

Hydrolysis of amino ester **14** with potassium hydroxide in methanol-water followed by acidification with hydrochloric acid and extraction into chloroform gave metal salt **26**,² whose mass spectrum contained the molecular ion of the salt. When barium hydroxide was substituted for potassium hydroxide and after the chloroform-extracted product was chromatographed on silica gel, a complex of the composition of **27**^{2a,b} was isolated. A solution of **27** in methanol when treated with sulfuric acid did not give a precipitate. When a tenfold excess of barium hydroxide 0.8% in strontium hydroxide was used to hydrolyze **12**, strontium ion was scavenged and carried into the chloroform with diacid **17**. The mass spectrum of the mixture produced a parent ion for **28**. Salts **28–32**² were prepared by neutralizing their acids with appropriate bases in methanol and evaporating the resulting homogeneous solutions to give powders. Salts **28–32** analyzed for one-to-one compositions.

Thus acids **17**, **19**, **20**, and **21** bind and lipophilize metal ions. When the average hole size of the host matches the ionic diameter of the guest ion and the number of carboxyl groups of the host equals the number of positive charges of the guest ion, stable one-to-one complexes form. The hole diameters (Å) are estimated from CPK models to vary with naphthyl-naphthyl dihedral angles (45–135°) as follows: [17]crown-5, 1.7–2.2; [20]crown-6, 2.4–3.1; [23]crown-7, 3.4–4.1. The most probable diameters (Å) in ionic crystals of metals used here are⁶ Na⁺, 2.24; K⁺, 2.88; NH₄⁺, 3.32; Ca²⁺, 2.36; Sr²⁺, 2.64; and Ba²⁺, 2.98. To our knowledge, no one has introduced before the counterions into the host ethers and varied their number.⁷ Proper design of hole size, heteroatom type, and the number of "built-in" counterions should provide host molecules with a wide range of differential complexing abilities of many of the metal cations of the periodic table. Ion lipophilization is important to ion transport through membranes, to homogeneous catalysis, and to inorganic reagent design for use in organic solvents.

(6) M. F. C. Ladd, *Theor. Chim. Acta*, **12**, 333 (1968).

(7) C. J. Pedersen, *J. Amer. Chem. Soc.*, **92**, 386 (1970), and ref 3, and H. K. Frensdorff, *ibid.*, **93**, 600 (1971), correlated hole size of crown ethers with ionic diameters of complexing metal cations.

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Thermal Rearrangement of Dewar Benzenes to Benzene Triplet States. Examples of Spin Forbidden Nonadiabatic Pericyclic Reactions

Sir:

Thermal rearrangements of Dewar benzenes (**D**) to benzenes (**B**) are exothermic by about 60 kcal/mol.¹ These valence isomerizations also have substantial activation energies,^{2,3} e.g., ΔH^\ddagger equals 19, 23, and 30

(1) (a) W. Schaffer, *Angew. Chem., Int. Ed. Engl.*, **5**, 669 (1966); (b) J. F. M. Oth, *ibid.*, **7**, 646 (1968); (c) H. C. Volger and H. Hoogveen, *ibid.*, **87**, 1185 (1968); (d) W. Adam and J. C. Chang, *Int. J. Chem. Kinet.*, **1**, 487 (1969); (e) A. H. Schmidt, unpublished results.

(2) R. Breslow, J. Napierski, and A. H. Schmidt, *J. Amer. Chem. Soc.*, **94**, 5906 (1972).

(3) In the case of hexamethyl(Dewar benzene) a range of values for ΔH^\ddagger have been reported; see ref 1.

