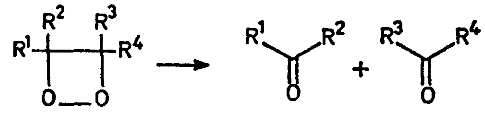
CNDO/S Calculations of the Thermal Dissociation of 1,2-Dioxetan

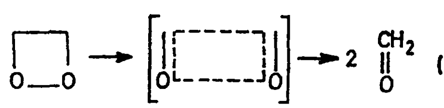
By DAVID R. ROBERTS

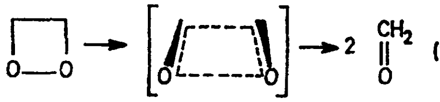
(*Department of Chemistry, The Open University, Walton Hall, Milton Keynes* MK7 6AA)

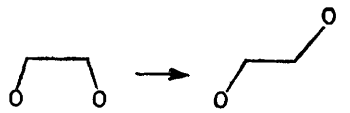
Summary CNDO/S Calculations, with configuration interaction between singly excited states, of the dissociation of 1,2-dioxetan to two formaldehyde molecules indicate a possible mechanism for the observed chemiluminescent nature of this process.

THE thermal dissociation (1) of 1,2-dioxetans to carbonyl compounds is a reaction known to be accompanied by chemiluminescence.[1] The quantum yield of excited product has been shown to be up to 50% and the excitation to be located almost wholly in the lowest triplet state.[2] There have been a number of attempts, based chiefly on the use of correlation diagrams, to provide a qualitative explanation for the occurrence of excited product.[3] There has also been a recent calculation[4] which gave consideration to the ground and singlet excited states involved. However, the nature of the excitation process has not yet been elucidated.


(1)


(2a)


(2b)


(3)

We report the application of the CNDO/S CI MO method to the thermal dissociation of 1,2-dioxetan. The results obtained, though not in quantitative agreement with experiment, do provide a qualitative explanation for the observed chemiluminescent properties of 1,2-dioxetans.

The method used was that of Del Bene and Jaffe[5] with minor modification. The original parameterization was used with the Mataga–Nishimoto formula for the repulsion integrals.[6] To avoid the totally unreal dissociation energies obtained with the original version, the core–core repulsion term was replaced by the modified expression used in the MINDO/2 method.[7] This leads to a value of 265 kJ mol^{-1} for the heat of dissociation compared with the value of 230 kJ mol^{-1} as estimated by O'Neal and Richardson.[8] Standard bond lengths and angles were used for 1,2-dioxetan and formaldehyde.[9]

The energies of the ground state and the lower singlet and triplet excited states were calculated for various nuclear configurations intermediate between the two extremes. Both 'concerted' and 'biradical' pathways were investigated [equation (2)] together with the electronic properties of the *cis-trans* interconversion [equation (3)]. The 'biradical' reaction co-ordinate was that leading to the conformation of lowest energy (dihedral angle *ca.* 60°).

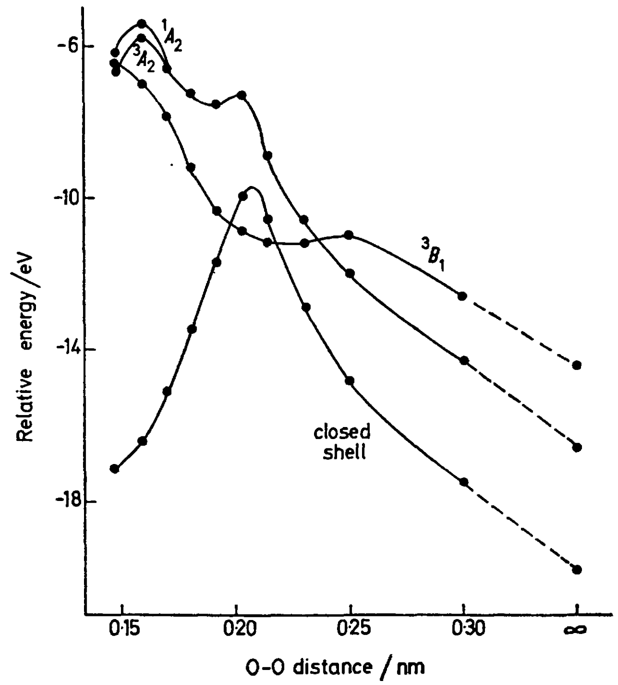


FIGURE 1. The 'concerted' (C_{2v}) pathway for the conversion of 1,2-dioxetan into 2HCHO showing the energies of the closed-shell configuration and the lowest $^3B_1$, $^1A_2$, and $^3A_2$ singly-excited states plotted against the oxygen–oxygen distance.

