

corresponding yields reported for **1** at 366 nm are 10 and 43%.⁹

In summary, the efficient spin inversion during photochemical and thermochemical decomposition of **1** is not found with **2**. Initial formation of ground-state 2-hexanone from **2** accounts for nearly all (>90%) of the products derived thermally or photochemically; thus **2** resembles most of the previous dioxetanes in its low excitation yield.

Kearns has offered a possible explanation of how chemical excitation might occur in 1,2-dioxetane systems.¹⁰ A crossing between the ground-state energy surface of the dioxetane and an upper level surface, which correlates with an excited state of the product, was proposed as a possible concerted pathway. Turro has pointed out that the orbital symmetry change corresponding to a shift from an all- σ to an n, π^* system could give strong spin-orbital coupling leading to enhanced spin inversion.⁵ However, Richardson has suggested that diradical states are intermediate, because of compelling energy considerations.¹¹

We believe that the contrasting behavior of **1** and **2** represents either (a) differences in partitioning of an intermediate species such as a diradical or (b) differences in efficiency of vibronic coupling between nonintersecting segments of ground- and excited-state energy surfaces. We are not able to account for these differences at the present time. It is particularly important that the *photochemical* and *thermochemical* triplet excitation yields *do not differ* significantly within each system.^{12,13} Unique behavior in this system on photosensitized decomposition will be reported shortly.

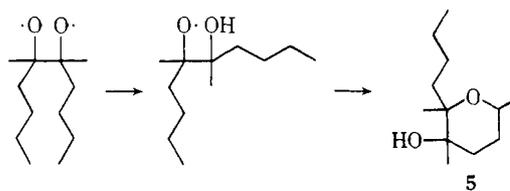
(9) N. J. Turro, P. Lechtken, A. Lyons, R. R. Hautala, E. Carnahan, and T. J. Katz, *J. Amer. Chem. Soc.*, **95**, 2035 (1973).

(10) D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971).

(11) H. E. O'Neal and W. H. Richardson, *J. Amer. Chem. Soc.*, **92**, 6553 (1970); W. H. Richardson, M. B. Yelvington, and H. E. O'Neal, *ibid.*, **94**, 1619 (1972).

(12) This observation suggests that in the case of a spin-forbidden concerted process, similar spin-orbital factors must couple both the ground and first excited state surfaces of the dioxetane with those of the n, π^* triplet ketone.

(13) A referee has questioned whether some of the products might not derive from γ -hydrogen abstraction in a diradical intermediate. In our consideration of this possibility, we felt that **5** should accompany any such process, and no evidence for **5** was found.



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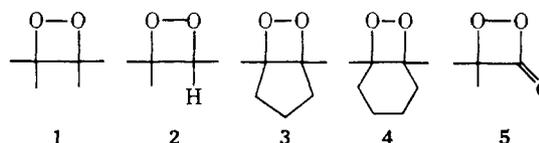
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Indirect Chemiluminescence by 1,2-Dioxetanes. Evaluation of Triplet-Singlet Excitation Efficiencies. A Long Range Singlet-Singlet Energy Transfer and an Efficient Triplet-Singlet Energy Transfer

Sir:

A great deal of recent research in chemiluminescence has been focused on the mechanism of conversion of chemical energy into electronic energy¹ and in the

utilization² of the thermally generated electronically excited states for "photochemistry in the dark." Indirect chemiluminescence (*i.e.*, emission from an additive rather than a primary chemiexcited product) has been employed to both amplify the intensity of emission and to study the mechanism of energy transfer processes. For example, Belakov and Vasilev³ have extensively studied the use of anthracenes as energy acceptors for triplet ketones and Wilson and Schaap⁴ have used anthracenes as energy acceptors in their study of the thermolysis of *cis*-diethoxy-1,2-dioxetane. These earlier reports^{3,4} assumed that the indirect chemiluminescence of anthracene (identified as anthracene fluorescence) was due exclusively to triplet (carbonyl) to singlet (anthracene) energy transfer and that the rate constant for this spin-forbidden process is, at best, about 100 times less than that for the spin-allowed alternative, triplet (carbonyl) to triplet (anthracene) energy transfer. We provide evidence that indirect chemiluminescence by singlet-singlet energy transfer is dominant in the case of "nonheavy atom" substituted anthracenes (*e.g.*, 9,10-diphenylanthracenes, DPA) and that triplet-singlet energy transfer is the dominant mechanism in the case of "heavy atom" substituted anthracenes (*e.g.*, 9,10-dibromoanthracene, DBA). We then use our observations to (a) evaluate the triplet-singlet excitation efficiencies of several 1,2-dioxetanes (**1-5**) and (b) evaluate



