]^{1/2}$
Perylene	1.52×10^{-3}	1.98×10^{-7}
Rhodamine B	6.77×10^{-4}	9.46×10^{-8}
9,10-Diphenylanthracene	3.77×10^{-4}	5.78×10^{-8}
Anthracene	2.34×10^{-4}	3.19×10^{-8}
Fluorescein	3.45×10^{-3}	2.74×10^{-7}
Tetrabromofluorescein	3.15×10^{-3}	1.32×10^{-7}
Tetraiodofluorescein	1.45×10^{-2}	1.05×10^{-7}
Tetrachlorodibenzanthrone	6.55×10^{-2}	3.15×10^{-7}
Dibenzanthrone	2.75×10^{-1}	2.29×10^{-7}

[a] Data evaluated in terms of T → S DD energy transfer from benzaldehyde triplet.

Chemiluminescence from the decomposition of dibenzophenone diperoxide, di-p-chlorodibenzal diperoxide, and di-p-nitrodibenzal diperoxide in the presence of perylene also was studied. The chemiluminescence matched the fluorescence spectrum of perylene. For the case of triplet → singlet dipole–dipole energy transfer to a particular acceptor species from different donors

$$k_{et} = a/\tau_D \sqrt{\phi_D J(\bar{\nu})} \qquad (23)$$

since

$$\phi_D = \tau_D/\tau_D^0 \qquad (24)$$

where $\tau_D^0 = $ inherent radiative lifetime of donor. Then

$$k_{et} = \left(a/\sqrt{\tau_D \tau_D^0}\right)\left(\sqrt{J(\bar{\nu})}\right) \qquad (25)$$

At the high temperature of the system, τ_D for the carbonyl compounds produced by decomposition of the corresponding cyclic diperoxide should be nearly equal. If one assumes that the term $\phi_C/k_{ic}(S) + k_Q(Q)$ does not change significantly with different carbonyl donors, then k_{et} and Ck_{et} should be approximately proportional to $\sqrt{J(\bar{\nu})}/\tau_D^0$. The data for these systems are listed in Table VI. The plot of Ck_{et} vs. $\sqrt{J(\bar{\nu})}/\tau_D^0$ is shown in Figure 6.

Table VI. Chemiluminescence from Decomposition of Cyclic Diperoxides in Diethylene Glycol Solution of Perylene at 175°

Peroxide decomposed	Donor	τ_D^0, msec[a]	k_1, sec^{-1}	Ck_{et}	$\sqrt{J(\bar{\nu})/\tau_D^0}$
Dibenzal diperoxide	Benzaldehyde	1.8	9.10×10^{-3}	1.35×10^{-3}	4.67×10^{-6}
Di-p-chlorodibenzal diperoxide	p-Chlorobenzaldehyde	1.6	4.15×10^{-3}	2.09×10^{-3}	5.35×10^{-6}
Di-p-nitrodibenzal diperoxide	p-Nitrobenzaldehyde			0^b	
Dibenzophenone diperoxide	Benzophenone	5.8	3.7×10^{-3}	6.75×10^{-4}	2.13×10^{-6}

[a] τ_D^0 determined for compound in EPA glass, $T = 77°$K, using 20-μsec flash incorporated into the photomultiplier–oscilloscope system. [b] p-Nitrobenzaldehyde has a phosphorescence quantum yield ~ 0: S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969.

The value of k_{et} was evaluated by comparison of the chemiluminescence data for decomposition of dibenzal diperoxide with acceptor present and in the absence of acceptor. In the absence of acceptor, chemilumines-
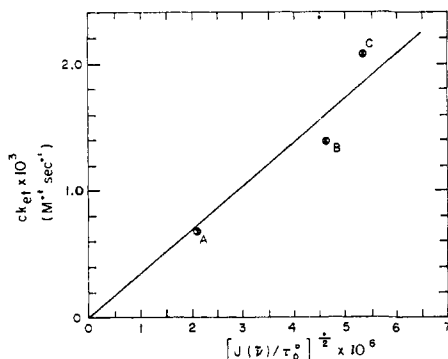

Figure 6. Plot of Ck_{et} vs. $[J(\bar{\nu})/\tau_D^0]^{1/2}$ for triplet → singlet energy-transfer chemiluminescence, perylene acceptor, carbonyl donors: (A) benzophenone, (B) benzaldehyde, (C) p-chlorobenzaldehyde.

cence is due to benzaldehyde phosphorescence. q_T is defined as the number of triplets which emit per total number of benzaldehyde molecules formed. Thus

$$q_T = (\phi_T \phi_C)(k_p/[\Sigma k_1 + \Sigma k_2(X)]) \qquad (26)$$

where ϕ_1 and ϕ_C are as defined previously, and the term in the brackets is the sum of all processes deactivating the triplet.