The results are presented in Figures 1—3. The method gives a good description of the excited states of formaldehyde.[10] In contrast the lowest excited states of 1,2-dioxetan are predicted to be *ca.* 10·5 eV above the ground state; however, it is likely that the first absorption band lies no higher than about 6 eV. Calculation of the excited states of oxetan for comparison gives very similar results; the first observed valence shell transitions occur at 6·6 eV.[11] This failure of the CNDO/S parameterization to account satisfactorily for transitions involving σ orbitals has been noted previously.[12] Further, in the region of the transition state the energies of the two lowest closed shell configurations are very close; it is therefore to be expected that interaction would be very strong leading to a much lower activation energy. Nevertheless the value obtained for the pathway to the 'biradical' configuration (*ca.* 7 eV) compares favourably with the value of 6 eV obtained[4] with the CNDO/2 parameterization when CI between doubly excited configurations was taken into account.

The most significant result is the intersection of a triplet-state surface with the 'ground' state near the transition state. A reaction co-ordinate involving a crossing to the triplet surface requires an activation energy 1 eV less than the lowest energy singlet pathway. Though such a pathway has a low intrinsic probability, the dioxetan molecule requires so much more energy to dissociate *via* the singlet pathway that it is essentially trapped until crossing to the triplet surface does occur. Such a mechanism would account for the low values of the activation energies and pre-exponential factors (indicating low transmission coefficients) of dioxetan decompositions[8,13] compared with the values for the closely related thermal decomposition of oxetans and cyclobutanes.[14] Once on the triplet surface the dioxetan molecule can dissociate rapidly to two formaldehyde molecules with too short a time spent at the second crossing of the triplet and closed shell potential surfaces for a diabatic transition to occur. The product corresponds to a singly excited state involving both formaldehyde molecules; with increasing separation this exciton state would degenerate to one excited and one ground state formaldehyde molecule. The maximum quantum yield of triplet states of 0·5 found experimentally[2] for some systems requires 100% decomposition by this pathway. The small number of molecules found in a singlet excited state presumably could arise by intersystem crossing from the triplet product, a process with a relatively high probability for n–π^* states.

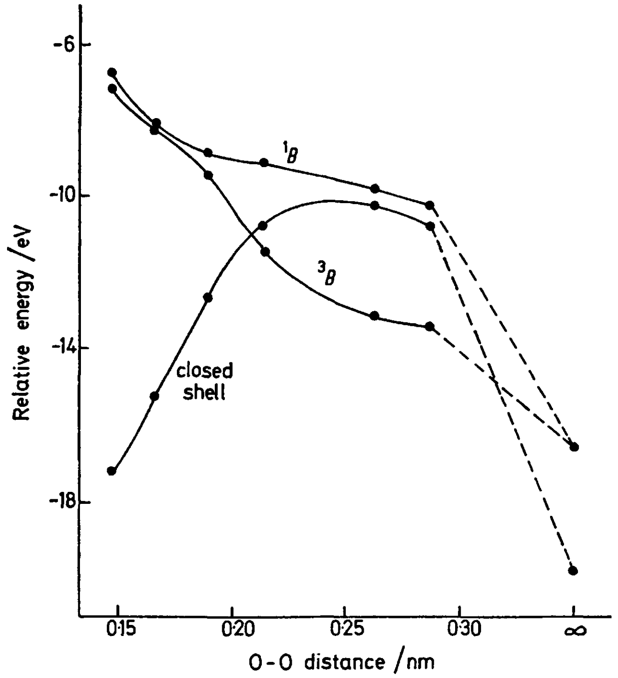


FIGURE 2. The 'biradical' (C_2) pathway for the conversion of 1,2-dioxetan into 2HCHO showing the energies of the closed-shell configuration and the lowest ^1B and ^3B singly excited states plotted against the oxygen–oxygen distance.