the rate constants for singlet-singlet and triplet-singlet energy transfer and compare these to values for triplet-triplet energy transfer.

The key experiments of this study involve the measurements of the indirect chemiluminescence (fluorescence) of DPA and DBA, chemiexcited by thermolysis of the 1,2-dioxetanes **1**, **2**, **3**, **4**, and **5**. In all cases, the change in concentration of dioxetane is small (<0.1%) during the period of measurement. The intensity of indirect chemiluminescence, I_{CL} , is given in eq 1, where

$$I_{CL} = R[(\phi_*^S \phi_{ET}^{SS} \phi_{FA}^A) + (\phi_*^T \phi_{ET}^{TS} \phi_{FA}^A)] \quad (1)$$

R is the rate of disappearance of dioxetane, ϕ_*^S (ϕ_*^T), ϕ_{ET}^{SS} (ϕ_{ET}^{TS}), and ϕ_{FA}^A are the efficiencies of singlet (or triplet) formation from the dioxetane, singlet-singlet (or triplet-singlet) energy transfer from excited donor to anthracene, and anthracene fluorescence, respectively. Experimentally, it is found that specific triplet ketone quenchers (1,3-dienes, oxygen, acrylonitrile) *dramatically decrease the indirect chemiluminescence of DBA, but have a negligible effect on the indirect chemiluminescence of DPA.* From this striking result we conclude that the dominant mechanism for indirect chemiluminescence of DBA is triplet-singlet energy transfer whereas the dominant mechanism for indirect chemilumines-

(1) N. J. Turro and P. Lechtken, *Pure Appl. Chem.*, **33**, 363 (1973); *J. Amer. Chem. Soc.*, **95**, 264 (1973), and references therein.

(2) E. White, J. Wiecko, and C. C. Wei, *J. Amer. Chem. Soc.*, **92**, 2167 (1970); E. White, J. Wiecko, and D. F. Roswell, *ibid.*, **91**, 5194 (1969); H. Gisten and E. F. Ullman, *Chem. Commun.*, 28 (1970).

(3) V. A. Belakov and R. F. Vasilev, *Photochem. Photobiol.*, **11**, 179 (1970).

(4) T. Wilson and A. P. Schaap, *J. Amer. Chem. Soc.*, **93**, 4126 (1971).

cence of DPA is singlet-singlet energy transfer.⁵ Thus, the indirect chemiluminescence intensities for DPA and DBA (I_{CL}^{DPA} and I_{CL}^{DBA}), respectively, are given by eq 2 and 3. The ratio of eq 3 to eq 2 leads to eq 4, which is

$$I_{CL}^{DPA} = R(\phi^S \phi_{ET}^{SS} \phi_F^{DPA}) \quad (2)$$

$$I_{CL}^{DBA} = R(\phi_*^T \phi_{ET}^{TS} \phi_F^{DBA}) \quad (3)$$

$$\frac{I_{CL}^{DBA}}{I_{CL}^{DPA}} = \frac{\phi_*^T \phi_{ET}^{TS} \phi_F^{DBA}}{\phi_*^S \phi_{ET}^{SS} \phi_F^{DPA}} \quad (4)$$

