dipole nature of the triplet-singlet process allows for large intermolecular distances; and consequently, the efficiency of the triplet-singlet process may be orders of magnitude larger than the triplet-triplet process in solution, which proceeds *via* an exchange mechanism. The kinetics of the thermal decomposition of various aromatic peroxides have been stuided by Abbott and Hercules,[28] using triplet-singlet energy transfer as a mechanistic tool. Recently, White, *et al.*,[32] have

(32) E. H. White, D. R. Roberts, and D. F. Roswell, "Molecular

postulated the occurrence of triplet-singlet energy transfer in the chemiluminescence of phthalic hydrazide derivatives. It will be interesting to look into the role of the triplet-singlet energy process in certain bioluminescence reactions.

Luminescence," E. C. Lim, Ed., W. A. Benjamin and Co., New York, N. Y., 1969.

Intermolecular Triplet Energy Transfer. II. From Benzene, Acetone, and Biacetyl to π-Bonded Molecules

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Abstract: The relative rates of the triplet electronic energy transfer from benzene to olefinic hydrocarbons (mono- and diolefins) and CS_2 have been measured in competition with *cis-trans* isomerization of *cis*-2-butene in the gas phase. In some cases, deuterated olefinic acceptor molecules have been used and varying degrees of deuterium isotope effects on rate have been observed. The rates of the triplet electronic energy transfer from acetone and and biacetyl to some π-bonded molecules have also been measured by the quenching of the direct phosphorescence emission. So far, CS_2 is found to be the most efficient quencher of the triplet benzene and acetone. These and other rate-energetics data will be discussed in reference to existing mechanistic models of triplet energy transfer processes.

The kinetics of the intermolecular triplet electronic energy transfer processes in the gas phase involving simple organic molecules of photochemical interest have been studied extensively in the recent years. These molecular energy transfer systems are expected to be simpler than those studied in the condensed media where the environmental effects are usually not negligible and therefore they can be used for a rigorous test of various mechanistic models in the laboratory.

Benzene in its lowest triplet state ($^3B_{1u}$) having an electronic excitation energy of 84.4 kcal/mol was first used by Ishikawa and Noyes to sensitize the phosphorescence emission from biacetyl.[1] Since then, the triplet benzene photosensitization method has been widely used for mechanistic diagnosis of primary photochemical processes,[2-6] and systematic studies of the triplet energy transfer rates involving various hydrocarbons, ketones, aldehydes and ethers as acceptors have been conducted.[2,7-9] Triplet energy transfer

from acetone to biacetyl was studied by Heicklen and Noyes[10a] 10 years ago, and the relative rates of triplet energy transfer from acetone and biacetyl, having triplet excitation energies of 79-82 and 57 kcal/mol, respectively, to a variety of olefinic molecules were measured by Rebbert and Ausloos.[10b] The observation of substantial deuterium isotope rate effects for these systems as well as for the benzene-olefin systems studied in our laboratory has been recently reported.[8] Only recently an interesting study of the H atom scrambling and *cis-trans* isomerization of dideuterioethylene sensitized by triplet benzene and its derivatives has been reported.[11]

We have carried out additional measurements of the triplet energy transfer rates from the above-mentioned donors to a few more hydrocarbons and their deuterated analogs and CS_2, and we now wish to discuss in detail the experimental fit of the rate and energetics data to existing mechanistic models.

Experimental Section

Most of the chemicals used in this work are of the same grade as those used in the earlier study[7c] and they were handled similarly. Acetylene was generated from calcium carbide and purified on a vacuum line before use. A commercial grade 1,4-pentadiene was purified by gas chromatography before use. Acetone (Baker "Analyzed") was used directly. The following deuterated olefins were obtained from Merck Sharp and Dohme of Canada and used

(1) H. Ishikawa and W. A. Noyes, Jr., *J. Chem. Phys.*, **37**, 583 (1962).
(2) (a) R. B. Cundall and D. G. Milne, *J. Amer. Chem. Soc.*, **83**, 3902 (1961); (b) R. B. Cundall, F. J. Fletcher, and D. G. Milne, *Trans. Faraday Soc.*, **60**, 1146 (1964).
(3) M. Tanaka, T. Terao, and S. Sato, *Bull. Chem. Soc. Jap.*, **38**, 1645 (1965).
(4) (a) N. E. Lee and E. K. C. Lee, *J. Phys. Chem.*, **71**, 1167 (1967); (b) E. K. C. Lee, *ibid.*, **71**, 2804 (1967); (c) H. O. Denschlag and E. K. C. Lee, *J. Amer. Chem Soc.*, **90**, 3628 (1968).
(5) R. E. Rebbert and P. Ausloos, *ibid.*, **89**, 1573 (1967).
(6) F. S. Wettack and W. A. Noyes, Jr., *ibid.*, **90**, 3901 (1968),
(7) (a) G. A. Haninger, Jr., and E. K. C. Lee, *J. Phys. Chem.*, **71**, 3104 (1967); (b) E. K. C. Lee, H. O. Denschlag, and G. A. Haninger, Jr., *J. Chem. Phys.*, **48**, 4547 (1968); (c) G. A. Haninger, Jr., and E. K. C. Lee, *J. Phys. Chem.*, **73**, 1815 (1969).
(8) M. W. Schmidt and E. K. C. Lee, *J. Amer. Chem. Soc.*, **90**, 5919 (1968), paper I in the series.

(9) A. Morikawa and R. J. Cvetanović, *Can. J. Chem.*, **46**, 1813 (1968).
(10) (a) J. Heicklen and W. A. Noyes, Jr., *J. Amer. Chem. Soc.*, **81**, 3858 (1959); (b) R. E. Rebbert and P. Ausloos, *ibid.*, **87**, 5569 (1965).
(11) S.-I. Hirokami and S. Sato, *Can. J. Chem.*, **45**, 3181 (1967).

