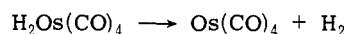


not by itself imply a dinuclear elimination mechanism. A traditional mononuclear reductive elimination followed by



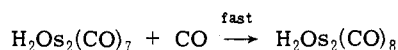
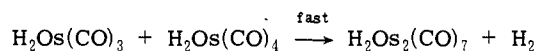
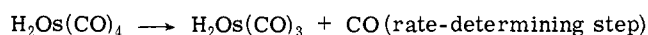
the insertion of  $\text{Os}(\text{CO})_4$  into an  $\text{Os}-\text{H}$  bond of another  $\text{H}_2\text{Os}(\text{CO})_4$  molecule would also result in the formation of  $\text{H}_2\text{Os}_2(\text{CO})_8$ . Indeed, Moss and Graham originally proposed<sup>6</sup> that their polynuclear osmium dihydridocarbonyls resulted from such a reaction sequence. Simple elimination of  $\text{H}_2$  might also have been expected as the reverse of the original synthesis<sup>2</sup> of  $\text{H}_2\text{Os}(\text{CO})_4$  by the oxidative addition of hydrogen to  $\text{Os}(\text{CO})_5$ —a process likely to involve intermediate  $\text{Os}(\text{CO})_4$ .

The distinction between dinuclear and mononuclear elimination mechanisms was most easily made through labeling experiments.  $\text{D}_2\text{Os}(\text{CO})_4$  was readily prepared (71% yield, 86% isotopic purity) from  $\text{Na}_2\text{Os}(\text{CO})_4$  and  $\text{D}_3\text{PO}_4$  in tetraglyme. Thermolysis of mixtures of the deuteride and hydride at  $105^\circ$  gave HD as well as  $\text{H}_2$  and  $\text{D}_2$ , indicating a dinuclear mechanism. The exact isotopic composition of the product gas reflects the operation of small isotope effects:  $k_{\text{HH}}/k_{\text{HD}} = 1.4 \pm 0.2$ ,  $k_{\text{HH}}/k_{\text{DD}} = 2.9 \pm 0.4$ .<sup>10</sup>

The possible presence of an  $\text{H}_2-\text{D}_2$ -HD equilibration catalyst was checked by the prolonged thermolysis of  $\text{H}_2\text{Os}(\text{CO})_4$  under excess  $\text{D}_2$ . Although the principal product was  $\text{H}_2$ , a small amount of HD (16% of  $\text{H}_2$ ) was formed, suggesting that the  $\text{H}_4\text{Os}_4(\text{CO})_{12}-\text{Os}_3(\text{CO})_{12}$  secondary product system is capable of slow isotopic equilibration. (This conclusion was confirmed by observing the slow equilibration of an  $\text{H}_2-\text{D}_2$  mixture by these compounds.) This experiment also rules out any mechanism involving the reversible dissociation of hydrogen prior to the bimolecular step; such a process would have formed  $\text{D}_2\text{Os}(\text{CO})_4$  and thus much HD as in the previous experiment.

A quantitative study of the kinetics of  $\text{H}_2\text{Os}(\text{CO})_4$  decomposition was then undertaken.<sup>11</sup> Under small CO pressures the reaction is first-order in  $\text{H}_2\text{Os}(\text{CO})_4$ , the rate constant at  $125.8^\circ$  being  $6.1 \pm 0.2 \times 10^{-5} \text{ sec}^{-1}$ .  $\Delta H^*$  is  $33.7 \pm 0.6 \text{ kcal/mol}$  and  $\Delta S^*$  is  $+6 \pm 2 \text{ eu}$ . The rate law and activation parameters suggest a rate-determining step involving carbon monoxide dissociation.<sup>12</sup>

Taken together, the deuterium labeling data and the kinetic results suggest the following mechanism.<sup>13,14</sup>



The empty coordination site formed in the first step may allow the formation of one or more hydride bridges necessary for the dinuclear step.