The yield of triplets which undergo energy transfer is equivalent to the yield of excited singlet state molecules q_A'

$$q_A' = \phi_T \phi_C \frac{k_{et}(A)}{[\Sigma k_1 + \Sigma k_2(X)] + k_{et}(A)} \qquad (27)$$

Since ϕ_T and ϕ_C are not affected by the presence of acceptor, and assuming $k_{et}(A)$ to be small relative to $[\Sigma k_1 + \Sigma k_2(X)]$, we arrive at

$$q_T/q_A' = k_p/k_{et}(A) \qquad (28)$$

$$k_{et} = \frac{k_p q_A'}{q_T(A)} = \frac{k_p(Ck_{et})}{q_T} \qquad (29)$$

For benzaldehyde, $k_p = 1/\tau_D^0 = 556$ sec^{-1}; Ck_{et} values for the CL systems at 160° are listed in Table IV. q_T at 160° in diethylene glycol was determined to be 4.92×10^{-10}. The values of k_{et} thus determined from eq 28 agree well with those expected for T → S energy transfer in fluid solution,[23] and are listed in Table VII.

(23) A. F. Vaudo and D. M. Hercules, *J. Amer. Chem. Soc.*, in press.

Table VII. Determination of k_{et} by Energy-Transfer Chemiluminescence–Decomposition of Dibenzal Diperoxide in the Presence of Fluorescent Acceptors[a]

Donor	Acceptor	k_{et}(exptl), M^{-1} sec^{-1}
Benzaldehyde	Perylene	1.72×10^9
Benzaldehyde	Rhodamine B	7.65×10^8
Benzaldehyde	Anthracene	2.64×10^8
Benzaldehyde	9,10-Diphenylanthracene	4.27×10^8

[a] Diethylene glycol solvent, at 160°.

Role of Singlet Oxygen in CL. The data of Table V indicate high CL yields for decomposition of dibenzal diperoxide in diethylene glycol containing fluorescein, tetrabromo- and tetraiodofluorescein, tetrachlorodibenzanthrone, and dibenzanthrone. The data are consistent with a CL mechanism involving energy transfer to the acceptor from a singlet oxygen species.

Singlet oxygen in either the $^1\Delta_g$ or $^1\Sigma_g^+$ state can be generated by peroxide decomposition (eq 6) and by quenching of triplet benzaldehyde by ground-state oxygen. The latter process should be more efficient in the decomposition "cage" than in solution.

Once formed, singlet oxygen can transfer its excitation energy to a suitable acceptor by a two-step mechanism (mechanism D of Table I), or through formation of a collisional pair ($^1O_2^*$)$_2$, which transfers its combined energy to an acceptor (mechanism E of Table I). Both processes are second order in oxygen.

A study of the dependency of CL yield on initial peroxide concentration in the tetrachlorodibenzanthrone system showed a second-order dependency, which thus fits a CL mechanism involving two $^1O_2^*$ states. Evidence of the existence of the ($^1\Delta_g$)$_2$ collisional pair state of oxygen was presented earlier in this paper.

Studies have been reported in the literature on the generation of singlet oxygen by radiofrequency discharge and by the reaction of chlorine and alkaline hydrogen peroxide. In an rf discharge, Noxon[24] found relative concentrations of the $(^3\Sigma_g^-):(^1\Delta_g):(^1\Sigma_g^+)$ states of 1:0.005:0.00015, and for a similar system Clyne and coworkers[25] reported the values 1:0.01:0.001. Khan and Kasha,[4] in work on the Cl_2–H_2O_2 system, detected far stronger emission at 633.5 nm $[(^1\Delta_g)_2 \rightarrow 2(^3\Sigma_g^-)]$ than at 478.0 nm $[(^1\Delta_g + ^1\Sigma_g^+) \rightarrow 2(^3\Sigma_g^-)]$, and failed to detect emission at 381.0 nm $[(^1\Sigma_g^+)_2 \rightarrow 2(^3\Sigma_g^-)]$. Abbott and coworkers[26] studied the same

(24) J. F. Noxon, *Can. J. Phys.*, 39, 1110 (1961).
(25) M. A. A. Clyne, R. P. Wayne, and B. A. Thrush, *Photochem. Photobiol.*, 4, 957 (1965).
(26) S. R. Abbott, S. Ness, and D. M. Hercules, unpublished studies, M. I. T., 1969.