Table I. Observed Relative Rates of Quenching the Triplet Benzene ($C_6H_6 = 2.5$ Torr and $\lambda_{ex} = 253.7$ nm)

| Quencher (Q, Torr)[a]		Competing pressure (P_c, Torr)[b]	(k_Q/k_{CB})[c]	$(\sigma_Q^2/\sigma_{CB}^2)$
CH≡CH	(0–120)	≥5 × 10²	≤0.005	≤0.004
CD₂=CD₂	(0–27)	19.3	0.13_0	0.10_9
CH₂=CD₂	(0–18)	18.0	0.13_9	0.11_3
CH₂=CH₂	(0–20)	10.6	0.23_6	0.18_7
CH₂=C=CH₂	(0–10)	10.2	0.25	0.22
CD₃—CD=CD₂	(0–18)	7.7	0.32	0.31
CH₃—CD=CD₂	(0–11)	8.5	0.29	0.28
CH₃—CH=CH₂	(0–8)	6.4	0.39	0.36
			(0.43)[d]	(0.40)[d]
CH₃—CH=CH—CH₃ (cis)			(1.00)	(1.00)
CH₂=CH—CH₂—CH=CH₂	(0–10)	2.5	1.0	1.0_6
CD₂=CD—CD=CD₂	(0–0.2)	0.18	14	14
CH₂=CH—CH=CH₂	(0–0.5)	0.18	14	14
CH₃—CH=CH—CH=CH₂ (trans)		0.16	16	17
CH₃—CH=CH—CH=CH₂ (cis)		0.15	17	18
S=C=S	(0–0.2)	0.084	30	32

[a] Pressure ranges of Q used in the experiment. [b] P_c is the pressure of the quencher molecule at which it competes equally with 2.5 Torr of cis-2-butene used in the experiment. [c] $k_Q/k_{CB} = 2.5$ Torr/P_c. [d] Average of the three literature values.[7b,c,10b]

without further purification: C_2D_4 (99 atom % D), CH₂=CD₂ (98 atom % D), C_3D_6 (99 atom % D), CH_3CDCD_2 (98 atom % D), and 1,3-C_4D_6 (98 atom % D).

The vacuum and fluorescence–phosphorescence apparatus were the same as those described earlier.[7c,12] The phosphorescence emission intensity from acetone was determined as the difference between the total observed emission intensity in the absence of O_2 and that in the presence of 5 Torr of O_2. A procedure similar to this has been used earlier by Rebbert and Ausloos.[10b] The experimental procedure and set-up for the competitive quenching study of the triplet benzene were identical with those employed in our earlier studies.[7b]

Results

The relative rate of quenching of the triplet benzene by an acceptor molecule has been monitored by the
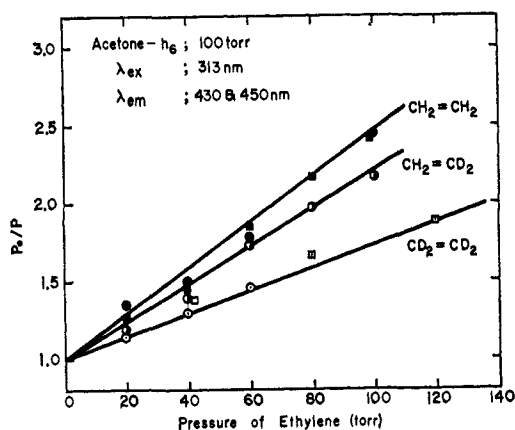
Figure 1. A Stern–Volmer plot of the acetone phosphorescence quenching as in Figure 2 but at 100 Torr of acetone: C_2H_4 (filled circles, $P_{1/2} = 129$ and 142 Torr), CH_2CD_2 (half-filled circles, $P_{1/2} = 82$ Torr), C_2D_4 (open circles, $P_{1/2} = 64$ and 72 Torr).

yields of trans-2-butene from cis-2-butene at varying quencher pressures and at 2.5 Torr each of benzene and cis-2-butene. It has been shown that eq 1 results from a linear Stern–Volmer plot, particularly at 2.5 Torr of cis-2-butene.[7b]

$$\frac{(\Phi_{c \to t})_0}{(\Phi_{c \to t})} = 1 + \frac{k_Q(Q)}{\tau_T^{-1} + k_{CB}(CB)} \approx 1 + \frac{0.40 k_Q}{k_{CB}}(Q) \quad (1)$$

(12) E. K. C. Lee, M. W. Schmidt, R. G. Shortridge, Jr., and G. A. Haninger, Jr., *J. Phys. Chem.*, 73, 1805 (1969).

Here $(\Phi_{c \to t})_0$ and $(\Phi_{c \to t})$ are the quantum yields of trans-2-butene in the absence and in the presence of the added quencher, respectively, τ_T is the lifetime of the triplet benzene in the absence of the quencher (Q), and k_Q and k_{CB} are the bimolecular quenching rate coefficients of the quencher and cis-2-butene (CB), respectively.[13] The results are summarized in Table I. Pressures of the conjugated dienes and CS_2 were low enough in the present study so that no appreciable quenching of the singlet benzene was observed.[12]

The quenching rate of an acceptor for the triplet acetone (or biacetyl) has been monitored by the variations in intensity of the phosphorescence emission directly excited by 313-nm light (or 435 nm) as a function of the quencher pressure. The result of a linear Stern–Volmer relationship is shown as

$$(P_0/P) = 1 + \tau_P k_Q(Q) \quad (2)$$

where P_0 and P are the phosphorescence intensities in the absence and in the presence of the added quencher molecules, respectively, τ_P is the phosphorescence decay time of the donor, and k_Q is the bimolecular rate coefficient for the triplet energy transfer. At the half-quenching pressure $(P_{1/2})$, $\tau_P k_Q(Q) = 1$; the values of k_Q will then be deduced from the known values of τ_P, 0.20 msec for acetone[14,15] 1.8 msec for biacetyl,[14] and the corresponding values of $P_{1/2}$. Typical results are shown in Figures 1 and 2 with the least-squares fitted lines, and they are summarized in Table II. The quenching of the acetone phosphorescence by CS_2 was measured at 0.105 and 0.50 Torr of CS_2.

Discussion

Triplet Energies and Rates

Typical accuracy of the relative rates of quenching the triplet benzene is approximately 10%. Within this accuracy of measurement, our values of k_Q/k_{CB} agree with the previously reported values for C_2H_2,[2b] C_2H_4,[7,9]

(13) A value of $k_{CB} = 1.0 \times 10^{10}$ l. mol⁻¹ sec⁻¹ has been deduced from a value of $\tau_T = 70$ μsec observed by C. S. Parmenter and his associates (see C. S. Parmenter and B. L. Ring, *J. Chem. Phys.*, 46, 1998 (1967), and footnote 25 of ref 7b). Therefore τ_T^{-1} is ∼0.01 times as large as k_{CB}(CB) at 2.5 Torr of cis-2-butene.

(14) W. E. Kaskan and A. B. F. Duncan, *ibid.*, 18, 427 (1950).

(15) A. Gandini, D. A. Whytock, and K. O. Kutschke, *Ber. Bunsenges. Phys. Chem.*, 72, 296 (1968).