an experimentally tractable expression since it requires only a simple measurement (ratio of intensities) to obtain efficiencies. We have measured $\phi_F^{DBA}/\phi_F^{DPA}$ to be approximately 0.1 under our conditions. Furthermore, at extrapolation to infinitely high concentrations of acceptor, all singlet states, and all triplet states are trapped so that ϕ_{ET}^{SS} should go to a value of one and ϕ_{ET}^{TS} should go to a value dependent only on the competition between triplet-singlet and triplet-triplet energy transfer (*vide infra*, eq 5 and 6). From our previous chemical titration⁶ experiments we estimate the limiting value of ϕ_{ET}^{TS} to be approximately 0.25. Thus, eq 5 allows ready evaluation of ϕ_*^T/ϕ_*^S . The results

$$\frac{I_{CL}^{DBA}}{I_{CL}^{DPA}} = 0.025 \frac{\phi_*^T}{\phi_*^S} \quad (5)$$

based on this method are given in Table I. In all cases,

Table I. Singlet and Triplet Yields from Indirect Chemiluminescence Experiments

Dioxetane ^a	ϕ_*^T/ϕ_*^S	ϕ_*^S	ϕ_*^T
1	200	0.0025 ^b	0.5 ^b
2	>300	~0.002 ^c	~0.5 ^c
3	30	0.003	~0.2 ^c
4	~30 ^d		
5	20	0.01	0.2

^a Benzene solutions except for 5 (CCl₄). Dioxetane concentrations 10^{-2} to 10^{-3} M. Concentrations of acceptors 10^{-2} to 10^{-4} M. ^b From chemical titration experiments. See ref 6. ^c Estimated from direct comparison with the emission of 1 and the assumption of comparable rate constants for energy transfer of all excited carbonyl components to acceptors. ^d Impure sample. An approximate value only.

a strong preference for triplet formation relative to singlet formation was observed. The rate constants for singlet-singlet (k_{ET}^{SS}) and triplet-singlet (k_{ET}^{TS}) energy transfer from acetone donor to anthracene can be evaluated by a Stern-Volmer analysis.⁷

In eq 4, under our experimental conditions, ϕ_{ET}^{TS} (or ϕ_{ET}^{SS}) depend on the concentration of DBA (or DPA) as follows

$$\phi_{ET}^{TS} = \frac{k_{ET}^{TS}[DBA]}{(k_{ET}^{TS} + k_{ET}^{TT})[DBA] + k_T} \quad (6)$$

$$\phi_{ET}^{SS} = \frac{k_{ET}^{SS}[DPA]}{k_{ET}^{SS}[DPA] + k_S} \quad (7)$$

where k_T (or k_S) is the rate constant for decay of acetone triplet (or singlet) under our conditions but in the

(5) The fluorescence of neither DPA nor DBA was significantly affected by the quenchers in the concentration ranges employed.

(6) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **94**, 2886 (1972).

(7) For a detailed analysis of the kinetics see H. C. Steinmetzer, P. Lechtken, and N. J. Turro, *Justus Liebig Ann. Chem.*, in press.

absence of DBA (or DPA). Thus, a Stern-Volmer analysis (plot of $1/I_{CL}^{DBA}$ vs. $1/[DBA]$ or $1/I_{CL}^{DPA}$ vs. $1/[DPA]$) will yield values of $(k_{ET}^{TS} + k_{ET}^{TT})/k_T$ and k_{ET}^{SS}/k_S . We have independently evaluated k_S to be equal to 2×10^{-9} sec and estimate k_T to be 1×10^{-7} sec under our experimental conditions.⁸ From the value of ϕ_{ET}^{TS} measured above, we now have enough information to evaluate k_{ET}^{SS} and k_{ET}^{TS} (Table II). The rate constant

Table II. Rate Constants for Singlet-Singlet and Triplet-Singlet Energy Transfer from Indirect Chemiluminescence^a

Acceptor	Donor ^b	k_{ET}^{SS}	k_{ET}^{TS}
9,10-Diphenylanthracene	Acetone	6×10^{10}	$<1 \times 10^6$
9,10-Dibromoanthracene	Acetone	5×10^{10}	1×10^9

^a Rate constants (in $M^{-1} \text{sec}^{-1}$) evaluated from Stern-Volmer analysis of indirect chemiluminescence emission, benzene solution. ^b Chemiexcited acetone from 1.

