

posed effect due to accompanying changes in σ_w and in σ_E . It is interesting, however, to note that the chloroform in III, as compared with those in the other solvents, shows the marked pressure shift, since the aromatic solvent shifts (ASIS) of chloroform resonance induced by I, II, and by III are shown to be nearly identical with each other at ordinary pressure.⁵ Thus the observation (d) can hardly be explained by the simple model in which the chloroform proton in III is located much closer to the ring and consequently displays much larger pressure shift. One plausible explanation may be that the approach of the chloroform proton, with increasing pressure, to the ring of III overcrowded on its periphery with bulky side chains might be allowed only in the limited region near the sixfold axis of the ring where the proton feels the highest diamagnetic field.

Continuing studies, examining the pressure dependence of chloroform resonance in various solvents in relation to the density changes of the solutions are now being carried out, and a more detailed discussion will appear in the near future.

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(5) H. Yamada, T. Ishihara, and T. Kinugasa, unpublished data.

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Quantum Chain Processes. A Novel Procedure for Measurement of Quenching Parameters. Evidence That Exothermic Triplet-Triplet Energy Transfer Is Not Diffusion Limited and an Estimation of the Efficiency of Exothermic Quenching in a Solvent Cage

Sir:

The assumption of diffusion-limited exothermic triplet-triplet energy transfer in fluid organic solvents has allowed the calculation of the lifetimes of electronically excited molecules and the rate constants of many important photochemical processes.¹ However, inspection of the literature reveals that the assumption of diffusion controlled quenching is moot.² One of the

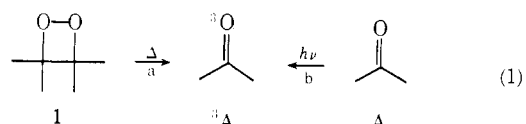
(1) For an excellent review see A. A. Lamola in "Energy Transfer and Organic Photochemistry," Wiley-Interscience, New York, N. Y., 1969.

(2) (a) For examples supporting the contention that exothermic triplet-triplet energy transfer is diffusion limited in low viscosity organic solvents see G. Porter and F. Wilkinson, *Proc. Roy. Soc., Ser. A*, **264**, 1 (1961); K. Sandros, *Acta Chem. Scand.*, **18**, 2355 (1964); A. D. Osborne and G. Porter, *Proc. Roy. Soc., Ser. A*, **264**, 9 (1965). These papers appear to assume high fluidity ($\eta \sim 0.01$ P) and a transfer exothermicity of $\sim 2-3$ kcal/mol. (b) For a contrasting point of view see P. J. Wagner, *J. Amer. Chem. Soc.*, **89**, 5715 (1967); P. J. Wagner and I. Kochevar, *ibid.*, **90**, 2232 (1968); K. S. Y. Lau, R. O. Campbell, and R. S. H. Liu, *Mol. Photochem.*, **4**, 315 (1972). In these latter studies only indirect evidence for nondiffusion limited triplet-triplet transfer was presented. (c) Research concerned with the occurrence of pure steric effects on the rate constant for exothermic triplet-triplet energy transfer is presently an active area and has resulted in both positive [P. J. Wagner, M. J. May, A. Haug, and D. R. Graber, *J. Amer. Chem. Soc.*, **92**, 5268 (1970); C. C. Wamser and P. L. Chang, *ibid.*, **95**, 2044 (1973)] and negative [P. J. Wagner, J. M. McGrath, and R. G. Zepp, *ibid.*, **94**, 6883 (1972), and references therein] results.

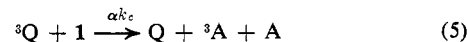
problems which arises in evaluating the reported data is the variation of methods employed to measure the important quantity k_q , the rate constant for quenching.³

The key idea of this report is that if a quantum chain reaction (a chain reaction in which electronic excitation is cycled through a number of steps) occurs, then the measurement of Stern-Volmer triplet quenching kinetics can lead to observed $k_q\tau$ values which differ significantly from the $k_q\tau$ values measured in the absence of a quantum chain. The difference between these measured $k_q\tau$ values can lead to information on the nature of the electronically excited triplet quencher 3Q , the rate constant of the quenching process, and the efficiency of exothermic triplet-triplet energy transfer in a solvent cage. Based on these ideas, we report here experiments which involve quantum chain reactions⁴ and which allow rapid determination of quenching parameters, evaluation of the assumption of diffusion limited triplet-triplet energy transfer, and an estimation of the efficiency of energy transfer within a solvent cage.