Table II. Observed Relative Rates of Quenching of Triplet Acetone and Biacetyl

Quencher (Q)	Half-pressure ($P_{1/2}$, Torr)	k_Q,[a] l. mol^{-1} sec^{-1}	Half-pressure ($P_{1/2}$, Torr)	k_Q,[a] l. mol^{-1} sec^{-1}
	50 Torr of acetone		100 Torr of acetone	
C_2D_4	99	0.93×10^6	113	0.99×10^6
CH_2CD_2	69	1.34×10^6	82	1.12×10^6
C_2H_4	52	1.77×10^6	68	1.35×10^6
CS_2	~0.028	3×10^9	~0.025	4×10^9
	0.56 Torr of biacetyl		1.00 Torr of biacetyl	
1,3-C_4D_6	0.30	3.3×10^7	0.27	3.7×10^7
1,3-C_4H_6	0.12	8×10^7	0.16	6×10^7

[a] Phosphorescence lifetimes at room temperature of 0.20 msec measured at 110 Torr of acetone in the mercury-free system (ref 15) and 1.8 msec measured in 2–30 Torr of biacetyl (ref 14) were used.

and 1,3-C_4H_6;[7b,9] on the other hand, the present value of 0.39 for propylene appears to be in agreement with a value of 0.42 obtained from the sensitized biacetyl phosphorescence, but it is too low compared to the other reported values (0.53[7b] and 0.47[9]) obtained by the cis–trans isomerization method. If 0.53 is omitted for the averaging, a mean value of 0.43 is obtained and it is likely to be nearer to the true value. The most striking observation is that CS_2 is by far the most efficient quencher and that a methyl group substitution in 1,3-butadiene does not significantly enhance the triplet energy transfer efficiency as it does in C_2H_4.[7,9]

The observed half-quenching pressure of C_2H_4 for the triplet acetone at 100 Torr of acetone pressure is in good agreement with the previously reported value at 103 Torr of acetone pressure.[10b] Since the phosphorescence lifetime of acetone becomes longer at lower acetone pressure,[14,15] the observed half-quenching pressure of ethylene at 50 Torr of acetone pressure is somewhat lower than that observed at 100 Torr of acetone pressure. The change corresponds to ~20%. It is obvious that CS_2 is almost 3000 times more efficient than C_2H_4 in quenching the triplet acetone, since $P_{1/2}$ for CS_2 is ~0.03 Torr.

The observed half-quenching pressure of 1,3-C_4H_6 for the triplet biacetyl at 1.0 Torr of biacetyl and 18 Torr of propane is about 30% lower than the value obtained at 15.8 Torr of biacetyl pressure by Rebbert and Ausloos.[10b] The discrepancy is not too serious for the present purpose, since the chief difference sought here is a consistent isotopic difference between 1,3-C_4H_6 and 1,3-C_4D_6.

The values of the lowest triplet energy levels of the acceptors reported in the literature are listed in Table III,[16–24] except in the case of O_2 for which two low-lying

(16) (a) S. Trajmar, J. K. Rice, P. S. P. Wei, and A. Kuppermann, *Chem. Phys. Lett.*, **1**, 704 (1968); (b) A. Kuppermann, J. K. Rice, and S. Trajmar, *J. Phys. Chem.*, **72**, 3894 (1968).

(17) D. F. Evans, *J. Chem. Soc.*, 1735 (1960).

(18) (a) A. Kuppermann and L. M. Raff, *Discuss. Faraday Soc.*, **35**, 30 (1963); (b) J. P. Doering and A. J. Williams, III, *J. Chem. Phys.*, **47**, 4180 (1967); (c) S. Trajmar, J. K. Rice, and A. Kuppermann, *Advan. Chem. Phys.*, in press; (d) R. S. Berry, *Annu. Rev. Phys. Chem.*, **20**, 357 (1969).

(19) H. H. Brongersma, J. A. v. d. Hart, and L. J. Oosterhoff in "Fast Reactions and Primary Processes in Chemical Kinetics," S. Claesson, Ed., Interscience Publishers, New York, N. Y., 1967, p 211.

(20) R. J. Campbell, Ph.D. Thesis, Northwestern University, 1967.

(21) S. R. La Paglia and B. C. Roquitte, *J. Phys. Chem.*, **66**, 1739 (1962).

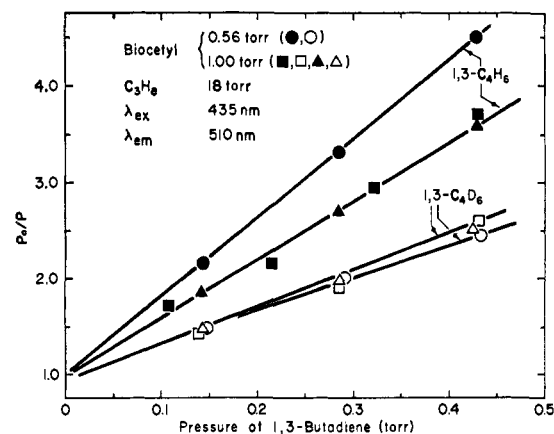(22) See G. Herzberg, "Molecular Spectra and Molecular Structure,"

Figure 2. A Stern–Volmer plot of the biacetyl phosphorescence quenching at 0.56 and 1.00 Torr of biacetyl in the presence of 18 Torr of propane as pressure stabilizer. Reciprocal emission intensity vs. pressure of isotopic 1,3-butadienes: 1,3-C_4H_6 (filled circles, $P_{1/2}$ = 0.12 Torr at BA = 0.56 Torr and $P_{1/2}$ = 0.16 Torr at BA = 1.00 Torr), 1,3-C_4H_6 (open circles, $P_{1/2}$ = 0.30 Torr at BA = 0.56 Torr and $P_{1/2}$ = 0.26 and 0.27 Torr at BA = 1.00 Torr).

singlet levels are of interest. The energy levels of the triplet donors are also listed in Table III. The 0–0 band of the S → T transition of acetone has been interpreted to be between 350 and 360 nm.[25] The observed rates of the triplet energy transfer found in this work and others[7,9,10,26] which will be correlated with the triplet energies of the acceptors are also listed in Table III.

Mechanistic Models

There is little doubt that the Wigner spin conservation rule is not violated in any serious manner for the triplet energy transfer processes under consideration. Thus we will simply express the processes in generalized forms as follows

$$^3D^* + {}^1A \longrightarrow {}^1D + {}^3A^* \tag{3}$$

or

$$^3D^* + {}^3A \longrightarrow {}^1D + {}^1A^* \tag{4}$$
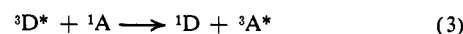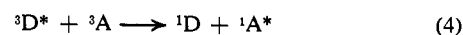
where superscripts 1 and 3 refer to the electronic spin multiplicities, the asterisk indicates an electronic excitation, D and A are donors and acceptors, respectively, and eq 4 is for the particular case of O_2 whose ground state is a triplet state, $^3\Sigma_g^-$. When the lowest triplet state benzene (E_T = 84.4 kcal/mol) is a donor and the ground state Xe,[9] CO_2,[2b] C_3H_8,[9] C_2H_2[2b] ($E_T \approx 105$ kcal/mol), and N_2O[9] (E_T = 93.3 kcal/mol) are acceptors, the energy transfer processes were either absent or greatly inefficient. Furthermore, acetylene and benzene were found to be extremely poor quenchers of the triplet state acetone,[10b] while isobutylene[27] and cis-2-butene[28] were very inefficient in quenching the triplet state biacetyl. These extremely inefficient quenchers

Vol. 3, D. Van Nostrand, Co., Inc., New York, N. Y., 1966, Appendix VI.