Table VIII. CL Due to Singlet Oxygen Energy-Transfer Processes

Acceptor	ϕ_e'	$\sqrt{J(\bar{\nu})/(O_2)_2} \rightarrow S$	$S_0 \rightarrow T_1$	$T_1 \rightarrow S_1$	$S_0 \rightarrow S_1$, kcal/mol
Dibenzanthrone	8.75×10^{-5}	$(^1\Delta_g)_2$, 8.17×10^{-7}	?	?	47
Tetrachlorodibenzanthrone	6.18×10^{-6}	4.69×10^{-7}	?	?	49
Tetraiodofluorescein	6.99×10^{-7}	$(^1\Delta_g + {}^1\Sigma_g)$, 2.12×10^{-7}	$\sim 40^a$	13	53
Tetrabromofluorescein	1.10×10^{-7}	2.67×10^{-7}	$\sim 40^a$	14	54
Fluorescein	7.00×10^{-8}	4.27×10^{-7}	$\sim 40^a$	17	57
Perylene	~ 0	$(^1\Sigma_g)_2$	$\sim 36^b$	31	65
Rhodamine B	~ 0		~ 40 (?)	12	52
9,10-Diphenylanthracene	~ 0		39^c	33	72
Anthracene	~ 0		43^b	32	75

a K. Golnick, *Advan. Photochem.*, **6**, 1 (1968).   *b* Footnote *b*, Table VI.   *c* C. H. Ting, *Chem. Phys. Lett.*, **1**, 335 (1967).

system and recorded emission intensities at 633.5 nm and 478.0 nm in the ratio of 1:0.01, and detected emission at 381.0 nm *ca.* a factor of 10^4 weaker than the 633.5-nm emission. These studies indicate that either $^1\Sigma_g^+$ forms in much lower yields than the $^1\Delta_g$ state and/or $^1\Delta_g$ has a much greater lifetime in both gas phase and solution than $^1\Sigma_g^+$. The radiative lifetimes have been estimated by Noxon to be 7 and 3600 sec for $^1\Sigma_g$ and $^1\Delta_g$, respectively. Although thermal quenching in solution will reduce the respective $^1O_2$ state lifetimes to more similar values, the lower lifetime for $^1\Sigma_g^+$ in solution is quite plausible.

A greater lifetime of the $^1\Delta_g$ state relative to that of $^1\Sigma_g^+$ would favor energy-transfer processes involving the $^1\Delta_g$ state, as indicated by the data of Table VIII. The yield of excited state formation for transfer from the benzaldehyde triplet can be predicted from the plot of Ck_{et} *vs.* $[J\bar{\nu})]^{1/2}$ of Figure 5.[27] This value is subtracted from the observed ϕ_e (given in Table V) to give ϕ_e', the excited state yield due to singlet oxygen processes.

Considering transfer from a singlet oxygen collisional pair, spin considerations allow the dipole–dipole interaction and forbid the exchange (collisional) interaction. The transfer probability will thus depend on $J(\bar{\nu})$. Dibenzanthrone (DBA) and tetrachlorodibenzanthrone (TCDBA) have good overlap with the $(^1\Delta_g)_2$ emission. Fluorescein (F), tetraiodofluorescein (FI$_4$), and tetrabromofluorescein (FBr$_4$) have good overlap with the $(^1\Delta_g + {}^1\Sigma_g^+)$ emission and negligible overlap with the $(^1\Delta_g)_2$ emission. Anthracene, 9,10-diphenylanthracene, rhodamine B, and perylene have good overlap with the $(^1\Sigma_g^+)_2$ emission and negligible overlap with the $(^1\Delta_g)_2$ and $(^1\Delta_g + {}^1\Sigma_g^+)$ emissions. The data of Table VIII show higher ϕ_e' for compounds capable of accepting excitation energy from the $(^1\Delta_g)_2$ state than for compounds which accept excitation energy from the $(^1\Delta_g + {}^1\Sigma_g^+)$ state, and a negligible ϕ_e' for the compounds capable of accepting excitation energy from only the $(^1\Sigma_g^+)_2$ state.

