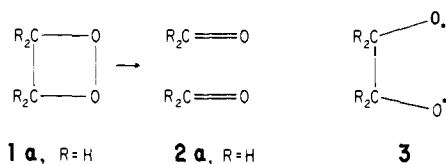


We have had considerable success in studying the mechanisms of other "forbidden" pericyclic reactions by the MINDO/3<sup>9</sup> method, the calculated activation energies usually agreeing with experiment to within 5 kcal/mol.<sup>10</sup> It occurred to us that a similar calculation for the dissociation of a dioxetane might throw light on the origin of the intersystem crossing, particularly since we had used MINDO/3 very successfully in a study of the analogous dissociation of cyclobutane into ethylene.<sup>11</sup>

The MINDO/3 potential surface for dissociation of dioxetane (**1a**) into formaldehyde (**2a**), by reverse ( $2\pi + 2\pi$ )



cycloaddition, proved very similar to that for dissociation of cyclobutane, having the "two-valley" structure characteristic of "forbidden" pericyclic reactions,<sup>11,12</sup> where reactant and product are lumomers.<sup>13</sup> A two-dimensional contour map was therefore constructed, using the carbon-carbon and oxygen-oxygen bond lengths as reaction coordinates. For each value of the reaction coordinates the energy was, as usual, minimized with respect to all the other geometrical variables, no assumptions whatsoever being made. While we did not locate the transition state with any high precision, we were able to establish that it must lie at least 65 kcal/mol above **1**. This is so much greater than the activation energies reported for thermolysis of substituted dioxetanes (21–29 kcal/mol<sup>2–6</sup>) that we feel the mechanism can be excluded. It is in any case difficult to see why it should lead exclusively to triplet excited products.

The second alternative would be conversion of **1** to an intermediate biradicaloid<sup>14</sup> **3** which in turn dissociates. This possibility has been favored by Richardson, *et al.*<sup>15</sup> Since biradicals are also species where the ground state and excited state become degenerate, **3** could very well dissociate into excited products; though here again it is difficult to see why triplets should be formed.

If MINDO/3 is to be used for biradicals or biradical-like species, it is necessary to include configuration interaction (CI) with the lowest doubly excited configuration.<sup>16</sup> The potential surface was therefore recalculated including such CI. While the corresponding activation energy (45 kcal/mol) was much less than for the pericyclic route, it was still much greater than experiment.

These results seemed to suggest rather strongly that the dissociation of **1a** into **2a** cannot be a ground state process. We therefore decided to study the corresponding triplet surface. MINDO/3 calculations for triplets are carried out using the "half-electron" approximation.<sup>17,18</sup> This has been shown to give good values for the energies of triplet CH<sub>2</sub> and O<sub>2</sub>.<sup>19</sup> As a further check, we calculated the lowest triplet and singlet excited states of formaldehyde; the corresponding excitation energies ( $\Delta E^*$ ) were:  $\Delta E^*$  (singlet), calcd, 78.0; obsd,<sup>20</sup> 80.6 kcal/mol;  $\Delta E^*$  (triplet), calcd, 72.9; obsd,<sup>20</sup> 72.0 kcal/mol. The triplet surface for dioxetane was then calculated using the same reaction coordinates as before. This was indeed found to intersect the singlet surface between dioxetane and the transition state, at a point 38.3 kcal/mol above **1**. The triplet surface curves down to a minimum corresponding to excited **2**. The structure corresponding to the crossing point is shown in the figure. It will be seen that the O–O bond is still quite short, implying that this "transition state" is by no means a biradical.

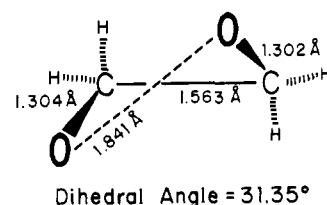


Figure 1. Calculated geometry of transition state for intersystem crossing in the thermal conversion of **1** to **2**.

These calculations seem to provide very strong evidence that the conversion of **1** to **2** does in fact involve an integral intersystem crossing. The calculated activation energy (38.3 kcal/mol) is in reasonable agreement with experiment, given that substituents would be expected to lower the activation energy. It therefore seems clear that reactions can take place by intersystem crossing without necessarily having small frequency factors. The implications are self-evident and far reaching.