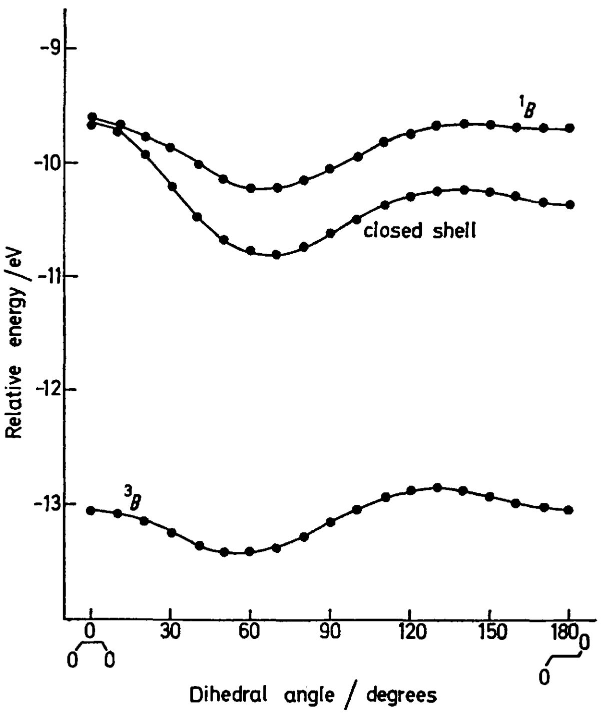


FIGURE 3. The *cis–trans* interconversion (3) of the 'biradical' configuration showing the variation of the energies of the closed shell configuration and the lowest ^3B and ^1B (C_2) singly excited states with dihedral angle.

Of the pathways considered, that of lowest energy involves an intermediate species of geometry that would be called a 'biradical'. However, it is clear from Figure 3 that the interaction of the (incipient) π–π^* singlet and triplet states is unusually large, and as such the species does not satisfy Salem and Rowland's criteria for a biradical.[15] In addition a different part of the same triplet surface lies below the closed shell surface for a geometry characteristic of a 'concerted' dissociation. The calculations are not sufficiently extensive to indicate whether or not a potential well exists in the triplet surface, but it is apparent that the distinction between 'concerted' as opposed to 'biradical' pathways is not as clearcut as previously supposed.

The author thanks Imperial Chemical Industries Ltd. for a Fellowship and Professor S. F. Mason, King's College, London, for his kind hospitality.

(*Received, 4th June* 1974; *Com.* 638.)

---

[1] N. J. Turro and P. Lechtken, *Pure Appl. Chem.*, 1973, **33**, 363; N. C. Yang and R. V. Carr, *Tetrahedron Letters*, 1972, 5143; T. R. Darling and C. S. Foote, *J. Amer. Chem. Soc.*, 1974, **96**, 1625; W. H. Richardson, F. C. Montgomery and M. B. Yelvington, *J. Amer. Chem. Soc.*, 1972, **94**, 9277; and references therein.

[2] N. J. Turro, P. Lechtken, G. Schuster, J. Orell, H.-C. Steinmetzer, and W. Adam, *J. Amer. Chem. Soc.*, 1974, **96**, 1627.

[3] D. R. Kearns, *Chem. Rev.*, 1971, **71**, 395; F. McCapra, *Chem. Comm.*, 1968, 155; N. J. Turro and P. Lechtken, *J. Amer. Chem. Soc.*, 1973, **95**, 264.

[4] E. M. Evleth and G. Feler, *Chem. Phys. Letters*, 1973, **22**, 499.

[5] J. Del Bene and H. H. Jaffe, *J. Chem. Phys.*, 1968, **48**, 1807, 4050.

[6] R. L. Ellis, G. Kuehnlenz, and H. H. Jaffe, *Theor. Chim. Acta*, 1972, **26**, 131.

[7] N. Bodor, M. J. S. Dewar, A. Harget, and E. Haselbach, *J. Amer. Chem. Soc.*, 1970, **92**, 3854.

[8] H. E. O'Neal and W. H. Richardson, *J. Amer. Chem. Soc.*, 1970, **92**, 6553.

[9] 'Tables of Interatomic Distances and Configuration in Molecules and Ions,' Special Publication No. 11, London, The Chemical Society, 1958.

[10] R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, 1970, **53**, 1368.

[11] G. J. Hernandez, *J. Chem. Phys.*, 1963, **38**, 2233;

[12] A. Tajiri, N. Ohmichi, and T. Nakajima, *Bull. Chem. Soc. Japan*, 1971, **44**, 2347.

[13] W. H. Richardson, M. B. Yelvington, and H. E. O'Neal, *J. Amer. Chem. Soc.*, 1972, **94**, 1619.

[14] H. M. Frey and R. Walsh, *Chem. Rev.*, 1969, **69**, 103.

[15] L. Salem and C. Rowland, *Angew. Chem. Internat. Edn.*, 1972, **11**, 92.