(23) R. E. Kellogg and W. T. Simpson, *J. Amer. Chem. Soc.*, **87**, 4230 (1965).

(24) D. F. Evans, *J. Chem. Soc.*, 1351 (1957).

(25) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

(26) R. G. Shortridge, Jr., and E. K. C. Lee, *J. Amer. Chem. Soc.*, in press.

(27) N. A. Coward and W. A. Noyes, Jr., *J. Chem. Phys.*, **22**, 1207 (1954).

(28) R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, **56**, 1211 (1960).

Table III. The Lowest Triplet Energies of Acceptors and the Triplet Energy Transfer Rates Observed in the Gas Phase at Room Temperature

Donor (E_T, kcal/mol)	Acceptor (A)		k_Q, l. mol⁻¹ sec⁻¹
	Molecule	E_T, kcal/mol	
C₆H₆ (84.4)[p]	CH≡CH	~104[a,q]	≤5 × 10⁷
	N₂O	93.3[g,r] ($^3\Pi$)	Very small[i]
	CH₂=CH₂	≤82,[b,s] ~78[c,d,q] ($^3B_{1u}$)	0.24 × 10¹⁰
	cis-2-C₄H₈	~76[d,q]	1.0 × 10¹⁰
	Cyclobutanone	~76[e,t]	0.25 × 10¹⁰ [j]
	Cyclopentanone	75–80[f]	≥0.1 × 10¹⁰ [j]
	Cyclohexanone	75–80[f]	0.26 × 10¹⁰ [k]
	4-Pentenal		4 × 10¹⁰ [l]
	CS₂	74.8 ($^3A_2$)[g,s]	32 × 10¹⁰
	1,3-C₄H₆	59.6,[b,s] 59.7[h,s]	14 × 10¹⁰
	trans-1,3-C₅H₈	59.2,[b,s] 59.2[h,s]	16 × 10¹⁰
	cis-1,3-C₅H₈	58.4[b,s]	17 × 10¹⁰
	(CH₃CO)₂	57.0 (^3B_g)[g,t]	3.8 × 10¹⁰
	O₂($^3\Sigma_g^-$)	22.7 ($^1\Delta_g$); 37.6 ($^1\Sigma_g^+$)[g,r]	~1 × 10¹⁰ [m]
Acetone (79–82)[p]	CH₂=CH₂	82,[b] 78[c,d]	~1.4 × 10⁸
	CS₂	74.8[g,r]	0.4 × 10¹⁰
	1,3-C₄H₆	59.6[b,s]	0.8 × 10¹⁰ [n]
	(CH₃CO)₂	57.0[t]	2 × 10¹⁰ [n]
	C₆H₅CH=CH₂	62.0[o,s]	30 × 10¹⁰ [n]
Biacetyl (57.0)[p]	1,3-C₄H₆	59.6[b,s]	6 × 10⁷
	C₆H₅CH=CH₂	62.0[o,s]	0.2 × 10⁷ [n]

[a] Reference 16, probable accuracy of ±0.2 eV. [b] Reference 17. [c] Reference 18, probable accuracy of ±0.2 eV. [d] Reference 19, probable accuracy of ±0.2 eV. [e] Reference 20, probable error of ±3 kcal/mol. [f] Estimated on the basis of ref 7c, 12, 20, and 21. [g] Reference 22. [h] Reference 23. [i] Reference 9. [j] Reference 4b and 4c. [k] Reference 26. [l] Reference 4a. [m] A value given in ref 7a was revised on the assumption that $^1B_{2u}$ benzene becomes $^3B_{1u}$ benzene upon collisions with O₂. [n] Reference 10. [o] Reference 24. [p] Estimated on the basis of ref 25 and references therein. [q] Onset of scattering due to energy loss in the low-energy electron impact spectroscopy. [r] Optical data from S → T absorption spectroscopy. [s] Onset of the optical S → T absorption induced by O₂ perturbation. [t] Optical data from T → S emission spectroscopy.

have their lowest triplet levels far above the triplet level of the specified donor. Therefore, a quenching mechanism requiring a strong chemical interaction, e.g., radical addition to a double bond and subsequent radical elimination—"Schenck mechanism"[29,30]—can be easily ruled out here.

It is well known that Förster's theory of radiationless energy transfer involving "coulombic interaction" has been successfully used in the interpretation of various energy transfer experiments in the condensed media.[31,32] We shall restrict our discussion to the energy transfer processes involving the ground and the first excited (singlet and triplet) states. The energy transfer efficiency is usually measured as R_0, the distance at which the transfer rate equals the normal decay rate of the donor. This efficiency is proportional to the efficiency of the donor luminescence (ϕ_D) and the spectral overlap of the donor emission with the acceptor absorption.[33] Since the triplet–triplet energy

(29) For a discussion see N. J. Turro, Photochem. Photobiol., 9, 555 (1969).

(30) M. W. Schmidt and E. K. C. Lee, J. Chem. Phys., 51, 2024 (1969). An example for a chain process was found in the gas phase.

(31) (a) T. Förster, Discuss. Faraday Soc., 27, 7 (1959), and references therein; (b) in "Modern Quantum Chemistry: Istanbul Lectures," Vol. 3, O. Sinanoğlu, Ed., Academic Press, New York, N. Y., 1965, p 93.

(32) See reviews by (a) F. Wilkinson, Quart. Rev. (London), 20, 403 (1966); (b) R. G. Bennett and R. E. Kellogg, Progr. React. Kinet., 4, 215 (1967); (c) P. J. Wagner and G. S. Hammond, Advan. Photochem., 5, 21 (1968).

(33) Förster's formulation simplifies to $R_0^6 = 8.79 \times 10^{-25} K^2 \phi_D \Omega/n^4$, where Ω is the overlap integral for the donor emission and the acceptor absorption, K is an orientation factor, and n is the index of refraction. Other useful expressions are found in ref 32b. R_0 can be very large (30–50 Å) for the following two processes

$$^1D^* + {}^1A \longrightarrow {}^1D + {}^1A^* \quad\quad (i)$$

$$^3D^* + {}^1A \longrightarrow {}^1D + {}^1A^* \quad\quad (ii)$$
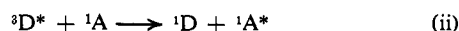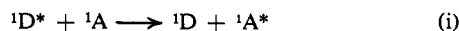
However, the process shown in eq iii, which is a complementary set of

transfer process as indicated in eq 3 is very inefficient by the coulombic interaction but can be very efficient by the "exchange interaction" formulated by Dexter,[34] we shall no longer be concerned with the former. Although the energy transfer rate by the exchange interaction is expected to be independent of the magnitude of the oscillator strength of the acceptor for the S₀ → T transition, the value of R_0 can be large, comparable with the van der Waals distance.[32]