This mechanism makes one unusual prediction, namely that  $\text{H}_2\text{Os}(\text{CO})_4$  successfully competes with carbon monoxide for the coordinatively unsaturated intermediate  $\text{H}_2\text{Os}(\text{CO})_3$ , so that decomposition will occur faster than carbonyl exchange. The entire scheme could thus be tested by heating  $\text{H}_2\text{Os}(\text{CO})_4$  under an atmosphere of  $^{13}\text{C}$ O and stopping the reaction after one half-life. Mass spectroscopic analysis of the isolated components showed only 4% label incorporation in the recovered  $\text{H}_2\text{Os}(\text{CO})_4$ , while there was 51% label incorporation in the product  $\text{H}_2\text{Os}_2(\text{CO})_8$ . The latter result exceeds the minimum (12.5%) required by the last step of the proposed mechanism and shows that  $\text{H}_2\text{Os}_2(\text{CO})_8$ , unlike  $\text{H}_2\text{Os}(\text{CO})_4$ , undergoes rapid carbonyl exchange under the reaction conditions.

Thus, in this dihydride at least, thermal reductive elimination of molecular hydrogen does not occur, loss of carbon

monoxide and subsequent dinuclear elimination occurring instead. It is worth noting that (1) loss of CO is also the primary photoprocess occurring upon irradiation of  $\text{H}_2\text{Os}(\text{CO})_4$  in an argon matrix at  $20^\circ\text{K}$ <sup>15</sup> and (2) loss of molecular hydrogen does occur as the principal fragmentation mode of the parent ion  $\text{H}_2\text{Os}(\text{CO})_4$  in the mass spectrometer. We are currently investigating the extent to which these dinuclear processes also occur in the reactions of the related alkyl species.

**Acknowledgment** is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the Research Corporation, and to the National Science Foundation (GP-38907X) for support of this work, to Dr. A. J. Rest for unpublished results, and to Matthey-Bishop, Inc., for a generous loan of osmium tetroxide.

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- (10) The stated uncertainty reflects the slow  $\text{H}_2-\text{D}_2$  equilibration (*vide infra*).
- (11) The reactions were run in concentrated mesitylene solution and followed by nmr with octamethylcyclotetrasiloxane as internal standard.
- (12) Although the rate is independent of  $p_{\text{CO}}$  up to the highest experimentally practical pressure (600 mm), this observation is not at all inconsistent with a dissociative mechanism; the concentration of CO in the liquid phase is quite small compared to the concentration of  $\text{H}_2\text{Os}(\text{CO})_4$  (about 0.4 M). Since the rate-determining step must be unimolecular and is demonstrably not the loss of molecular hydrogen, there is in any case no chemically plausible alternative.
- (13) A similar mechanism has been proposed for the loss of hydrogen from the monohydride  $\text{HCo}(\text{CO})_4$  by Ungvary and Marko.<sup>14</sup> However, they postulate *equilibrium* dissociation of a carbonyl group prior to the bimolecular elimination step.
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John Evans, Jack R. Norton\*

Department of Chemistry, Princeton University  
Princeton, New Jersey 08540

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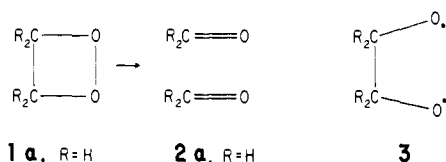
## MINDO/3 Study of the Thermolysis of Dioxetane. Role of the Triplet State<sup>1</sup>

Sir:

The thermolysis of derivatives (1) of 1,2-dioxetane to pairs of carbonyl derivatives (2) is a well known chemiluminescent process. The emission of light is due to phosphorescence of one of the product molecules, this being formed in its triplet state. While estimates of the quantum yield vary,<sup>2-6</sup> most lie in the range 0.5-1.0, implying that intersystem crossing is taking place with high efficiency. As Kearns<sup>7</sup> has pointed out, it is difficult to see how this could be the case unless the intersystem crossing is an integral part of the reaction, the transition state corresponding to the point at which the singlet and triplet surfaces cross. This argument has not, however, been pressed, presumably because of the long held view that such a process would necessarily have a very low frequency factor.<sup>8</sup> The frequency factors for dissociation of dioxetanes seem in fact to be "normal."

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 ( $2\pi + 2\pi$ )

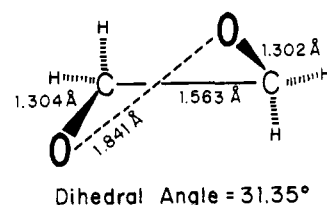


cycloaddition, proved very similar to that for dissociation of cyclobutane, having the "two-valley" structure characteristic of "forbidden" pericyclic reactions,<sup>11,12</sup> where reactant and product are lumomers.<sup>13</sup> A two-dimensional contour map was therefore constructed, using the carbon-carbon 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.

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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/