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Decomposition of 1,2-Dioxetane

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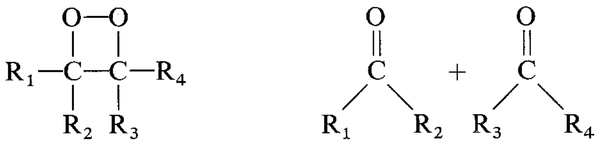
The thermal decomposition of 1,2-dioxetane to two formaldehyde molecules is investigated theoretically. Three different reaction paths are followed by calculating the energies for the different nuclear conformations using a previously developed semiempirical MCSCF procedure. This method is specifically designed to give a correct description of bond breaking and bond forming processes, correcting the well known Hartree-Fock dissociation error afflicting all conventional SCF techniques. The lowest energy path found corresponds to a concerted lengthening of the O–O and C–C bonds, accompanied by a twisting of the four-membered ring, with the C–C bond stretching (breaking) earlier than the O–O bond. In contrast to earlier calculations on this reaction, the calculated activation energy and heat of reaction agree reasonably with experimental values, lending credence to the reality of the reaction path determined.

Key words: 1,2-Dioxetane, decomposition of ~

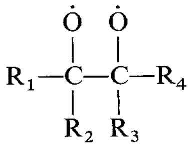
1. Introduction

The thermal decomposition of dioxetanes to carbonyl compounds



(1)

is of great interest, since it is accompanied by chemiluminescence of relatively high quantum yield. The reaction has been investigated experimentally for several different dioxetanes under different conditions [1]. Qualitative explanations, based mainly on orbital correlation diagrams, have been proposed for the mechanism of this reaction [2], allowing for either a concerted mechanism or for a biradical intermediate. A detailed thermochemical analysis [3] indicated that a biradical intermediate of the type



$$R_1\text{—}\overset{\dot{\mathrm{O}}}{\underset{R_2}{\mathrm{C}}}\text{—}\overset{\dot{\mathrm{O}}}{\underset{R_3}{\mathrm{C}}}\text{—}R_4 \tag{2}$$

is consistent with the experimental data for the activation energy of reaction (1).

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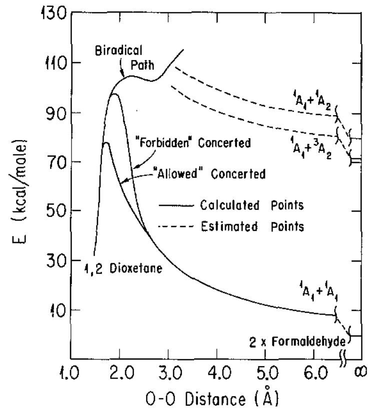
The specific decomposition of dioxetane to two formaldehydes has been the subject of two independent MO calculation studies [4]. Unfortunately these calculations are of a level inadequate to interpret the dynamics of this reaction for two reasons: (a) energies were calculated only for selected nuclear conformations believed to be representative of the reaction path, rather than systematically searching for the lowest energy path by letting the molecule relax at each step; (b) the relative energies obtained, particularly the activation energies are completely unrealistic. In both calculations activation energies in excess of 130 kcal/mole were obtained in gross disagreement with the experimental value of about 25 kcal/mole. In both calculations the high activation energy obtained was associated with a biradical intermediate of type (2). The reason for this large discrepancy can in part be looked for in (a), i.e. a lower energy path might have been found via a more systematic variation of the nuclear conformation. But more important than this is the well known fact that the Hartree-Fock model, on which both calculations were based (CNDO/2 and CNDO/S by Evleth [4a] and Roberts [4b] respectively), cannot describe correctly processes which involve bond breaking and bond formation. The well known Hartree-Fock dissociation error encountered in the description of such processes can be corrected adequately only with a nearly complete configuration mixing calculation in the SCF orbital space. To be sure, some configuration mixing was included by Evleth [4a], but the high activation energy obtained indicates that this was by far not sufficient to correct for the Hartree-Fock dissociation error.

After our work had been submitted for publication a third MO study of the thermolysis of dioxetane by Dewar and Kirschner [5] appeared. These authors have apparently carried out a systematic search for the reaction path using a modified MINDO/2 (MINDO/3) approach, the details of the modification have not been published as yet. It is thus difficult to judge why such a high activation energy (>65 kcal/mole) was found for the ground state reaction path, this might be either due to an inadequately corrected Hartree-Fock dissociation error, or due to the fact that the O–O bond with its lone pair repulsions is calculated too stable (*vide infra*).

We have developed a semiempirical MCSCF (multi-configuration self-consistent field) model [6] in which orbitals and configuration mixing coefficients are simultaneously optimized. With the specific inclusion of all the pair and double pair replacements, as demanded by this model, processes of bond breaking and bond formation are described correctly i.e. the Hartree-Fock dissociation error is adequately corrected. We have used this model to study reaction (1).