Exchange Mechanism

Triplet–triplet energy transfer in solution has been shown to occur with unit collisional efficiency if the energy transfer was at least 3 kcal/mol exothermic,[35] and back-transfer from the acceptor to the donor occurs with a rate coefficient k_b, where k_f is the forward

$$k_b = k_f \exp(-\Delta E_T/RT) \quad\quad (5)$$

transfer rate coefficient, ΔE_T is the exothermicity of the triplet energy transfer process (eq 3), R is the gas constant, and T is the temperature.[36] According to eq 5, the back-transfer probability is only $^1/_{100}$th of the forward-transfer probability if $\Delta E_T = 2.8$ kcal/mol and T

eq ii, is expected to have a low value of R_0, because the acceptor transition is typically forbidden and Ω is relatively small.

$$^1D^* + {}^1A \longrightarrow {}^1D + {}^3A^* \quad\quad (iii)$$
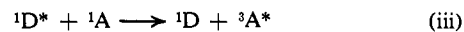
(34) D. L. Dexter, J. Chem. Phys., 21, 836 (1953).

$$n_{DA} = \frac{K^2}{h} \exp(-2R/L) \int_0^\infty f_D(\bar{\nu})\epsilon_A'(\bar{\nu}) \, d\bar{\nu}$$

where n_{DA} is the transfer rate, K and L are constants, f_D is the normalized donor luminescence, ϵ_A' is the normalized acceptor absorption, and ν is the wave number.

(35) (a) G. Porter and F. Wilkinson, Proc. Roy. Soc., Ser. A, 264, 1 (1961); (b) G. Porter and M. R. Wright, Discuss. Faraday Soc., 27, 18 (1959).

(36) K. Sandros, Acta Chem. Scand., 18, 2355 (1964).

= 300°K, and therefore it is unlikely that the inefficient energy transfer from the triplet benzene to monoolefins and carbonyl compounds in the gas phase (see Tables I and III) is due to back-transfer. Rebbert and Ausloos have already pointed out that the energy transfer processes between the triplet acetone and the conjugated dienes (1,3-butadiene and styrene) do not necessarily become more efficient with the increase in the exothermicity of the acetone.[10b] Our results obtained in the triplet benzene system certainly support a similar conclusion, because E_T for benzene is clearly higher than those for various π-bonded molecules listed in Tables I and III. For the exothermic energy transfer processes, we still need to explain why the collisional efficiencies are quite low in monoolefins and carbonyl compounds. We must first recognize the presence of a significant difference between the gas-phase encounter of the donor–acceptor pair and that in solution, since a cage is absent in the gas phase. For example, the donor–acceptor pair in the fluid or rigid medium is held in a fixed position for a long time compared to the time scale of molecular vibrations or rotations; the collision complex for the triplet acetone–2-pentene pair in solution at room temperature has been estimated to have a relatively long lifetime, $\sim$0.2 $\times$ 10^{-9} sec.[37] On the other hand, the duration of a hard-sphere collision between two simple molecules at room temperature can be estimated as only $\sim$5 $\times$ 10^{-13} sec,[38] and the unusually long-lived complexes found in the crossed molecular beam experiments have lifetimes either close to or longer than one rotational period of such a complex, 5 $\times$ 10^{-12} sec.[39] If the lifetime of the collision pair (triplet benzene–monoolefin) is comparable to those observed in the beam experiments, then it is much shorter than the lifetime of the collision pair studied typically in solution or the time scales involved in the measurement of the energy transfer in the frozen medium.[32,37] Therefore, to some extent, one must expect the collisional energy transfer efficiency in the gas phase to be determined by the duration of the actual collision complex.

One of the rate-determining factors in the collisional energy transfer in the gas phase is then the mean lifetime of the excited donor–acceptor pair ($\tau_{DA}*$), for which little direct experimental information is available. However, it is very unlikely that this lifetime-limiting factor *alone* can adequately account for the factor of 20 variation in the triplet energy transfer cross section (from the triplet benzene to ethylene and tetramethylethylene), since propylene, 1-butene, 1-pentene, and ethyl vinyl ether have practically identical values of the energy transfer cross section.[7] The interaction potential parameters involving the three monoolefins and the olefinic ether must be sufficiently different to provide a significant increase in $\tau_{DA}*$ for the 1-pentene–benzene pair compared to the propylene–benzene pair.[40] One expects the mean dissociative lifetime of the vibrationally excited, deuterated hydrocarbons (and radicals) to

be longer since the specific rate constant for these species have been found to be lower in general.[41] Thus, the fact that the triplet energy transfer cross section of C_2D_4 is smaller than that of C_2H_4 by a factor of 1.7 (see Table I for other comparisons) implies the presence of an additional and more important isotope effect in the opposite direction. It should also be mentioned that the deuterium isotope effect for the pairs $^3(C_6H_6)$–1,3-butadiene and –1,3-butadiene-d_6 disappears. So, it is reasonable to argue that the cross-section variation due to the variation in $\tau_{DA}*$ is of minor importance in the systems just discussed.

The other rate-determining factor to consider in the collisional triplet energy transfer in the gas phase is the extent of the spectral overlap between the donor emission and the acceptor absorption as proposed briefly in our first paper.[8] We shall discuss it in the context of Dexter's formulation of the exchange interaction model.[32,34] This kind of theoretical treatment has also been given recently to a triplet energy transfer system where *cis*- and *trans*-stilbene were used as acceptors in solution.[42,43] We will regard the donor emission intensity plotted in linear energy scale as a donor deexcitation function and analogously the acceptor absorption intensity plotted in linear energy scale as an acceptor excitation function. The former for the $T_1 \rightarrow S_0$ transition is obtained from phosphorescence emission studies, while the latter for the $S_0 \rightarrow T$ transitions is obtained from direct or O_2-induced optical absorption measurement[17,24] or from electron impact spectroscopy.[18,19] Particularly, the electron scattering measurement could be better than the optical one for obtaining the excitation spectrum, since the former is free from a complication due to the charge transfer spectra and the O_2 absorption in the latter; furthermore, the transition to the spin-forbidden state is no longer forbidden in the former whereas the intensity of the transition in the latter is dependent on the O_2 pressure.[24] Of course, all of these transitions must obey the Franck–Condon principle, and therefore the shape of the excitation and deexcitation functions is a measure of the Franck–Condon factors involved.

