

THE IMPORTANCE OF SPIN MULTIPLICITY IN THE ELECTROCYCLIC ELIMINATION  
OF O=C=C=O (ETHYLENEDIONE)

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It has recently been reported that substituted and annelated derivatives of bicyclo[2.2.2]octadiene-2,3-dione do not undergo a ready thermal elimination of C<sub>2</sub>O<sub>2</sub> (ethylenedione)<sup>2</sup> or 2CO to yield the corresponding aromatic compounds.<sup>3</sup> This is further confirmed by the apparent stability of the parent system.<sup>4</sup> As elimination of ethylenedione is a disrotatory reverse [2+4] addition it is allowed by the Woodward-Hoffman rules<sup>5</sup> and in the case of those compounds which would lead to benzene derivatives, elimination might well be expected to take place with ease. The alternative concerted pathway leading to two molecules of carbon monoxide is not allowed as a disrotatory process.

Application of the orbital symmetry rules does not take cognizance of the spin multiplicities of the reactants and products and it is thus possible that a reaction which is allowed by the former may be forbidden by the latter. Hirst, Hopton and Linnett<sup>6</sup> have made the qualitative prediction, based on MO considerations, that the ground state of ethylenedione is a triplet.

We have investigated the potential surfaces of ethylenedione by the INDO method<sup>7</sup> and have found the equilibrium geometries for the lowest singlet and triplet states. The bond lengths and binding energies are given in Table 1, and

it may be seen that the triplet is more stable<sup>8</sup> by 18.6 kcal mole<sup>-1</sup>. Thus the

Table 1. INDO Calculations on Ethylenedione

	Bond Lengths (°A)		Binding Energy (kcal mole <sup>-1</sup> )
	C-O	C-C	
O=C=C=O (singlet)	1.251	1.287	-1174.7
O=C=C=O (triplet)	1.252	1.283	-1193.2

concerted reactions of bicyclo[2.2.2]octadiene-2,3-diones leading to ground state products are spin forbidden and the triplet-singlet separation for ethylenedione is sufficiently large to account for the failure of these compounds to undergo the reverse Diels-Alder reaction (in analogy with the behavior of the trans-annular peroxides of benzenoid hydrocarbons).

Photochemical bisdecarbonylation of bicyclo[2.2.2]octadiene-2,3-diones to carbon monoxide and aromatic compounds apparently occurs very readily.<sup>3,9,10</sup> Orbital symmetry rules cannot, however, be applied since the excited state undergoing the reaction has not been identified<sup>11</sup> nor it is known whether a triplet or singlet state is involved. However, we do not believe that ethylenedione is the primary product, as its dissociation to carbon monoxide (the observed photolysis product) is forbidden by orbital symmetry rules.

The heats of formation of the carbon oxides calculated by the MINDO method<sup>12</sup> are given in Table 2. The MINDO calculations,<sup>12-15</sup> like those by the extended Huckel method,<sup>3</sup> do not preclude the existence of ethylenedione as a stable entity. The results of this study suggest, however, that bicyclo[2.2.2]octadiene-2,3-diones are unlikely to serve as precursors for ethylenedione.

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Table 2. MINDO Calculations on Carbon Oxides

Molecule	Method	Bond Lengths (°A)		Heat of Formation (kcal mole <sup>-1</sup> ) calcd (obsd)	Ref.
		C-O	C-C		
O=C=C=O (singlet)	MINDO/1	1.198 <sup>a</sup>	1.291 <sup>a</sup>	-10.5	d
	MINDO/2	1.198	1.291	-20.2	e
O=C=C=C=O	MINDO/2	1.187	1.278	-41.9 (-23.4, -47.4)	e
O=C=O	MINDO/2	1.189		-91.4 (-94.0)	e
C≡O	MINDO/1	1.129 <sup>b</sup>		-11.9 (-26.4)	f
<sup>-</sup> O-C≡C-O <sup>-</sup>	MINDO/1	1.28 <sup>c</sup>	1.21 <sup>c</sup>	70.6	d

<sup>a</sup>Bond lengths taken from MINDO/2 calculation of ref. 15.

<sup>b</sup>Observed bond length (see refs. 12 and 13).

<sup>c</sup>Observed bond length: E. Weiss and W. Büchner, *Helv. Chim. Acta*, **46**, 1121 (1963).

<sup>d</sup>This work.

<sup>e</sup>Ref. 15.

<sup>f</sup>Ref. 13.

#### ----- References

1. Present address: Department of Chemistry, University of Texas at Austin, Austin, Texas, 78712.
2. To date, there has been no systematic attempt to name the oxides of carbon O=C<sub>n</sub>=O. However, it appears to us that the normal rules of nomenclature, based on cumulenes as the parent hydrocarbons, can be applied. Thus O=C=C=O becomes ethylenedione, O=C=C=C=O ("carbon suboxide") becomes allenedione, O=C=C=C=C=O butatrienedione, etc.
3. J. Stratig, B. Zwanenburg, A. Wagenaar, and A. C. Udding, *Tetrahedron Lett.*, 125 (1969).
4. H.-D. Scharf and R. Klar, *Tetrahedron Lett.*, 517 (1971).
5. R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Verlag Chemie, GmbH, Weinheim, Germany, 1970.
6. D. M. Hirst, J. D. Hopton and J. W. Linnett, *Tetrahedron*, **19**, Suppl. 2, 15 (1963).
7. J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N.Y., 1970.
8. MO theory leads to the general prediction that all diones of the form O=C<sub>2n</sub>=O, n = 0, 1, 2, ... will have triplet ground states.

9. D. Bryce-Smith and A. Gilbert, Chem. Comm., 1319 (1968).
10. D. L. Dean and H. Hart, J. Amer. Chem. Soc., 94, 687 (1972).
11. See ref. 5, pp. 20-22.
12. N. C. Baird and M. J. S. Dewar, J. Chem. Phys., 50, 1262 (1969).
13. N. C. Baird, M. J. S. Dewar and R. Sustmann, J. Chem. Phys., 50, 1275 (1969).
14. M. J. S. Dewar and E. Haselbach, J. Amer. Chem. Soc., 92, 590 (1970).
15. N. Bodor, M. J. S. Dewar, A. Harget and E. Haselbach, J. Amer. Chem. Soc., 92, 3854 (1970).