Equations 1-4 represent a standard scheme for exo-



thermic triplet-triplet energy transfer,¹ based on triplet acetone (^3A) as donor. This mechanism predicts that entry to ^3A via thermolysis⁵ of tetramethyl-1,2-dioxetane (1) or via photoexcitation⁶ of acetone, i.e., path a and path b, respectively, in eq 1, should lead to the same Stern-Volmer constant (K_{sv}) which in turn will equal⁷ $k_q\tau_A$. A quantum chain reaction involving ^3Q and 1 requires addition of steps 5 and 6 to the mechanism.



Notice that, although ^3A is quenched in step 2, a new ^3A reappears some of the time as a result of step 5. "Effective net quenching" of ^3A depends on the extent of occurrence of step 5. The factors which determine the

(3) We feel that the best available data for the value of k_q will be obtained from studies in which the lifetime of the donor is measured. In this regard we take the value of k_q^{DIF} to be $\sim 1-2 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ for acetonitrile solutions: A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968); W. R. Ware and H. P. Richter, *J. Chem. Phys.*, **48**, 1595 (1968).

(4) P. Lechtken, A. Yekta, and N. J. Turro, *J. Amer. Chem. Soc.*, **95**, 3027 (1973).

(5) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **94**, 2886 (1972); *Pure Appl. Chem.*, **33**, 363 (1973).

(6) For recent studies involved with acetone triplet in fluid solution see (a) R. W. Yip and W. Siebrand, *Chem. Phys. Lett.*, **13**, 209 (1972); (b) G. Porter, R. W. Yip, J. W. Dunston, A. J. Cessna, and S. E. Sugamori, *Trans. Faraday Soc.*, **67**, 3149 (1972) (c) R. O. Loutfy and R. O. Loutfy, *Can. J. Chem.*, **50**, 4052 (1972); (d) R. W. Yip, *et al.*, *ibid.*, **50**, 3426 (1972); (e) S. K. Dogra, R. O. Loutfy, S. E. Sugamori, and R. W. Yip, *J. Chem. Soc., Faraday Trans. 1*, **69**, 1462 (1973).

(7) Direct measurement of quenching of acetone triplet by naphthalene in our laboratory (by single photon counting technique) results in a value of $k_q \sim 5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. The only other value of a presumed triplet-triplet quenching rate constant for acetone in acetonitrile is the value reported in ref 6b where $k_q \sim 4 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$ for 2,4-hexadien-1-ol as quencher.

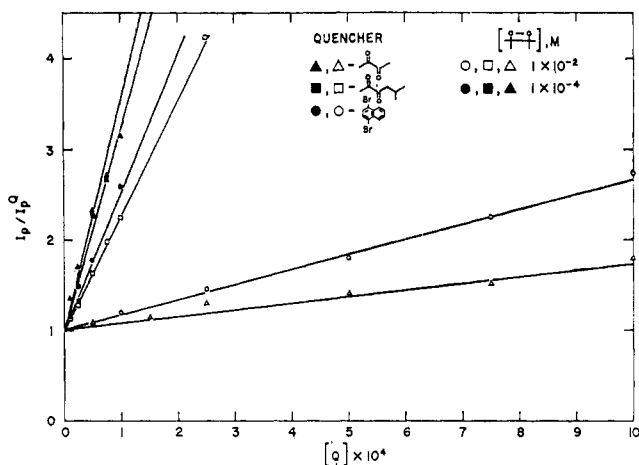


Figure 1. Stern-Volmer quenching of acetone phosphorescence by biacetyl, 5-methyl-2,3-hexanedione and 1,4-dibromonaphthalene at high and low concentrations of 1.