for diffusion controlled quenching⁹ in benzene is approximately $5 \times 10^9 M^{-1} \text{sec}^{-1}$. From Table II it is seen that (a) k_{ET}^{SS} is considerably larger than the rate constant for diffusion of small molecules in benzene and (b) k_{ET}^{TS} is nearly comparable in value to the rate constant for diffusion. Both conclusions are of considerable interest to those involved in the study of energy transfer processes in solution.^{10,11}

In summary, our results support the following conclusions. (a) In the decomposition of 1,2-dioxetanes triplet formation is preferred over singlet formation, in general. (b) A long range interaction is involved in the singlet-singlet energy transfer between acetone and anthracene singlets. (c) The efficiency of triplet-singlet energy transfer in the case of DBA is remarkably high and comparable to that of triplet-triplet energy transfer. Furthermore, the indirect chemiluminescence technique is much faster than the previously reported chemical titration for determining excitation efficiencies and can be applied without previous detailed knowledge of the specifics of the photochemistry of the carbonyl fragments.

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(8) The rate constant for quenching of acetone triplets by benzene has been determined to be $\sim 10^6 M^{-1} \text{sec}^{-1}$: R. O. Loutfy and R. W. Yip, *Can. J. Chem.*, **51**, 1881 (1973). We thus assume that in pure benzene (~ 10 M) the pseudounimolecular decay of acetone triplet will thus be $\sim 10^1 \text{sec}^{-1}$.

(9) A. Yekta and N. J. Turro, *Mol. Photochem.*, **3**, 307 (1972).

(10) Apparently, energy transfer is occurring by a long range (probably dipole-dipole) mechanism. Two pertinent reports of a comparable phenomenon have been published, but without consideration of the dipole-dipole mechanism as the basis for a "faster than diffusional quenching": A. J. Robinson, M. A. J. Rodgers, J. P. Keene, and C. W. Gilbert, *J. Photochem.*, **1**, 379 (1972); J. C. W. Chien and W. P. Conner, *J. Amer. Chem. Soc.*, **90**, 1001 (1968).

(11) After submission of this publication, we were informed by Professor Vasilev that a value of k_{ET}^{TS} of $1.5 \times 10^9 M^{-1} \text{sec}^{-1}$ was now accepted as the "best" value to be used for the transfer from triplet ketones to DBA. We thank Professor Vasilev for his correspondence and for pointing out this reevaluation. See, also, Y. M. Berenfeld, E. V. Chumavskii, M. P. Grinev, Y. I. Kuryatnikov, E. T. Artemev, and R. V. Dzhagatspayan, *Bull. Acad. Sci. USSR, Div. Chem.*, **34**, 597 (1970).

leum Research Fund, administered by the American Chemical Society, for their generous support of this work.

(12) Also of the University of Puerto Rico during the year 1972.

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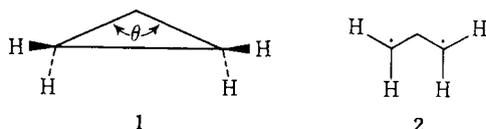
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Thermal $\sigma_2 + \sigma_2$ Isomerizations of the Conformationally Restricted Cyclopropanes 2,4-Dehydroadamantane and 2,4-Dehydrohomoadamantane

Sir:

The cyclopropane to propene rearrangement is the prototype $\sigma_2 + \sigma_2$ cycloreaction. According to current understandings, it proceeds in a nonconcerted fashion by way of a trimethylene diradical intermediate which may revert to cyclopropane or react with a C-H bond to give olefinic product.¹

Molecular orbital and valence bond calculations of several types and degrees of complexity on the trimethylene diradical are in general agreement:¹ the energy of the 90,90 form (1)² increases monotonically as the angle θ increases, reaching no energy well corresponding to an intermediate. Near $\theta = 110^\circ$, the 0,0-trimethylene species (2) becomes the lower energy



form, and it may exist as a discrete entity. Thus, the transformation of cyclopropane into the trimethylene diradical intermediate, according to these calculations, involves both increasing the angle θ and rotating C(1) and C(3) methylene hydrogens in a conrotatory or disrotatory manner into the plane defined by the carbon atoms.