Consider transfer from singlet oxygen monomers in two consecutive steps, involving an acceptor triplet intermediate, *i.e.*, mechanism D of Table I. The energy required for the $S_0 \rightarrow T_1$ and $T_1 \rightarrow S_1$ absorptions will determine which singlet oxygen state is required for steps 1 and 2, respectively. The triplet state energies of DBA and TCDBA are not known. However, Ogryzlo[5] has presented evidence that in the presence of $^1O_2^*$, DBA is excited in the two-step process involving $^1\Delta_g$ states. It is assumed that TCDBA behaves similarly.

Fluorescein and its halo derivatives have $S_0 \rightarrow T_1$ values of *ca.* 40 kcal/mol and $T_1 \rightarrow S_1$ values of *ca.* 15 kcal/mol. These energy values require a $^1\Sigma_g^+$ and a $^1\Delta_g$ state in steps 1 and 2, respectively. Perylene, anthracene, and 9,10-diphenylanthracene have $S_0 \rightarrow T_1$ values greater than 35 kcal/mol and $T_1 \rightarrow S_1$ values of greater than 30 kcal/mol. These energy values require $^1\Sigma_g^+$ states in both steps 1 and 2. The triplet value of rhodamine B should lie in the same region as the fluorescein compounds (due to structural similarity), requiring $^1\Sigma_g^+$ and $^1\Delta_g$ states in steps 1 and 2, respectively. However, the negligible ϕ_e' of rhodamine B places it in the class of compounds requiring two $^1\Sigma_g^+$ states. Its low yield may be due to other factors. Thus, with the exception of rhodamine B, the compounds follow the rule of greater transfer yield for transfers involving $^1\Delta_g$ states.

Examination of the relative yields of DBA and TCDBA and of fluorescein and its halo derivatives allows one to distinguish somewhat between the two singlet oxygen mechanisms. Whereas $[J(\bar{\nu})]^{1/2}$ for dipole–dipole transfer from $(^1\Delta_g)_2$ to DBA is about 1.7 times that for TCDBA, ϕ_e of DBA is 14 times that of TCDBA. These values can be explained by the two-step mechanism. The first step is spin-forbidden (see Table II) for both the exchange and dipole–dipole interaction. Greater spin-orbit coupling in DBA relative to TCDBA (evidenced by the respective fluorescence quantum yields of 0.14 and 0.44) would relax the forbiddenness for both types of interaction and thus enhance the transfer to DBA relative to that of TCDBA. For the fluorescein compounds, the values of $[J(\bar{\nu})]^{1/2}$ for dipole–dipole transfer from $(^1\Delta_g + {}^1\Sigma_g^+)$ are in the ratio 1.0 (F):0.63(FBr$_4$):0.45(FI$_4$), yet the values of ϕ_e' are in the ratio 1.0 (F):1.6 (FBr$_4$):10.0 (FI$_4$). This can be explained by spin-orbit coupling effects in step 1 of the two-step mechanism. The internal heavy atom effect due to the Br and I atoms greatly enhances spin-orbit coupling.[28]

This effect is similar to the enhancement of CL yield observed by Vassil'ev and coworkers[8] in the oxidation of hydrocarbons. Enhancement of the rate of energy transfer for 9,10-dibromoanthracene *vs.* anthracene was attributed to the heavy atom effect enhancing the exchange mechanism.

Generation of singlet oxygen by the Cl_2–alkaline H_2O_2 reaction, in ethanolic solutions of the compounds of Table VIII, produced relatively strong acceptor CL for DBA and TCDBA and moderate CL for F, FBr$_4$, and FI$_4$. No CL other than that of the $(^1\Delta_g)_2 \rightarrow$

(27) $\phi_e = 5.10 \times 10^{-5}$ (Ck_{et}). This can be derived from the relationships $I_0 = 2k_1qP_0$ and eq 7 and 21.

(28) M. Z. Hoffman and G. Porter, *Proc. Roy. Soc., Ser. A*, **268**, 46, 1962.

$2^3\Sigma_g^-$ emission was observed in solutions of perylene, 9,10-diphenylanthracene, anthracene, and rhodamine B. The data of Table VIII agree with these results.