efficiency of step 5 are (a) the quencher lifetime τ_Q , (b) the factor α , and (c) the concentration of 1. The Stern-Volmer constant, when steps 5 and 6 occur, is equal to $k_q\tau_A$ times the probability that 3A which is quenched in step 2 will "stay quenched," i.e., $(\tau_Q^{-1} + (1 - \alpha)k_q[1])(\tau_Q^{-1} + k_q[1])^{-1}$. Thus, the equation for Stern-Volmer quenching of acetone phosphorescence in the presence of steps 5 and 6 will have the form

$$\left(\frac{I_p}{I_p^0} - 1\right) = k_q\tau_A[Q] \left(\frac{1 + (1 - \alpha)k_q\tau_Q[1]}{1 + k_q\tau_Q[1]}\right) \quad (7)$$

We see that eq 7 predicts that $(I_p/I_p^0 - 1)$ will depend linearly on $[Q]$ at fixed $[1]$ but that the measured K_{sv} ($= k_q^{obsd}\tau_A$) will be different from that obtained by Stern-Volmer quenching of photoexcited acetone triplet ($k_q^{lim}\tau_A$). Indeed, this is found (Figure 1) to be the case for exothermic triplet-triplet quenching (quencher such as naphthalene, 1,4-dibromonaphthalene, biacetyl, anthracenes). Furthermore, consider the relationship of k_q^{obsd} to k_q^{lim} (eq 8).

$$(k_q^{obsd})^{-1} = (k_q^{lim})^{-1} \left(\frac{1 + k_q\tau_Q[1]}{1 + (1 - \alpha)k_q\tau_Q[1]}\right) \quad (8)$$

We see that if $\alpha = 1.0$, eq 8 simplifies to eq 9f or all $[1]$.

$$(k_q^{obsd})^{-1} = (k_q^{lim})^{-1}(1 + k_q\tau_Q[1]) \quad (9)$$

However, for values of $\alpha \neq 1.0$, we obtain the following expressions, eq 10 at low $[1]$ and eq 11 at high $[1]$.

$$(k_q^{obsd})^{-1} = (k_q^{lim})^{-1}(1 + \alpha k_q\tau_Q[1]) \quad (10)^8$$

$$(k_q^{obsd})^{-1} = (k_q^{lim})^{-1}(1 - \alpha)^{-1} \quad (11)^9$$

Figure 2 shows the data for biacetyl and 1,4-dibromonaphthalene as quenchers plotted according to eq 8. The plots appear to be linear at low $[1]$ (eq 10) and then curvature appears and finally a flattening out of the plot occurs.

It is significant that 5-methyl-2,3-hexanedione behaves quite differently from biacetyl (Figure 2) in that k_q^{obsd} is much closer to k_q^{lim} for the former dione and little,

(8) Derived from eq 8 via Maclaurin series expansion, i.e., $f([1]) = f(0) + [1]f'(0)$, dropping all further terms.

(9) Derived from eq 8 using L'hospital rule, i.e.

$$\lim_{[1] \rightarrow \infty} \frac{f([1])}{g([1])} = \lim_{[1] \rightarrow \infty} \frac{f'([1])}{g'([1])}$$

