

Next let us consider the HOMO/LUMO crossing. The ground state in its vicinity corresponds to a hybrid of the configurations derived by double occupation of one or other of the two near-degenerate MO's.¹² It is easily shown that this hybrid has an energy in between those of the singlet and triplet configurations in which the two MO's are each singly occupied. Since the latter singlet correlates with singly excited structures in regions away from the orbital crossing, it is evident that the singlet excited surface can never intersect the ground state surface. The triplet surface on the other hand must do so since it lies lower at the orbital crossing point. A thermal pericyclic chemiluminescent reaction should therefore give almost exclusively triplet excited structures. All the cases so far reported seem to conform to this.

A final proviso comes from the need for a reaction to be extremely exothermic if it is to lead to excited states of "normal" molecules with correspondingly high excitation energies. The potential surface for such a reaction must be correspondingly highly skewed and the triplet surface must slope steeply down to a minimum over the product. If the ground state potential surface is of the type involved in $3 \rightarrow 4$, where the transition state precedes the HOMO/LUMO crossing, the triplet surface is then likely to intersect the ground state surface *after* the transition state has been passed (*cf.* Figures 1 and 3). The efficiency of intersystem crossing will then be very low. For high chemiluminescent efficiency, it is therefore necessary not only that a pericyclic reaction be "forbidden" and highly exothermic but also that the geometrical constraints should be such as to make the HOMO/LUMO crossing correspond to the transition state (see ref 8). This condition is met in the case of **1** but not **3**.

Reversing these arguments, we would then predict that *any* forbidden pericyclic reaction which is highly exothermic, and in which the geometrical constraints indicated above are present, should give triplet excited product with high efficiency. Whether or not the process is actually chemiluminescent will of course depend on the fate of the triplet.

References and Notes

- (1) This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and the Robert A. Welch Foundation through Grant F-126. The calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computation Center.
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- (11) Our calculations were sufficient to establish the general shape of the surface but not to allow the construction of a detailed map.
- (12) Calculations of the potential surface in this region have therefore to be carried out with inclusion of CI with the lowest doubly excited configuration.¹³
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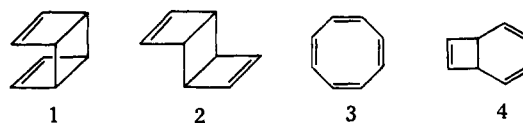
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Possible Intervention of Triplet States in Thermal Reactions of Hydrocarbons. A Study of the Rearrangements of Cyclobutadiene Dimers and Analogous Compounds¹

Sir:

On heating, the syn (**1**) and anti (**2**) dimers of cyclobutadiene are converted to cyclooctatetraene (**3**). We have now found that **1** reacts much faster than **2**, the ratio of rates at 97° being 20:1. The corresponding kinetic parameters are shown in Table I; it will be seen that both reactions have small positive entropies of activation, the difference in rates being due to the difference between their heats of activation.



A possible explanation seemed to lie in the fact that whereas **1** can give **3** directly by a ($\pi 2_s + \pi 2_s$) retrocycloaddition, **2** can do so only in two steps, *via* an intermediate bicyclooctatriene, **4**, formed by disrotatory electrocyclic opening of one cyclobutene ring in **2**. While both reactions are "forbidden," the retrocycloaddition could well be the more facile.

Since MINDO/3^{2,3} has proved successful and useful in the interpretation of other electrocyclic reactions⁴ we studied the rearrangements of **1** and **2** using the same technique. First we examined the direct conversion of **1** or **2** to **3** by retrocycloaddition. Both processes proved to be extremely unfavorable with calculated activation energies >75 kcal/mol. The energies of the transition states were indeed so high that we could not achieve SCF convergence in their vicinity.⁵ This result seems to exclude the possibility that **1** reacts faster than **2** because of a difference in mechanism.

The second path, *via* **4**, was next studied. As expected, the transition states for the overall reaction lay between **1** and **4**, the barrier between **4** and **3** being lower. The calculated activation energies (kcal/mol) were: $1 \rightarrow 4$, 57.7; $2 \rightarrow 4$, 56.1; $4 \rightarrow 3$, 22.8. Thus the calculated activation energies for $1 \rightarrow 4$ and $2 \rightarrow 4$ are not only too large by nearly 30 kcal/mol but also in the wrong order. Thus in so far as the calculations can be trusted, they seem to exclude *any* normal reaction mechanism involving only the ground state potential surface. In this connection it is interesting that our calculated activation energy for $4 \rightarrow 3$ agrees quite well with experiment (18.7 ± 0.08).⁶

Similar difficulties arose in a MINDO/3 study of the thermolysis of 1,2-dioxetane⁷ which apparently involves an intersystem crossing with efficient formation of triplet excited products. We therefore calculated the triplet surface for the $1 \rightarrow 3$ system as a function of the reaction coordinates used in studying the ground state.