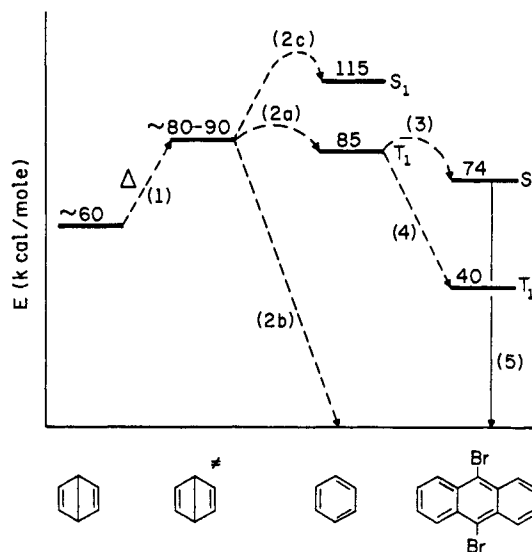
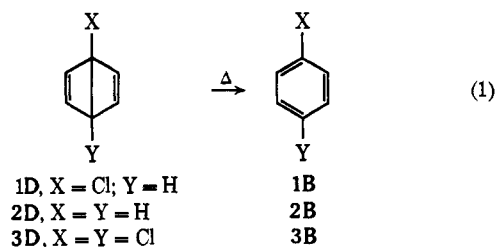


Figure 1. Schematic description of the energy levels involved in the Dewar benzene to benzene rearrangement. The ground-state enthalpy for the rearrangement is estimated to be ~ -60 kcal/mol and the activation enthalpies (step 1) are ~ 20 – 30 kcal/mol. From the transition state(s) of 1, 2, and 3 the major deactivation path is 2b, direct formation of ground-state benzene. Path 2c is a very minor path and path 2a, formation of benzene triplets, is a significant process, whose occurrence is monitored by the sequence 3 followed by 5, i.e., triplet to singlet transfer followed by fluorescence. Path 4 is, in fact, the major path of quenching of benzene triplets but is not directly detectable under our conditions.

kcal/mol for the Dewar benzene series **1D**, **2D**, and **3D**,



respectively. Figure 1 shows that the total transition state energy (as enthalpy relative to ground state benzenes) for the **D** \rightarrow **B** rearrangement is comparable to the electronic excitation energy required to produce benzene triplet states⁴ but is clearly less than the electronic excitation energy required to produce benzene singlets. Thermal population of benzene triplets in **D** \rightarrow **B** rearrangements thus seems to be energetically feasible and might occur if a mechanism were available which allows a spin flip to occur along the reaction coordinate. Such a process is particularly intriguing because it has important implications with respect to theories of orbital symmetry control of electrocyclic reactions⁵ (orbital symmetries do not allow a smooth and facile thermal **D** \rightarrow **B** conversion) and to ideas con-

(4) A similar analysis suggested that the singlet state of hexamethylbenzene might be energetically accessible from the transition state for the thermolysis of hexamethyl(Dewar benzene): C. C. Wamser, F. H. Dorer, L. T. Spada, and G. D. Pfeiffer, Abstracts, 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, ORGN 35. Attempts to observe excited state formation from this system were negative, however.

(5) (a) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970; (b) for a discussion of orbital symmetry disallowed, but energetically concerted reactions, see J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, *Accounts Chem. Res.*, **5**, 402 (1972).

cerning chemiluminescence mechanisms⁶ (*efficient* chemiluminescent reactions almost invariably involve complicated multistep reaction sequences). We report here that a detectable yield of benzene triplets is produced in the conversions $D \rightarrow B$.

Heating of dilute solutions⁷ of **1D**, **2D**, or **3D** ($\sim 10^{-2}$ M) results in clean rearrangement to **1B**, **2B**, and **3B**, respectively.² Although no light emission could be detected⁸ from these solutions during thermolyses, addition of 9,10-diphenylanthracene (DPA) or 9,10-diphenylethynylanthracene (DPEA) followed by heating results in generation of a weak emission characteristic of fluorescence from the anthracenes. Addition of 9,10-dibromoanthracene (DBA) to solutions of **1D**, **2D**, or **3D** followed by heating results in a much more intense emission, characteristic of DBA fluorescence. Both the rates of decay and the activation parameters for the reactions which lead to emission from DBA are in excellent agreement with those previously determined by nmr spectroscopy for the thermal rearrangements² $D \rightarrow B$. These results indicate that the thermal generation of anthracene fluorescence occurs after the transition state for the thermal rearrangements $D \rightarrow B$.