How will a cyclopropane behave if it is conformationally restricted so that the geometry required for a 0,0-trimethylene diradical intermediate may not be attained? Is the 0,0-diradical intermediate a necessary stage in thermal structural isomerizations of cyclopropanes?

We have studied the thermal chemistry of two cyclopropane derivatives restricted to bond elongating distortions and prevented from reaching the geometry characteristic of 0,0-trimethylene diradicals. They give $\sigma_2 + \sigma_2$ cycloreactions quite smoothly: 2,4-dehydroadamantane³⁻⁶ (3) rearranges to protoadamantene

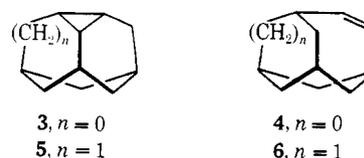
(1) R. G. Bergman in "Free Radicals," J. K. Kochi, Ed., Wiley-Interscience, New York, N. Y., 1973, and references cited.

(2) Conformational designations follow the conventions introduced by R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(3) J. Boyd and K. H. Overton, *Chem. Commun.*, 211 (1971); *J. Chem. Soc., Perkin Trans. 1*, 2533 (1972).

(4) A. C. Udding, Doctoral Thesis, University of Groningen, The Netherlands, 1968. We are indebted to Mr. Gerrit DeWilde for translations of parts of this thesis. See also A. C. Udding, J. Strating, H. Wynberg, and J. L. M. A. Schlatmann, *Chem. Commun.*, 657 (1966).

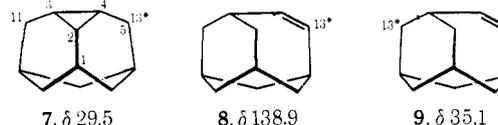
(4)^{3,7} in the gas phase with a first-order rate constant of about 10^{-5} sec^{-1} at 387° ; 2,4-dehydrohomoadamantane⁸ (5) is isomerized to homoadamantene (6)^{9,10} in the



gas phase with a first-order rate constant of about 10^{-4} sec^{-1} at 400° . These rearrangements proceed 20 and 80 times faster than the formally analogous conversion of methylcyclopropane to 1-butene at the respective temperatures.^{11,12}

To identify the bonds involved in the isomerization of 5, 2,4-dehydrohomoadamantane-5-¹³C (7) and 4-homoadamantene-4-¹³C (8) were prepared from adamantanone and potassium cyanide-¹³C (61% enriched) by way of the cyanohydrin, the amino alcohol, homoadamantan-4-one-5-¹³C, and thermal decomposition of the lithium or sodium salts of the corresponding tosylhydrazones.^{8,10}

Pyrolysis of 7 gave recovered 7 of undiminished isotopic integrity and a 1:2 mixture of 8 and 9. The syn-



thesized sample of 8 was subjected to the reaction conditions and found to suffer positional scrambling of the carbon-13 label to only a barely detectable extent. In a completely independent experiment, starting with adamantanone and labeled potassium cyanide, much larger samples of 7 and 8 were utilized; the same controls were run with the same findings, and the homoadamantene produced by pyrolysis of 7 at 400° for 3 hr was a 27:73 mixture of 8 and 9 according to the relative intensities of the cmr absorptions at δ 138.9 and 35.1.

These results are consistent with involvement of two $\sigma_2 + \sigma_2$ rearrangement modes: a [C(2)-C(4)/H-C(5)] bond reorganization and a [C(2)-C(4)/C(3)-C(11)] process. The more precise experimental results obtained with the larger sample of 7 correspond to these two modes obtaining in 54:46 proportions.¹³

We conclude that 0,0-trimethylene diradical intermediates are not required in $\sigma_2 + \sigma_2$ isomerizations of

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(12) D. W. Placzek and B. S. Rabinovitch, *J. Phys. Chem.*, **69**, 2141 (1965).

(13) There are other [C-C/C-C] cycloreaction modes which, followed by rapid 1,3-carbon migrations, would account for the 7 \rightarrow 9 reaction.