The triplet surface was indeed found to intersect the ground state surface between **1** or **2** and the transition states separating them from **3**. The relationship between the singlet and triplet surfaces is indicated in Figure 1. The minimum in the triplet surface corresponds to the triplet

Table I. Kinetic Parameters for the Thermal Reaction of Syn and Anti Dimers of Cyclobutadiene

	1	2
k at 97° (sec ⁻¹)	2.75×10^{-4}	1.40×10^{-5}
E (kcal/mol)	28.8 ± 0.6	32.4 ± 0.9
Log A	13.36 ± 0.34	14.18 ± 0.56
ΔS^\ddagger , eu	$+1 \pm 2$	$+4 \pm 3$

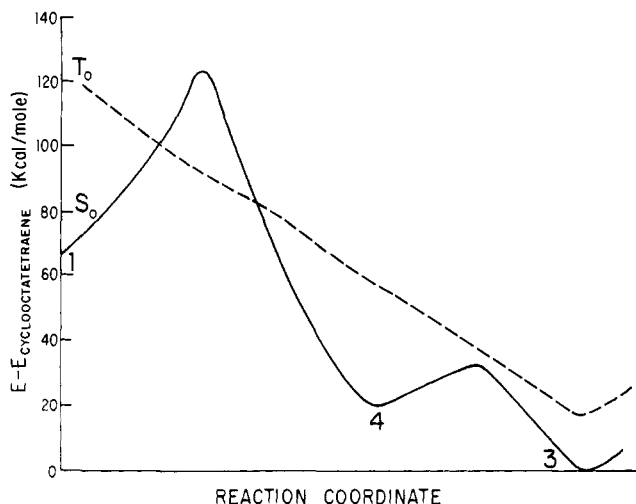
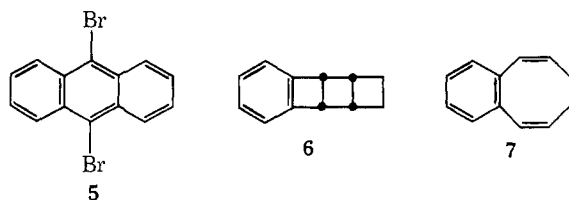


Figure 1. Cross section of S_0 and T_0 potential energy surfaces for the interconversion of **1** to **4**.

state of cyclooctatetraene; this is predicted to be planar, with D_{8h} symmetry, lying 17.8 kcal/mol above the ground state ($C-C$ bond length, 1.403 Å). There may be a small subsidiary minimum corresponding to **4**; if so, however, the barrier separating it from triplet **3** is very low.

According to these results there are direct low energy paths from **1** or **2** to **3** via triplet intermediates, the initial product in each case being the triplet excited form of **3**. (Intermediate deactivation might lead to **4** but this would rearrange rapidly to **3** under the conditions of the reaction). The corresponding activation energies are: $1 \rightarrow 3^*$, 36.0 kcal/mol; $2 \rightarrow 3^*$, 39.3 kcal/mol. The agreement with experiment is quite close and the difference between the two values (3.3 kcal/mol) is essentially identical with that observed (3.6 kcal/mol).

These results therefore seemed to suggest rather strongly that the conversions of **1** or **2** to **3** must involve intersystem crossing as an integral part of the reaction, as apparently does the thermolysis of dioxetanes. If so, **3** should be formed initially in its triplet state. Unfortunately the triplet state of **3** lies so close to the ground state that its detection would be very difficult; we therefore looked for analogous processes that might be expected to take place in a similar way and lead to products with a greater singlet-triplet separation. Such high energy triplets can be detected by adding to the reaction mixture agents which can be excited by energy transfer and will then emit light, e.g., 9,10-dibromoanthracene (**5**).⁸



An obvious choice seemed to be the *syn*-benzotricyclooctene (**6**) which can be made easily by reduction of the double bond in the codimer of cyclobutadiene and benzocyclobutadiene⁹ and which is converted quantitatively on heating to benzo[*c*]-1,3,5-cyclooctatriene (**7**). In repeated experiments where solutions of **6** and **5** in decalin (30 mg and 100 mg per ml, respectively) were heated to temperatures over the range 150–200°, visible light was emitted corresponding to fluorescence from **5**. No light was emitted in control experiments when **6** was omitted and light emission died away with the disappearance of **6** (the lifetime of which could of

course be estimated from the Arrhenius parameters). While the chemiluminescence was weak, Professor Turro (who is now examining the reaction in detail) has pointed out that the fluorescent efficiency of **5** at these temperatures is very low indeed so that the yield of triplet **7** must be quite high. There seems to be no case on record where a thermal reaction of a hydrocarbon has led with high efficiency to a triplet excited product.

This work reported here and in the two previous communications^{7,10} therefore leads to the quite unexpected conclusion that apparently "normal" reactions may take place by mechanisms involving intersystem crossing and so lead to products in triplet excited states. The kinetic data moreover indicate that such reactions can occur with normal frequency factors. If these conclusions can be substantiated, they will open a Pandora's box of hitherto unexpected new chemiluminescent processes and a complete rethinking of ideas concerning the possible role of triplet states in thermal reactions.

References and Notes

- (1) This work was supported by the Robert A. Welch Foundation through Grants No. F-067 and F-126, by the Air Force Office of Scientific Research through Contract No. F44620-71-C-0119, and by the National Science Foundation. The calculations were carried out using the CDC 6400/6600 computer at The University of Texas Computation Center.
- (2) MINDO/3 is an improved version of the MINDO/2 semiempirical SCF MO method; R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, in press.
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Total Synthesis of β -Lactam Antibiotics. VII.¹ Total Synthesis of (\pm)-1-Oxacephalothin

Sir:

Aside from the nitrogen atom, the cephalosporin and penicillin nuclei have sulfur as the only other heteroatom. Since the sulfur atom could possibly bind to an electrophilic site on the enzyme with which these molecules interact, it was of interest to determine whether sulfur is necessary for the biological activity of these compounds. Substitution of sulfur in the bicyclic system by a smaller atom could also result in higher strain in the system and, hence, a more reactive β -lactam moiety and therefore perhaps an antibiotic with increased activity.

Following the total syntheses of cephalothin (**13**) and cefoxitin (**14**) from our laboratories,² we now wish to report the total synthesis of a molecule with all the features of cephalothin in which the sulfur atom has been replaced by oxygen,³ and in the accompanying article a similar molecule in which the sulfur has been replaced by methylene.⁴

Treatment of benzyl α -aminodiethylphosphonoacetate²