Although the benzene singlet state was considered unlikely as a direct product of thermolyses of **1D**, **2D**, or **3D** (Figure 1), this possibility was easily excluded experimentally since only a minute amount of fluorescence was detected with 10^{-2} M DPA or DPEA present, even though at this concentration $\sim 50\%$ of the excited benzene singlets would be quenched⁹ by singlet-singlet transfer. Since benzene phosphorescence is undetectable¹⁰ in fluid solution near room temperature, an indirect but specific test for benzene triplets was designed. This new method is based on the observation that S_1 of DPA and DPEA is readily excited by a singlet donor whose S_1 level lies at energies >74 kcal/mol (the energy of S_1 of DPA and DPEA) but not by a triplet donor whose T_1 level lies at energies >74 kcal/mol. This contrasts with the ability of the S_1 level of DBA to accept electronic energy from both singlet and triplet energy donors.¹¹ The observation that DBA fluorescence is more efficient than DPA (or DPEA) fluorescence excited by thermolysis of Dewar benzenes **1D**, **2D**, and **3D** is clear evidence for the proposal that the benzene T_1 is produced directly and subsequently transfers energy to DBA. This hypothesis is in accord with the fact that triplet energies¹² of benzenes **1B**, **2B**, and **3B** are greater than 74 kcal/mol; it is corroborated by the observation that "high energy" triplet quenchers (2-methylpentene and *cis*-1,2-dimethoxyethylene, $84 > E_T > 74$ kcal/mol) quench the emission of DBA in our

(6) F. McCapra, *Pure Appl. Chem.*, **24**, 611 (1970); R. Dougherty, *J. Amer. Chem. Soc.*, **93**, 7187 (1971).

(7) No solvent effects on the rate of thermolyses were noted for solvents such as cyclohexane, tetrachloroethylene, or *m*-xylene.

(8) We estimate that an excitation yield of $\sim 10^{-4}$ could have been detected from fluorescence of benzene.

(9) We assume a diffusion controlled rate constant for singlet-singlet transfer and a benzene singlet lifetime of $\sim 10^{-9}$ sec; see, for example, J. Birks, "Photophysics of Aromatic Molecules," Wiley, New York, N. Y., 1970.

(10) The quantum yield of benzene phosphorescence at room temperature is estimated to be $\sim 10^{-9}$, based on its known radiative phosphorescence rate constant and its triplet lifetime; see, for example, ref 9 and R. B. Cundall, G. B. Evans, P. A. Griffiths, and J. P. Keene, *J. Phys. Chem.*, **72**, 3871 (1968).

(11) V. A. Belyakov and R. F. Vassilev, *Photochem. Photobiol.*, **9**, 35 (1967); *ibid.*, **11**, 179 (1970).

(12) From ref 9, E_3 of **1B**, **2B**, and **3B** is 83, 85, and 80.5 kcal/mol, respectively.

thermal rearrangement (under conditions such that they will not directly quench DBA fluorescence when it is simply excited by light). Furthermore, variations of the intensity of chemiluminescence as a function of the concentration of DBA allows us to determine the Stern-Volmer parameter $k_q\tau$ which, according to our hypothesis, reflects the competition between the major path for quenching of benzene triplets by DBA¹³ and unimolecular decay of benzene triplets. The value obtained (Table I) falls in the range measured in other

Table I. Activation Parameters for the Thermal Rearrangement of Dewar Benzenes **1-3** as Followed by Their Formation of Excited States. Yields of Generation of Excited States

No.	$\Delta H^\ddagger,^a$ kcal/ mol	$\Delta S^\ddagger,^a$ eu	$\phi^*,^c$ %	$\Delta H^\ddagger,^b$ kcal/ mol	$\Delta S^\ddagger,^b$ eu	$k_q\tau_T^d$
1	20.0	-4.2	0.07	19.1	-9.4	340
2	25.1	+0.8	0.02	23.0	-5.0	140
3	30.2	+14.0	0.1	30.5	+12.0	