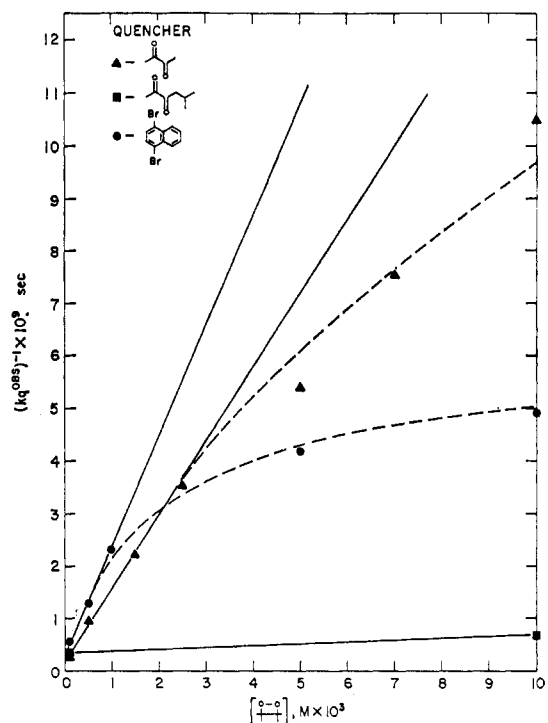


Figure 2. Relationship between k_q and $[1]$ for three quenchers. Solid lines correspond to region of low $[1]$ covered by eq 10. Dotted lines are calculated using eq 8 and the following parameters: for biacetyl, $\alpha = 0.992$ and $k_q\tau_Q = 7720$; for 1,4-dibromonaphthalene, $\alpha = 0.94$ and $k_q\tau_Q = 7000$; corresponding parameters for 5-methyl-2,3-hexanedione are $\alpha = 0.98$ and $k_q\tau_Q = 88$.

if any, flattening of a plot of eq 10 is observed with this quencher. However, these data are readily explained on the basis of a quantum chain mechanism, since τ_Q for 5-methyl-2,3-hexanedione is at least two orders of magnitude smaller than τ_Q for biacetyl.¹⁰ From eq 10 we expect that as τ_Q decreases the term $k_q\tau_Q[1]$ will become comparable in value to unity and that k_q^{obsd} will approach k_q^{lim} .

Based on our proposed mechanism, the equivalence of all the intercepts in Figure 2 implies that $k_q^{lim}\tau_A$ is essentially the same for each quencher. At low $[1]$, we have the relation slope/intercept $= \alpha k_q\tau_Q$ (eq 10), whereas the value of k_q^{obsd} at high $[1]$ allows the calculation of $(1 - \alpha)$ (eq 11). Our calculated values based on these ideas are given in Table I.

Notice that $k_q \sim 3-5 \times 10^9 M^{-1} sec^{-1}$ for quenchers of widely differing structure and triplet energy. The failure of k_q to vary with quencher structure and triplet energy may be considered as *prima facie* evidence for diffusional quenching. However, we have measured k_q for singlet-singlet energy transfer from acetone to camphorquinone and find $k_q^{ss} = 1.5 \times 10^{10} M^{-1} sec^{-1}$. This value is in excellent agreement with that proposed to reflect diffusional quenching in acetonitrile.³ Thus, we must conclude that exothermic triplet-triplet transfer is not diffusion controlled in acetonitrile. This conclusion is reinforced by consideration of the values of $(1 - \alpha)$, the "dark" interaction of 3Q and 1. There is reason to believe that the details of step 5 involve an energy transfer process to produce 3A and Q in the same solvent cage. Since τ_Q is probably limited by oxygen quenching in our system to $\sim 10^{-5}$ sec or less, the

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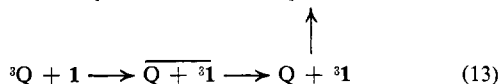
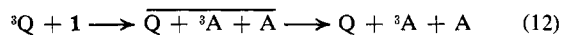
Table I. Quenching Parameters for Exothermic Triplet-Triplet Energy Transfer from Thermally Produced Acetone Triplets^a

Quencher	E_s , kcal/mol	$10^9 k_q^{\text{obsd}}$, $M^{-1} \text{sec}^{-1}$ ^b	$10^9 k_q^{\text{lim}}$, $M^{-1} \text{sec}^{-1}$	$(1 - \alpha)^c$
1,3-Dibromonaphthalene	60	2.0×10^8	2.7×10^9	0.06
Biacetyl	55	9.5×10^7	5.0×10^9	0.01
5-Methyl-2,3-hexanedione	55	1.7×10^9	2.9×10^9	0.02

^a Acetonitrile solutions at 48°, N₂ bubbled for 120 sec. The concentration of **1** was usually varied from 10⁻⁴ to 10⁻² M and the concentration of quencher was usually varied from 10⁻⁵ to 10⁻² M. k_q^{obsd} evaluated according to standard Stern-Volmer relation (I_p/I_p^0) - 1 = $k_q^{\text{obsd}} \tau_A [Q]$ at various [1] using $\tau_A = 8.4 \times 10^{-6}$ sec measured directly by the single photon counting techniques. k_q^{lim} evaluated from extrapolation of eq 10 to [1] = 0. ^b Value at [1] = 10⁻² M. ^c Calculated from eq 11.

large values of $k_c \tau_Q$ found (Figure 2) imply that k_c approaches 10⁹ sec⁻¹. This, together with the low values of 1 - α in Table I suggests that ³A, Q "cage partners" are capable of diffusing apart faster than exothermic triplet-triplet transfer can take place.