The two-step energy transfer mechanism involving singlet oxygen monomers and the fluorescer triplet as an intermediate has thus been shown to be more significant than the singlet oxygen collisional-pair mechanism. However, the data do not rule out the presence of the collisional pair transfer. Indeed, the $(^1\Delta_g)_2$ state was shown to be produced in the systems studied.

Transfer from collisional pair states would be expected to occur to those acceptors with absorption having a high degree of overlap with the collisional pair emission.

Optical Rotatory Properties of Vinyl Copolymers[1]

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Abstract: Variation of optical rotatory properties with copolymer composition was studied for some poly-α-olefin systems comprising two optical antipodes, and for those composed of an optically active monomer and inactive comonomer with isomeric structure. Optical activities of these polymers were evaluated within the framework of the revised version of the Whiffen–Brewster empirical rule. For a copolymer chain with moderately blocked structure, poly-$(R)(S)$-4-methylhex-1-ene exhibits sizable deviation from linearity in the optical rotation *vs.* copolymer composition plot, while poly-$(R)(S)$-5-methylhept-1-ene gives a nearly linear relation. The agreement with experimental observation is satisfactory in both cases. Extension of the treatment to the copolymer system derived from (S)-4-methylhex-1-ene and 4-methylpent-1-ene or 5-methylhex-1-ene again predicts some departure from linearity. The results compare favorably with experimental data for the former system. The conformational asymmetry characteristic of a copolymer system containing a comonomer having a branched structure at the position γ (or further) to the vinyl group is also discussed.

Theoretical interpretation of optical rotatory properties of poly-α-olefins such as poly-(S)-3-methylpent-1-ene, poly-(R)-3,7-dimethyloct-1-ene, poly-(S)-4-methylhex-1-ene, poly-(S)-5-methylhept-1-ene, and poly-(S)-6-methyloct-1-ene has been presented in the preceding paper.[2] Conformational analysis based on the rotational isomeric state approximation revealed that the rigidity of the backbone chain is largely influenced by the side chain configuration. When the asymmetric site is located at the α or β position with respect to the main chain tertiary carbon, the number of conformations permitted to the skeletal chain is severely restricted, due to the high energy four-bond steric interactions. Such considerations, combined with the Whiffen[3]–Brewster[4] empirical rule, lead to the prediction of a large optical rotatory power of these polymer systems, regardless of the tacticity of the chain. When the distance between the asymmetric site and the backbone chain is further apart, the chain becomes less stiff. It was shown as a consequence that configuration along the chain may be an important factor determining the optical rotatory properties of polymers such as poly-(S)-5-methylhept-1-ene. Conformational analysis of isotactic poly-(S)-4-methylhex-1-ene has been also reported independently by Luisi and Pino.[5]

Recently optical rotatory properties of copolymers prepared from the monomer mixture comprising (R) and (S) optical antipodes were studied by Pino, Ciardelli, Montagnoli, and Pieroni.[6] When the optical activity of the polymer was plotted against the optical purity of the starting monomer, sizable deviation from linearity was observed for poly-$(R)(S)$-3,7-dimethyloct-1-ene and poly-$(R)(S)$-4-methylhex-1-ene. In the case of poly-$(R)(S)$-5-methylhept-1-ene, however, the relation was nearly linear.

Extension of our previous treatment to such copolymer systems[7] is straightforward. Copolymers of optically active monomers like (S)-4-methylhex-1-ene with inactive symmetric comonomers are also examined. The results of calculations are compared with experimental data reported by Carlini, Ciardelli, and Pino.[8]

Stereochemistry of the Polymer System

Steric interactions here considered are those between the groups separated by three and by four C–C bonds. In keeping with the previous usage,[2,9] this paper intro-

(1) Presented at the 22nd Annual Meeting of Chemical Society of Japan, Tokyo, 1969.
(2) A. Abe, *J. Amer. Chem. Soc.*, **90**, 2205 (1968).
(3) D. H. Whiffen, *Chem. Ind.* (London), 964 (1956).
(4) J. H. Brewster, *J. Amer. Chem. Soc.*, **81**, 5475 (1959).
(5) P. L. Luisi and P. Pino, *J. Phys. Chem.*, **72**, 2400 (1968).

(6) P. Pino, F. Ciardelli, G. Montagnoli, and O. Pieroni, *J. Polym. Sci., Part B*, **5**, 307 (1967).
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