^a The decay of the Dewar benzene is followed by monitoring the intensity of DBA emission. Error limits 1.5-2 kcal, corresponding to 3-7 eu. ^b Measured by nmr in C_2Cl_4 : R. Breslow, J. Napierski, and A. H. Schmidt, *J. Amer. Chem. Soc.*, **94**, 5906 (1972). ^c The method of estimating ϕ^* was as follows. $\phi^* = \phi_{Cl}/\phi_{F\phi_{ET}}$ where ϕ_{Cl} is the yield of chemiluminescence, ϕ_F is the fluorescent yield of DBA and ϕ_{ET} is the efficiency of triplet to singlet transfer from benzene triplet to S_1 (DBA). Since ϕ^* is known for tetramethyl-1,2-dioxetane (T), comparison of ϕ_{Cl} induced by **D** with **T** allows calculation of ϕ^* if ϕ_{ET} is assumed to be comparable for both benzene triplets and acetone triplets. In fact, it is likely that ϕ_{ET} will be smaller for benzene triplets, so that ϕ^* is only a lower limit. ^d Values of $k_q\tau_T$ (rate constant for benzene triplet quenching by 9,10-dibromoanthracene) determined from plots of $1/I_{Cl}$ vs. $1/[DBA]$. Literature¹⁴ values of $k_q\tau$ where k_q is the rate constant for diffusion are in the range of 100-1000.

laboratories¹⁴ for diffusion controlled quenching of benzene triplets.

Finally, we are able to estimate a lower limit to the yield of benzene triplets produced in our thermolyses by application of results of other triplet-singlet transfer¹¹ studies (Table I). Although we estimate that only one molecule in 10^3 - 10^4 (a lower limit) actually produces a triplet benzene in our rearrangements, the ratio of rates of spin allowed to (electronically equivalent) spin forbidden processes is generally¹⁵ believed to be of the order of 10^6 . It seems likely that in the present case, the spin-orbital interaction needed to flip an electron spin is achieved by specific vibronic interaction during the rearrangement process, as appears to be the case in the pericyclic thermolyses of 1,2-dioxetanes.¹⁶ The estimated yields of triplets in our current case are apparently considerably smaller than for dioxetanes, presumably because of the absence of one crucial center spin-orbit interaction in the hydrocarbon system.⁷ Interestingly, the $D \rightarrow B$ triplet quantum yields, within our series, increase with increasing number of chlorine

(13) Due to the bromine atoms in DBA the spin conservation rule is not strictly adhered to, so that some fraction of the electronic energy of the triplet donor is transferred to the fluorescent singlet state of the DBA. See ref 11 for a discussion of this point.

(14) See ref 10 and R. B. Cundall and P. A. Griffiths, *Trans. Faraday Soc.*, **61**, 1968 (1965); J. T. DuBois and J. W. von Loben Sels, *J. Chem. Phys.*, **45**, 1522 (1966).

(15) M. Kasha, *Discuss. Faraday Soc.*, **9**, 14 (1950).

(16) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **94**, 2886 (1972); **95**, 264 (1973).

substituents (possibly a heavy atom effect¹⁷ on spin-orbit coupling) rather than with increasing activation energy.

In summary, we have provided evidence that if sufficient energy (as enthalpy) is available, the direct thermal population of triplet states is possible as a result of a molecular rearrangement.¹⁸

Acknowledgments. Support of this work by the National Institutes of Health, the Air Force Office of Scientific Research, and the National Science Foundation is gratefully appreciated.

(17) (a) It is interesting to note that benzene triplet is believed to possess D_{2h} symmetry, *i.e.*, belong to the same point group as Dewar benzene: M. S. de Groot and J. H. van der Waals, *Mol. Phys.*, **6**, 545 (1963). (b) See S. K. Lowen and M. A. El-Sayed, *Chem. Rev.*, **66**, 199 (1966), for a discussion of spin-orbit interactions in organic molecules.

(18) Nearly all reported chemiluminescent reactions involving organic molecules in solution are oxidative fragmentations or electron transfers.

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Tetramethyl-1,2-dioxetane. A Mechanism for an Autocatalytic Decomposition. Evidence for a Quantum Chain Reaction

Sir:

Studies directed toward an understanding of the mechanisms of chemiluminescent reactions of organic molecules in fluid solution currently provide an area of lively and expanding interest and importance. Recent breakthroughs¹ in the syntheses of 1,2-dioxetanes, molecules believed to be significant intermediates in many known chemiluminescent reactions,² allow a direct study of chemoelectronic generation of excited states. Because of their exceptionally high energy content and unique electronic structure, 1,2-dioxetanes might well be expected to be involved in unusual and novel mechanisms. We report here evidence for such a situation, namely the occurrence of a quantum chain reaction (eq 1 and 2) in which electronic excitation energy is cycled through a number of steps.