At least one other possible interpretation of our data is possible, namely the regeneration of ³A is not due to escape of Q and ³A from a common cage (eq. 12) but results from the formation of triplet **1**, followed by



diffusion of the latter out of the solvent cage with Q (eq 13) and eventual decomposition. We note, however, that this mechanism requires a lifetime of ³1 which is significantly greater than 10⁻¹⁰ sec, the time scale of cage dissolution.¹¹ Since the lifetime of singlet **1** has been estimated¹² to be less than 10⁻¹⁰ sec, such a mechanism would require an unexpectedly long lifetime for ³1.

In conclusion, we have provided a kinetic scheme and data which appear to vitiate the common assumption that exothermic triplet-triplet transfer is diffusion controlled in fluid organic solvents. Assuming that ³A and Q are produced in a solvent cage, our method also allows the estimation of the efficiency of cage effects. We also note that in principle, evaluation of τ_Q is available from our data. The determination of τ_Q by the use of the procedure described above will be the subject of a future report.

Acknowledgment. The authors thank the Air Force Office of Scientific Research (Grant AFOSR-70-1848) and the National Science Foundation (Grants NSF-GP-26602X and GP-40330X) for their generous support of this research.

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(12) (a) N. J. Turro, P. Lechtekn, A. Lyons, R. R. Hautala, E. Carnahan, and T. T. Katz, *J. Amer. Chem. Soc.*, **95**, 2035 (1973). (b) Under our conditions, a small molecule should diffuse approximately \sqrt{Dt} (where D is the diffusion coefficient) from its original site. Since $D \approx 10^{-5}$ cm²/sec, a molecule should not move a distance of more than the order of one diameter ($\approx 3 \text{ \AA}$) in 10⁻¹⁰ sec.

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The Octant Rule. II.¹ Anti-Octant Behavior of *exo*-2-Methylbicyclo[2.2.1]heptan-7-one²

Sir:

The breakdown of the octant rule^{3,4} for back octants has been invoked recently to explain the observed Cotton effects (CE's) of optically active twistanone⁵ and A/B cis 3-oxo steroids.⁶ However, at an even earlier date, an apparent breakdown, "anti-octant effect," could be recognized in the theoretical calculations of Pao and Santry.⁷ The results of these authors' Gaussian orbital calculations agreed with the predictions based on Moscowitz' original theoretical derivation of the octant rule^{8,9} for all configurations, except 3-axial,¹⁰ of various monoalkyl substituted chair cyclohexanones. In Pao and Santry's calculation, the 3-axial methyl substituent was predicted to have a CE sign opposite to that expected from normal back octant behavior. Subsequently, this prediction was verified experimentally by Snatzke and coworkers¹¹ for conformationally rigid 3-axially substituted adamantanones whose sole dissymmetric perturbers lay in back octants and whose CE magnitudes were very weak with signs usually *opposite* to those predicted by the octant rule. Interestingly, with a methyl perturber, in isooctane solvent the octant rule was obeyed, whereas in dioxane or ethanol "anti-octant" behavior was noted. Other apparent "anti-octant" effects have been claimed¹²⁻¹⁵ and calculated.¹⁶ Perhaps the most revealing of these is the work of Coulombeau and Rassat¹⁵ who explain "anti-octant" effects of methyl perturbers in terms of those perturbers lying in front octants. Despite the various proposals of an "anti-octant" effect, until now there have been no unambiguous experimental demonstrations of it with carbon and hydrogen as static, dissymmetric perturbers, except for the work of Snatzke in which a peculiar solvent effect was noted.¹¹ In the present work we report on the synthesis and circular dichroism (CD) of the stereochemically rigid, epimeric (1*R*)-*exo*-2-methylbicyclo[2.2.1]heptan-7-one (**1**) and (1*R*)-*endo*-2-methylbicyclo[2.2.1]heptan-7-one (**2**), of which

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