## References and Notes

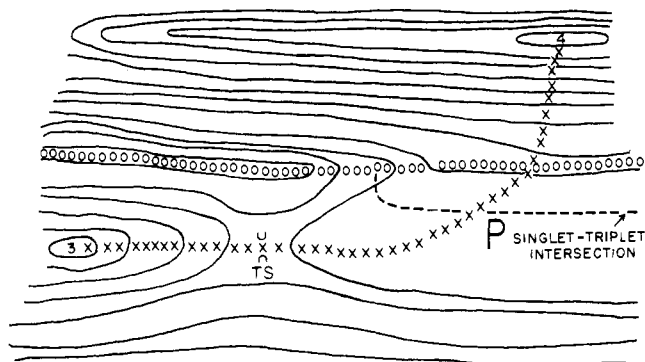
- (1) This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and the Robert A. Welch Foundation through Grant F-126. The calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computation Center.
- (2) T. Wilson and A. P. Schaap, *J. Amer. Chem. Soc.*, **93**, 4126 (1971).
- (3) N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, **94**, 2887 (1972).
- (4) P. Lechtken, A. Yekta, and N. J. Turro, *J. Amer. Chem. Soc.*, **95**, 3027 (1973).
- (5) N. J. Turro, H. C. Steinmetzer, and A. Yekta, *J. Amer. Chem. Soc.*, **95**, 6468 (1973).
- (6) E. H. White, P. D. Wildes, J. Weicho, H. Doshan, and C. C. Wei, *J. Amer. Chem. Soc.*, **95**, 7050 (1973).
- (7) D. Kearns, *Chem. Rev.*, **71**, 345 (1971).
- (8) See, e.g., S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes," McGraw-Hill, New York, N.Y., (1941), p 326.
- (9) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, in press.
- (10) For a summary of results, see M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **96**, 5244 (1974).
- (11) M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **96**, 5246 (1974).
- (12) M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **93**, 4292 (1971).
- (13) M. J. S. Dewar, S. Kirschner, and H. W. Kollmar, *J. Amer. Chem. Soc.*, **96**, 5240 (1974).
- (14) M. J. S. Dewar, S. Kirschner, H. W. Kollmar, and L. E. Wade, *J. Amer. Chem. Soc.*, **96**, 5242 (1974).
- (15) W. H. Richardson, M. B. Yelvington, and H. E. O'Neal, *J. Amer. Chem. Soc.*, **94**, 1619 (1972); W. H. Richardson, F. C. Montgomery, and M. B. Yelvington, *ibid.*, 9277.
- (16) See R. C. Bingham and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **94**, 9107 (1972).
- (17) M. J. S. Dewar, J. A. Hashmall, and C. G. Venier, *J. Amer. Chem. Soc.*, **90**, 1953 (1968).
- (18) M. J. S. Dewar and N. Trinajstić, *J. Chem. Soc. A*, 1220 (1971).
- (19) M. J. S. Dewar, R. C. Haddon, and P. K. Weiner, *J. Amer. Chem. Soc.*, **96**, 253 (1974).
- (20) G. Herzberg, "Molecular Spectra and Molecular Structure III. Electronic Spectra and Electronic Structure of Polyatomic Molecules," Van Nostrand-Reinhold, New York, N.Y., 1966.

Michael J. S. Dewar,\* Steven Kirschner  
 Department of Chemistry  
 The University of Texas at Austin  
 Austin, Texas 78712  
 Received June 20, 1974

## Cryptochemiluminescence in the Rearrangements of Dewar Benzenes. The Requirements for Pericyclic Reactions to Be Chemiluminescent<sup>1</sup>

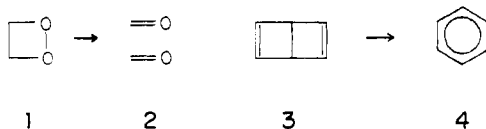
Sir:

The thermolysis of dioxetanes is a chemiluminescent process, leading with high efficiency to triplet excited product.<sup>2</sup> We have explained<sup>3</sup> this result by carrying out a MINDO/



**Figure 1.** Schematic potential surface for  $3 \rightarrow 4$ , indicating the minimum energy reaction path (XXX), HOMO/LUMO crossing (0000), and singlet-triplet intersection (0000).