The extent of the overlap between the excitation and deexcitation functions held responsible for the observed variation in the triplet energy transfer rates from the triplet benzene to C_2H_4 and 1,3-butadiene (or to C_2H_4 and C_2D_4) has already been illustrated in Figure 2 of our paper I.[8] An analogous illustration for the triplet energy transfer involving the triplet acetone and biacetyl as donors and the ground state 1,3-butadiene and styrene as acceptors is worthwhile for this discussion and it is shown in Figure 3. Recalling that the normalized excitation functions are to be used in the calculation of the overlap with the deexcitation function,[34] it is clear that the biacetyl phosphorescence spectrum overlaps better with that of 1,3-butadiene than it does with that of styrene. Therefore, the value of k_Q for biacetyl–1,3-butadiene is expected to be greater than that for biacetyl–styrene, and the former is observed to be greater than the latter by about a factor of 30, as shown in Table III.[10b] The spectral overlaps of the

(37) R. F. Borkman and D. R. Kearns, *J. Amer. Chem. Soc.*, **88**, 3467 (1966).

(38) See S. W. Benson, "The Foundations of Chemical Kinetics," McGraw-Hill Book Co., New York, N. Y., 1960, p 155.

(39) (a) D. O. Ham and J. L. Kinsey, *J. Chem. Phys.*, **48**, 939 (1968); (b) Y. T. Lee, J. D. MacDonald, P. R. LeBreton, and D. R. Herschbach, *ibid.*, **49**, 2447 (1968).

(40) See D. L. Bunker, "Theory of Elementary Gas Reaction Rates," Pergamon Press, New York, N. Y., 1966, Chapter 4.

(41) See B. S. Rabinovitch and D. W. Setser, *Advan. Photochem.*, **3**, 1 (1964).

(42) A. Bylina, *Chem. Phys. Lett.*, **1**, 509 (1968).

(43) W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).
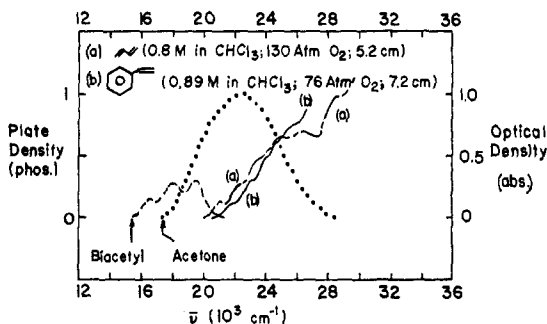
Figure 3. Right, absorption spectra of 1,3-butadiene and styrene recorded by Evans; left, emission spectra of acetone and biacetyl, uncorrected for the spectral sensitivity of the luminescence detector.

acetone phosphorescences with the excitation spectra of 1,3-butadiene and styrene are similar and occur over the upper third of the energy scale. Thus, the value of k_Q for acetone–1,3-butadiene and acetone–styrene can be expected to be nearly equal, but the former is smaller than the latter by a factor of $\sim$40 as shown in Table III.[10b] Obviously, one of the problems in estimating the extent of the overlap is the normalization of the excitation function for the first $S_0 \rightarrow T$ transition, and the spectra shown in Figure 3 were not properly normalized, since the location and the shape at the blue end of the transition are not well defined.[17,24,44] Another plausible source of complication is the solvent shift of the 1,3-butadiene spectra for the $S_0 \rightarrow T$ transition, since for the $S_0 \rightarrow S_1$ transition the liquid spectrum is red shifted as much as 1800 cm^{-1} from the gas spectrum.[12,17]

Of course, the present difficulty can be overcome to some extent,[44] if a comparison of the k_Q's for the same acceptor but with different donors is made. The energy transfer efficiency from acetone to 1,3-butadiene is at least two orders of magnitude greater than that from biacetyl to 1,3-butadiene (see Table III). Similarly, the energy transfer efficiency from acetone to styrene is five orders of magnitude greater than that from biacetyl to styrene. This latter example is very striking, since the overlap of the biacetyl spectra with styrene occurs near the threshold region of the styrene excitation spectra. Such an example was found earlier for the benzene–ethylene system.[8] It is also worth noting that the acetone phosphorescence profile overlaps well, but not entirely, with the presumed $S_0 \rightarrow T_1$ excitation spectra of biacetyl, if the latter is assumed to be the mirror image of the biacetyl phosphorescence as shown in Figure 3. Thus, the collision efficiency of $^1/_{10}$ for the transfer of the triplet excitation from acetone to biacetyl[10a] is quite reasonable.

The general lack of efficiency in the triplet benzene–cyclic ketone system, a collisional efficiency of $^1/_{100}$, can be rationalized on the basis of poor overlap,[45] and it is

likely to be so for many saturated ketones with similar excitation functions. The triplet energy transfer efficiency from benzene to biacetyl improves at least by a factor of 20, a collisional efficiency of $\sim$0.2, and it can be rationalized on the basis of an improved overlap.[46] It is generally accepted that aliphatic aldehydes have the triplet states at somewhat lower level than aliphatic ketones, but the triplet level and the excitation spectra for an unsaturated but unconjugated aldehyde are not known. Since the k_Q value of 4-pentenal is comparable to that of biacetyl, the favorable overlap for 4-pentenal is either due to its high value of the excitation function in the overlapping energy region or its low value of E_T, compared with aliphatic ketones. It should also be noted that K_Q for 1,4-pentadiene is greater than the value for propylene (or 1-pentene) by a factor of $\sim$2–3.

It is interesting to note that O_2 has a low collisional quenching efficiency of $\sim$0.03 for the triplet benzene. The reason again may lie in the fact that the excitation spectrum of O_2 for the $^3\Sigma_g^- \rightarrow {}^1\Sigma_g^+$ ($\sim$7600 Å) transition overlaps poorly with the benzene phosphorescence spectrum and the overlap for the $^3\Sigma_g^- \rightarrow {}^1\Delta_g$ is even worse. An additional factor contributing to the low efficiency could be the spin statistical factor ($^1/_9$) in the case of the triplet benzene–triplet O_2 pair.[35b] It is most likely that the energy transfer process 4 involving the $^1\Sigma_g^+$ state is favored over that involving the $^1\Delta_g$ state on the basis of the exchange interaction, but there is no definitive evidence for it.[47]

The unit collisional efficiency observed for the triplet benzene–CS_2 pair is very interesting, since CS_2 has a low-lying triplet state (26,187 cm^{-1})[22] and its optical excitation spectrum in the gas phase overlaps well only in the upper half of the benzene phosphorescence spectra. Therefore, its high efficiency appears anomalous to the expectations of the exchange interaction, since 1,3-butadiene and 1,3-pentadienes are somewhat less efficient than CS_2 even though these conjugated dienes have better overlaps than CS_2. Therefore, this anomaly for CS_2 suggests that an additional interaction mechanism such as coulombic interaction may be operative due to the relaxation of the spin-forbiddenness in CS_2.