2. Method of Calculation and Results

The semiempirical MCSCF procedure as described previously [6] was used without modification. Two different types of reaction paths were followed: (a) planar, the nuclear conformation constrained to C_{2v} symmetry, i.e. the carbon and oxygen atoms remained in the same plane; (b) twisted, the nuclear conforma-



tion constrained to C_2 symmetry with the C_2 axis bisecting the O–O and C–C bonds. In all calculations the hydrogen conformation relative to the C–C axis remained fixed with (C–H) = 1.09 Å, the angle (H–C–H) = 106.2° and the angle (C–C–H) = 116°.

For several given fixed O–O bond lengths the energy was minimized with respect to a variation of the C–O and C–C distances, and in type (b) calculations in addition with respect to the angle of twist. The resulting energies for these path ways are shown in Fig. 1. The upper two curves correspond to the planar, type (a) calculations where we found two local minima for O–O distances larger than 1.7 Å. The uppermost curve, labeled "biradical" corresponds to a biradical of type (2), i.e. the C–C bond stays short (1.54 to 1.59 Å). The curve labeled "forbidden concerted" corresponds to the lower local minimum found in the energy surface of the planar constrained calculations. Near its maximum r(O–O) = 1.88 Å the C–C bond is almost broken r(C–C) = 2.81 Å and the C–O bond has shortened to r(C–O) = 1.16 Å, which is .05 Å shorter than a normal C–O double bond. For longer O–O distances the C–C distance increases rapidly and the C–O distance becomes that of a normal C–O double bond in formaldehyde. A significant energy lowering was obtained by allowing the ringsystem to twist for r(O–O) > 1.7 Å. This led to the energy curve labeled "allowed concerted". Near its maximum r(O–O) = 1.88 Å the C–C bond is essentially broken, r(C–C) = 3.27 Å and the angle of twist is approximately 20°. This is approximate, because the minimum with respect to a variation of the twist angle is rather shallow, for a twist angle of 45° the energy is only 1.5 kcal/mole higher than at 20°. Since the C–C bond breaks much earlier than the O–O bond, it is possibly a misnomer to label this curve "concerted".

Unfortunately, our model at present does not yet allow a reliable description of excited states, therefore the curves labeled $^1A_1+^1A_2$ and $^1A_1+^3A_2$ for the singlet and triplet excited state reaction product are not computed, but sketched into Fig. 1. This is not too serious a shortcoming in the present study, since for the specific decomposition of dioxetane to two formaldehyde molecules our results as well as a previous thermochemical analysis [3a] indicate that the heat of reaction

(55 kcal/mole) plus the activation energy ($\simeq$25 kcal/mole) are probably insufficient to yield electronically excited products. Unfortunately, the specific reaction under investigation here has not been studied experimentally.

3. Discussion of Results

Our calculation yields an activation energy of 47 kcal/mole ("allowed concerted" path) and a heat of reaction, $\Delta H = 32$ kcal/mole. The latter is 23 kcal/mole lower than the thermodynamical estimate of O'Neal and Richardson [3a], who obtained $\Delta H = 55$ kcal/mole. Although an assumed ring strain energy of 26 kcal/mole entered into their estimate, we assume O'Neal and Richardson's ΔH to be essentially correct, since we know that our MCSCF procedure yields short O–O bonds too stable because the lone pair-lone pair repulsion is underestimated [6]. Any CNDO based semiempirical procedure must underestimate neighboring lone pair repulsions, since the diatomic exchange integrals, which are the principal cause of such a repulsion, are neglected. Assuming $\Delta H = 55$ kcal/mole requires that the energy of our calculated results for short O–O distances are raised by 23 kcal/mole. With this we obtain an activation energy for the "allowed" concerted path of 24 kcal/mole which is in good accord with the activation energy of 27 kcal/mole obtained experimentally for the decomposition of tetramethyldioxetane. One may object here that the empirically applied correction to the O–O bond which is calculated too stable, would alter our findings, however, this is hardly the case. Since in Fig. 1 the O–O distance is used as abscissa the correction would apply equally to all three curves and thus leave their order unchanged. In addition we know that the O–O bond is obtained too stable only for short distances, the error is due to the neglect of a two center exchange integral which diminishes exponentially with distance. At the position of the activated complex, $r(\mathrm{O–O}) = 1.88$ Å, the necessary correction would be certainly less than 5 kcal/mole, thus affecting our predicted activation energy only little, and the prediction of the preferred reaction path not at all.

From the discussion above, we predict the reaction barrier to lie 79 kcal/mole higher than the products, two ground state formaldehyde molecules, while the triplet excitation energy of formaldehyde is 72 kcal/mole (80 kcal/mole for the first excited singlet state). Since we would not expect an excited triplet and a ground state formaldehyde to be attractive in the conformation of the activated complex, but rather be repulsive by more than 10 kcal/mole, we conclude that the decomposition of unsubstituted dioxetane will not yield chemiluminescence. This is in agreement with the conclusion reached by O'Neal and Richardson [3a] and could be tested experimentally. In tetramethyldioxetane, where chemiluminescence is observed the heat of reaction is 13 kcal/mole larger [3a], and since the excitation energies of formaldehyde and acetone are nearly the same, sufficient energy is available to reach the excited triplet as well as the excited singlet product states.