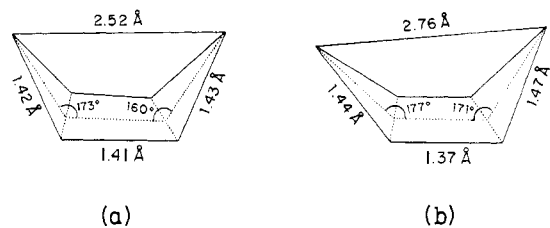
$3^4$  study of the potential surface for the conversion of dioxetane (**1**) to formaldehyde **2**. The calculated activation energy for the normal ground state retrocycloaddition was very high. However, the triplet surface was found to intersect the ground state surface between the minimum corresponding to **1** and the transition state for (**1**  $\rightarrow$  **2**). Intersystem crossing, to give one molecule of **2** in its ground state and the other in its lowest triplet state, should therefore be a relatively facile process.



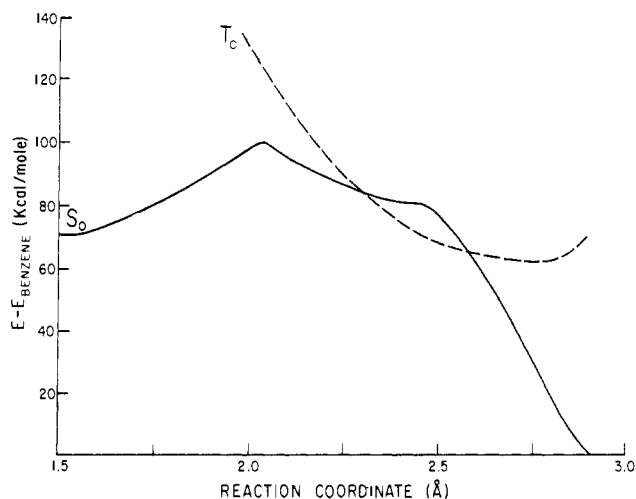
Recently Turro *et al.*,<sup>5</sup> have shown that triplet excited product is also formed in the thermolysis of Dewar benzene (**3**) to benzene (**4**). No phosphorescence could be observed under the conditions of the reaction; however, the formation of triplet **4** was indicated by fluorescence of added 9,10-dibromoanthracene, this being excited by energy transfer. While, however, the dioxetane fission gives triplet excited product with very high efficiency, thermolysis of **3** gives only *ca.* 0.02% of triplet excited **4**. This difference cannot be attributed to a lack of energy, for the transition state for (**3**  $\rightarrow$  **4**) lies above the lowest triplet of **4**. The experimental evidence also suggests that in this case intersystem crossing occurs after the transition state for the normal ground state reaction is passed, for the proportion of excited **4** formed is independent of temperature.

These results were of special interest to us since we had carried out a MINDO/3 calculation for the conversion of **3** to **4**.<sup>6</sup> This accounted well for the general course of the reaction, giving quite good estimates of the heat of reaction and activation energy. We have now supplemented this calculation by a study of the corresponding triplet surface.

The conversion of **3** to **4** is a typical "forbidden" electrocyclic process, involving the interconversion of lumomers<sup>7</sup> with a corresponding HOMO/LUMO crossing. As we have pointed out,<sup>8</sup> such reactions normally involve highly unsymmetrical transition states which precede the HOMO/LUMO crossing. The potential surfaces have a "two-valley" configuration,<sup>9</sup> the valleys corresponding to reactant-like and product-like structures and the intervening ridge to the biradical species<sup>10</sup> where HOMO and LUMO cross. We established<sup>6</sup> that (**3**  $\rightarrow$  **4**) showed these features, and located the transition state, by a two-dimensional grid search<sup>9</sup> using the length ( $r$ ) of the breaking bond in **3**, and the angle ( $\theta$ ) between the 1234 and 1456 planes as reaction coordinates. The shape of the surface is indicated by the idealized contour map in Figure 1.<sup>11</sup>



**Figure 2.** Structures for (a) a biradicaloid in the plateau P of Figure 1 and (b) triplet state of benzene.



**Figure 3.** Cross section of  $S_0$  and  $T_0$  potential energy surfaces for the interconversion of **3** to **4**.

The minimum energy reaction path (XXX) crosses the transition state (TS) and then descends gently to a wide plateau (P). The HOMO/LUMO crossing (0000), at low values of  $r$ , corresponds to a ridge. As  $r$  increases, this dies away and the crossing then follows the edge of the plateau, marking a precipitous drop to benzene (**4**). The triplet surface intersects the ground state surface along a line (---) crossing the plateau almost parallel to the  $r$  axis. At the transition state (TS), the surfaces are well separated (by 23.7 kcal/mol).