Deuterium Isotope Effect

A large deuterium isotope effect, $k_Q^H/k_Q^D \approx 2$, observed for the values of k_Q with the benzene–ethylene, acetone–ethylene, and biacetyl–1,3-butadiene systems has been explained earlier as the near-threshold phenomena,[8] since a substantial deuterium isotope effect is observed near the threshold of absorption spectra. In addition to an isotope shift for the zero-point energy levels, an isotope effect on the vibrational overlap is introduced.[22] Thus, absorption coefficients for many deuterated organic molecules near the absorption threshold are appreciably low compared with those for protonated molecules, and often this trend continues over a wide spectral region. Such isotope effects on the Franck–Condon factors have been observed

(44) The present difficulty may disappear when the appropriate excitation functions can be measured by electron impact spectroscopy, since the intensity of the transition does rise and fall like a broad peak.[18,19] The excitation functions of C_2H_4 and cis-2-C_4H_8 obtained by the electron spectroscopy in the gas phase are clearly normalizable,[19] and thus they can be of value when the presently lacking energy resolution improves.

(45) The benzene phosphorescence emission starts below 29,000 cm^{-1} for all practical purposes (see Figure 2, ref 8), and the 0–0 band of the $S_0 \rightarrow T$ transition of cyclic ketones is estimated to be near that of acetone around 28,000 cm^{-1} (ref 25). Thus the overlap region is only $\sim$1000 cm^{-1}.

(46) The 0–0 band of the $S_0 \rightarrow T$ transition for biacetyl is at 19,900 cm^{-1} and therefore the overlap with the benzene phosphorescence spectra should be reasonably good. A phosphorescence excitation spectrum of biacetyl would be useful but is not available at present.

(47) (a) D. R. Snelling, Chem. Phys. Lett., 2, 346 (1968); (b) see also A. U. Kahn and D. R. Kearns, Advances in Chemistry Series, No. 77, American Chemical Society, Washington, D. C., 1968, p 143. The $T_1 \rightsquigarrow S_0$ intersystem crossing enhanced by the ground state O_2 is not an efficient process.

for CH$_3$Br-CD$_3$Br,[48] C$_2$H$_4$-trans-C$_2$H$_2$D$_2$-C$_2$D$_4$,[17] n-C$_4$D$_{10}$,[49] and C$_2$H$_6$-C$_2$D$_6$.[50] As shown in Tables I and II, the deuterium isotope effects observed with partially deuterated olefins fall between the normal and completely deuterated olefins. More quantitative evaluation requires higher precision than that obtained in the present work, and therefore we will consider our results on the partially deuterated olefins to be qualitatively consistent with the others. It is significant to recognize that the deuterium isotope effect observed in the benzene-propylene system is only $^1/_3$ of that observed in the benzene-ethylene system and furthermore the isotope effect disappears entirely in the benzene-1,3-butadiene system. However, the deuterium isotope effect in 1,3-butadiene reappears when the triplet donor is biacetyl. All of these observations are entirely consistent with the preceding interpretation; the extent of the overlap near threshold affected by the Franck-Condon factors is an important rate-controlling factor in the triplet energy transfer. Although the S$_0 \rightarrow$ T excitation spectra for the deuterated propylenes and 1,3-butadienes are not available for examination, a substantial deuterium isotope effect in the absorption coefficients near the threshold region must be present. However, the fact that an intermolecular deuterium enhancement of fluorescence and phosphorescence from biacetyl has been observed recently in the condensed media using C$_6$H$_6$ and C$_6$D$_6$ as environmental bath molecules[51] cannot be rationalized in the present context.

Temperature Dependence of k_Q

The temperature effect on k_Q has been measured for the triplet benzene-olefin system by Morikawa and Cvetanović.[9] An activation energy difference of 2 kcal/mol between ethylene and tetramethylethylene was observed. One way to view this temperature effect within the context of the exchange interaction is to consider it to be a development of a hot band (or bathochromic shift) in the acceptor excitation spectra due to the temperature increase. Since the temperature effect on the lifetime of the triplet benzene is not known, it is very difficult to understand what the observed activation energy difference means in terms of the lifetime of the donor-acceptor pair and the efficiency of the energy transfer within the lifetime of this collision pair.

Comparison with Atomic Donors

It is a well-known fact that the triplet energy transfer from Hg (^{3}P$_1$, E_T = 112.7 kcal/mol) to an olefin or ketone has a unit collisional efficiency.[52] Furthermore, the energy transfer efficiency from the triplet cadmium (^{3}P$_1$, E_T = 87.7 kcal/mol) to an olefin (including acetylene) is virtually invariant.[53] With an exception of the

Cd-acetylene system, the rest of the energy transfer systems are entirely exothermic, and therefore high energy transfer efficiencies are expected from the exchange interaction due to the sharp line emission given off by these excited atoms. Since acetylene has a value of E_T = 104 kcal/mol,[16] it is not entirely clear that the quenching process involving the triplet cadmium atom and olefins is truly a triplet-triplet energy transfer process.

Other Mechanisms

An energy transfer mechanism involving an excitation of an acceptor via a nonvertical (or Franck-Condon forbidden) transition has been invoked to rationalize the unexpectedly efficient energy transfer for an endothermic process involving a sensitizer and cis-stilbene as an acceptor in solution.[29,32c,44,54] It has been argued recently that "nonvertical" mechanism is either unnecessary[42,43] or that it could be a consequence of an exciplex formation and is thus an intermediate case between the energy transfer mechanism and the Schenck mechanism.[29] We find it unnecessary to invoke the nonvertical mechanism to account for the triplet energy transfer data presented here.

One interesting consequence of a triplet exciplex formation is as follows. The energy transfer from the triplet donor moiety to the acceptor moiety can be viewed as an act of intramolecular radiationless excitation transfer and the theory of the radiationless transitions can be used to examine the energy transfer rates.[55-59] It is consistently observed that the greater the rate of the intramolecular radiationless relaxation processes (S$_1 \leadsto$ T$_1$, T$_1 \leadsto$ S$_0$, S$_2 \leadsto$ S$_1$), the less the energy gap between the two electronic states concerned, since the Franck-Condon factor dominates over other rated-etermining factors. Therefore, the rates of the intramolecular energy transfer within the exciplex lifetime should be slower, if the energy gap between the two triplet moieties [$\Delta E_T \approx E_T$(donor) $- E_T$(acceptor)] is larger, in contradiction to the present experimental observation. Furthermore, the rate of the intramolecular radiationless relaxation for the aromatic and carbonyl compounds becomes slower with the deuterium substitution and the deuterium rate isotope effect becomes more pronounced with the increasing energy gap.[8,51,55-57,60-62] This expectation is also in contradiction to the present experimental observation.

(48) A. A. Gordus and R. B. Bernstein, *J. Chem. Phys.*, 22, 790 (1954).

(49) H. Okabe and D. A. Becker, *ibid.*, 39, 2549 (1963).

(50) (a) C. Sandorfy, B. Lombos, and P. Sauvageau, *Coll. Spectrosc. Int. Proc. 13th*, 370 (1968); (b) B. Lombos, P. Sauvageau, and C. Sandorfy, *J. Mol. Spectrosc.*, 24, 253 (1967).