The chemiluminescent system studied was the decomposition of tetramethyl-1,2-dioxetane (**1**). Our experiments were run by using chemiluminescence, *i.e.*, acetone fluorescence, to monitor the relative concentration of **1** (benzene solution 0.3-1.0 *M* at 72°). The decay of fluorescence was found to be experimentally indistinguishable from the disappearance of **1** as monitored by quantitative nmr analysis. The disappearance of **1** is cleanly first order for aerated solutions but shows drastic deviation from first-order kinetics when degassed solutions are analyzed (Figure 1). Indeed the half-life of a 1 *M* degassed solution of **1** (benzene) at room

(1) K. R. Kopecky and C. Mumford, *Can. J. Chem.*, **47**, 709 (1969); W. Adam and J. C. Liu, *J. Amer. Chem. Soc.*, **94**, 2894 (1972).

(2) F. McCapra, *Pure Appl. Chem.*, **24**, 611 (1970).

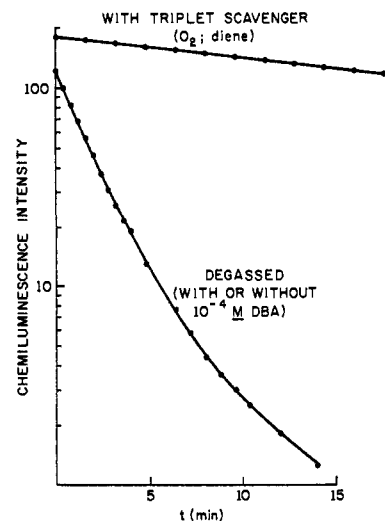
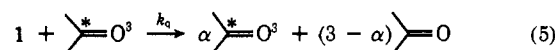
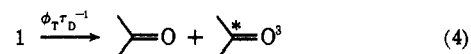
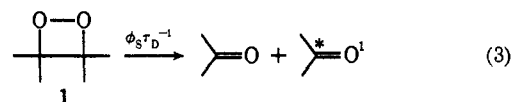


Figure 1. Typical decay of chemiluminescence intensity of **1** in aerated and degassed solution. In benzene solution at 72° the lifetime of **1** is $\tau_D = 42$ min in the presence of oxygen or 1,3-dienes.

temperature is of the order of 1-2 min, while a 1 *M* aerated solution is of the order of 10^3 - 10^4 min!

Our mechanism to explain these results is proposed in eq 3-5. In the presence of oxygen, triplet acetone is



generated³ as a result of reaction 3 only by intersystem crossing ($k_{ST} \sim 10^9 \text{ sec}^{-1}$) and with low efficiency ($\phi_s \sim 0.01$).³ Equation 4 represents the major path for production of acetone triplet. In aerated solutions the latter is deactivated by oxygen⁴ faster than it sensitizes destruction of a molecule of **1**. Significant formation of singlet acetone in a step analogous to (5) is rendered unlikely by the observation that the initial luminescence intensity in aerated solution is *higher* than in degassed solutions; thus, when "self-sensitization," such as reaction 5, occurs fewer singlets are produced than in the thermolysis when triplets are efficiently quenched by O_2 (Figure 1).

In order to calculate a rate expression for the proposed mechanism, we assume a steady state in excited acetone and thereby obtain⁵ eq 6, which provides a

$$\exp \left[\left(1 + \frac{1-\alpha}{\phi_s + \phi_T} \right) \left(\ln \left(\frac{F}{F_0} \right) + \frac{t}{\tau_D} \right) \right] = \frac{1 + (1-\alpha + \phi_s + \phi_T) k_q \tau_T [1]_0 (F/F_0)}{1 + (1-\alpha + \phi_s + \phi_T) k_q \tau_T [1]_0} \quad (6)$$

measurable relationship between the fluorescence intensity F (which measures the concentration of **1**) and time. In this equation, F_0 and $[1]_0$ are the fluorescence

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

(4) Oxygen and 1,3-pentadiene are excellent triplet scavengers; see N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, New York, N. Y., 1964.

(5) For a detailed derivation of eq 6, please write the senior author at Columbia University.