These results explain the experimental findings<sup>5</sup> very nicely. Since the singlet and triplet surfaces cross, the product can be formed in an excited state. Since the crossing occurs after transition state has been passed, the yield of excited product is independent of temperature and also small (since most of the molecules will lose their excess energy too quickly to undergo intersystem crossing). We had also studied the conversions of the 1-chloro and 1,4-dichloro derivatives of **3** to corresponding derivatives of **4**; we now find that the potential surfaces are similar to that for **3** itself, involving similar singlet-triplet intersections.

Points on the plateau P (Figure 1) correspond to biradicaloid<sup>10</sup> structures; a typical structure, near the edge of the plateau is shown in Figure 2a while Figure 2b shows the predicted structure of the resulting benzene triplet.

Apart from their significance in the immediate context, these results, combined with the ones<sup>3</sup> for (**1**  $\rightarrow$  **2**), lead to some general conclusions concerning chemiluminescent pericyclic reactions.

First, the reactions must clearly be of "forbidden" type, since otherwise the ground state and excited state surfaces could not intersect in any region of reasonably low energy. In a "forbidden" reaction the HOMO and LUMO cross so there must be a corresponding ground state-excited state crossing.

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.<sup>12</sup> 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

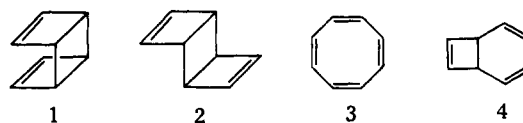
- (1) This work was supported by the Air Force Office of Scientific Research through Contract F44620-71-C-0119 and the Robert A. Welch Foundation through Grant F-126. The calculations were carried out using the CDC 6400/6600 computer at the University of Texas Computation Center.
- (2) N. J. Turro, H. C. Steinmetzer, and A. Yekta, *J. Amer. Chem. Soc.*, **95**, 6468 (1973).
- (3) M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **96**, 7578 (1974).
- (4) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Amer. Chem. Soc.*, in press.
- (5) P. Lechtken, R. Breslow, A. H. Schmidt, and N. J. Turro, *J. Amer. Chem. Soc.*, **95**, 3025 (1973).
- (6) M. J. S. Dewar and S. Kirschner, *Chem. Commun.*, in press.
- (7) M. J. S. Dewar, S. Kirschner, and H. W. Kollmar, *J. Amer. Chem. Soc.*, **96**, 5240 (1974).
- (8) M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **96**, 5244 (1974).
- (9) M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **93**, 4292 (1971).
- (10) M. J. S. Dewar, S. Kirschner, H. W. Kollmar, and L. E. Wade, *J. Amer. Chem. Soc.*, **96**, 5242 (1974).
- (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.<sup>13</sup>
- (13) See R. C. Bingham and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **94**, 9107 (1972).

Michael J. S. Dewar,\* Steven Kirschner, Herbert W. Kollmar  
 Department of Chemistry, The University of Texas at Austin  
 Austin, Texas 78712  
 Received June 20, 1974

## Possible Intervention of Triplet States in Thermal Reactions of Hydrocarbons. A Study of the Rearrangements of Cyclobutadiene Dimers and Analogous Compounds<sup>1</sup>

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<sup>2,3</sup> has proved successful and useful in the interpretation of other electrocyclic reactions<sup>4</sup> 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.<sup>5</sup> 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 ( $18.7 \pm 0.08$ ).<sup>6</sup>

Similar difficulties arose in a MINDO/3 study of the thermolysis of 1,2-dioxetane<sup>7</sup> 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 <sup>-1</sup> )	$2.75 \times 10^{-4}$	$1.40 \times 10^{-5}$
$E$ (kcal/mol)	$28.8 \pm 0.6$	$32.4 \pm 0.9$
Log $A$	$13.36 \pm 0.34$	$14.18 \pm 0.56$
$\Delta S^\ddagger$ , eu	$+1 \pm 2$	$+4 \pm 3$