(51) N. J. Turro and R. Engel, *J. Amer. Chem. Soc.*, 90, 2989 (1968).

(52) (a) R. J. Cvetanović, *Progr. React. Kinet.*, 2, 67 (1964); (b) A. B. Callear in "Photochemistry and Reaction Kinetics," by P. G. Ashmore, F. S. Dainton, and T. M. Sugden, Ed., Cambridge University Press, London, 1967, p 133.

(53) S. Tsunashima and S. Sato, *Bull. Chem. Soc. Jap.*, 40, 2987 (1967).

(54) G. S. Hammond and J. Saltiel, *J. Amer. Chem. Soc.*, 85, 2515, 2516 (1963).

(55) (a) G. W. Robinson and R. P. Frosch, *J. Chem. Phys.*, 37, 1962 (1962); (b) G. W. Robinson and R. P. Frosch, *ibid.*, 38, 1187 (1963); (c) G. W. Robinson, *ibid.*, 47, 1967 (1967).

(56) (a) E. F. McCoy and I. G. Ross, *Aust. J. Chem.*, 15, 573 (1962); (b) G. R. Hunt, E. F. McCoy, and I. G. Ross, *ibid.*, 15, 591 (1962).

(57) (a) W. Siebrand, *J. Chem. Phys.*, 46, 440 (1967); (b) W. Siebrand and D. F. Williams, *ibid.*, 43, 403 (1967); (c) W. Siebrand, *ibid.*, 47, 2411 (1967); (d) W. Siebrand in "The Triplet State," A. B. Zahlan, Ed., Cambridge University Press, London, 1967, p 31.

(58) D. P. Chock, J. Jortner, and S. A. Rice, *J. Chem. Phys.*, 49, 610 (1968).

(59) R. E. Kellogg and N. C. Wyeth, *ibid.*, 45, 3156 (1966).

(60) See S. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1969.

(61) G. M. Breuer and E. K. C. Lee, *J. Chem. Phys.*, 51, 3615 (1969); the rate of the S$_1 \leadsto$ T$_1$ intersystem crossing for C$_6$H$_6$ in the gas phase is greater than the rate for C$_6$D$_6$ by approximately a factor of 2.

(62) (a) D. R. Coulson and N. C. Yang, *J. Amer. Chem. Soc.*, 88, 4511 (1966); (b) N. C. Yang, S. L. Murov, and T.-C. Shieh, *Chem. Phys. Lett.*, 3, 6 (1969).

Therefore, it is difficult to use an exciplex model to explain the intermolecular triplet energy transfer processes in the gas phase as presently discussed.

Future Studies

The exchange interaction mechanism has given the most satisfactory account of most of the observed rate data and the spectral data for the intermolecular triplet energy transfer processes in the gas phase. In order to test this mechanism more thoroughly, however, more precise and extensive rate measurements must be carried out and a consistent and precise set of the electron energy-loss cross section measurements for all of the acceptor molecules concerned must be obtained. Particularly, isotopic substitution studies would be extremely valuable. It would also be useful to study the temperature effects on rates, provided that the necessary lifetime data for the excited donor molecules at varying temperatures are available.

Intramolecular Excimer Formation and Fluorescence Quenching in Dinaphthylalkanes[1]

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Abstract: The fluorescence spectra of various dinaphthylalkanes have been studied over the temperature range -100–$100°$. Strong intramolecular excimer formation is found only in the two symmetrical 1,3-dinaphthylpropanes, which implies that the stable excimer configuration is the symmetrical sandwich arrangement. Thermally activated self-quenching of fluorescence is important only in the two species which form stable excimers. The quenching path probably does not involve intersystem crossing to a triplet state and transient photodimer formation is suggested.

The question of the geometry of an excimer consisting of two identical (or nearly so) aromatic hydrocarbon nuclei has been discussed in the literature but has been largely unapproached from an experimental viewpoint. A sandwich configuration with an interplanar spacing less than the normal graphite distance of 3.5 Å was suggested by Ferguson[2] in his study of the pyrene crystal fluorescence. However there has been little work done to determine if there is a preference for a particular orientation of the two hydrocarbon nuclei with respect to each other and what such a preference might be. Various theoretical treatments[3-5] of the excimer pair have favored the symmetrical sandwich configuration which gives the largest exciton splitting. However Birks has suggested[6] that the preferred orientation might have one molecule displaced considerably (*ca.* 1.4 Å) from the other, along one of the molecular axes, so as to minimize van der Waals repulsion between corresponding carbon atoms in the two molecules.

The geometry of the excimer pair in the crystal is not necessarily that which would be favored in solution because of the constraints imposed by the lattice. Similarly, the geometries of the various ground state anthracene pairs in rigid glasses do not fix the geometries of the excimers although one can make some qualitative statements regarding the latter. Thus the anthracene pair, produced by the photolytic dissociation of dianthracene in a rigid glass, is known to have the symmetrical (long and short axes parallel) sandwich arrangement in the ground state.[7,8] It is unlikely that there could be any large rotation about the axis perpendicular to both rings during the lifetime of the excited state, simply because of the high viscosity of the surrounding medium. However one cannot preclude the possibility of small rotations and/or translations during conversion to the excimer. In this case the lifetime[9] (about 20 times the monomer lifetime) of the excimer indicates that the molecular axes must be essentially parallel. This is in accord with the prediction of the simple exciton model where the transition from the lower lying level to the ground state has no transition moment and is forbidden. A small rotation would increase the transition moment, as has been suggested by Chandra and Lim.[3]

The ground state sandwich dimer of 9,10-dichloroanthracene in a rigid matrix at low temperature is rather different from that of anthracene; here the molecular axes are angled at 60°.[8] This is presumably a reflection of van der Waals repulsion between adjacent chlorine atoms. These interactions would be even

(1) Presented in part at the 156th National Meeting of the American Chemical Society, Division of Physical Chemistry, Atlantic City, N. J., Sept 1968.
(2) J. Ferguson, *J. Chem. Phys.*, **28**, 765 (1958).
(3) A. K. Chandra and E. C. Lim, *ibid.*, **49**, 5066 (1968).
(4) J. N. Murrell and J. Tanaka, *Mol. Phys.*, **4**, 363 (1964).
(5) F. J. Smith, A. T. Armstrong, and S. P. McGlynn, *J. Chem. Phys.*, **44**, 442 (1966), and preceding papers.
(6) J. B. Birks, *Nature*, **214**, 1187 (1967).

(7) E. A. Chandross, E. G. MacRae, and J. Ferguson, *J. Chem. Phys.*, **45**, 3546 (1966).
(8) E. A. Chandross and J. Ferguson, *ibid.*, **45**, 3554 (1966).
(9) N. Mataga, Y. Torihashi, and Y. Ota, *Chem. Phys. Lett.*, **1**, 385 (1967).