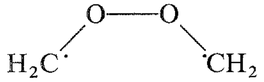
Our conclusions as well as those of O'Neal and Richardson [3a] are different from those reached in a recent calculation by Dewar and Kirschner. The ground state energy curve along the reaction path calculated by Dewar and Kirschner has a maximum of 65 kcal/mole (45 kcal/mole with some CI) above the energy of the reactant, unsubstituted dioxetane. It is difficult for us to determine why their maximum is so much higher than the one in our "allowed concerted" curve, since we do not know what modifications Dewar and Kirschner have made to MINDO/2 or how many and what configurations were used in the CI of their calculation. We suspect the difference to be associated with a not fully corrected Hartree-Fock dissociation error or with the fact that the O–O bond is obtained too stable because the lone pair repulsion is underestimated, as discussed above. Dewar and Kirschner predict the activation energy for the thermolysis of dioxetane as 38 kcal/mole, the energy of the crossing point of their triplet potential with the ground state potential along the reaction path. Assuming the triplet curve to be similar in tetramethyldioxetane, where ΔH is 13 kcal/mole larger and the excitation energy about the same, one would obtain from Dewar's results an activation energy of 25 kcal/mole in good agreement with experiment and our conclusions. Incidentally Dewar as we predicts a twisted activated complex of rather similar structure.

The difference between our conclusions and mechanism and that of Dewar could be tested experimentally in a study of the thermolysis of unsubstituted dioxetane. Dewar predicts chemiluminescence in this case and an activation energy of 38 kcal/mole, we predict an activation energy of 24 kcal/mole and very likely no chemiluminescence.

Surprising and at first somewhat puzzling is the conformation of the dioxetane near the maximum of the lowest energy "allowed" concerted reaction path; the ring is twisted (in agreement with Dewar [5]), the C–C bond is almost broken, $r(\text{C–C}) = 3.27$ Å, while the O–O distance is still relatively short, $r(\text{O–O}) = 1.88$ Å. From bond energy arguments, $D(\text{O–O}) \simeq 40$ kcal/mole and $D(\text{C–C}) \simeq 80$ kcal/mole, one would expect the O–O bond to break first. The puzzle is resolved once one realizes that with the C–C bond broken the C–O bond has become short $r(\text{C–O}) = 1.20$ Å indicating significant double bond character. In the case where the O–O bond breaks first, the $\simeq 25$ kcal/mole higher "biradical" path, the C–O bond remains long, $r(\text{C–O}) = 1.35$ Å, indicating no double bond character. In the former case, the lone electrons on carbon get drawn into the bonding region by the more electronegative oxygen, thus contributing to binding, while in the latter case the lone electrons remain localized on oxygen. This double bond formation is expected to compensate for the difference in bond dissociation energy of the C–C and O–O bonds.

Our results, as well as other quantum chemical studies [4, 5] are at variance with those of O'Neal and Richardson [3a], who, using thermochemical arguments, prefer a biradical pathway and obtain for it a low (21.5 kcal/mole) activation energy. It is well known that thermochemical methods give heats of formation of stable molecules reliably – in fact, we have used such data to correct our results for the error in the O–O bond, which is obtained too stable, *vide supra*. However the heats of formation obtained for biradicals from thermochemical arguments appear to be much less reliable, and what is more important, the heat of formation obtained for a possible biradical intermediate is not yet directly related to the activation energy for its formation or for the reaction. To obtain these activation energies O'Neal and Richardson [3a] needed in addition the ring closing activation energy, E_{-1} in their notation. To determine E_{-1}, the experimental activation energy of the thermal decomposition of 3,3,4 trimethyldioxetane was used, and it is not surprising that reasonable activation energies resulted for the biradical mechanism of the decomposition of other dioxetane homologues.

In conclusion, we believe our "allowed" concerted pathway to be realistic, since it reproduces expected activation energies well and its ring twisted form brings the bond breaking orbitals into proper geometrical relation for the formation of $n \rightarrow \pi^*$ excited products which become energetically accessible in the pyrolysis of substituted dioxetanes. We believe to have effectively ruled out biradical intermediates of type (2). A biradical is still possible but then of the form,



although it is not a metastable intermediate. To what extent such a mechanism can be consistent with the insensitivity of the activation energy to benzyl and phenyl substitution as found by Richardson *et al.* [3c], remains an open question, but it is hoped that future theoretical studies of substituted dioxetane, with a detailed treatment of excited states will lead to a more complete understanding of the mechanism involved, including the intersystem crossing required to obtain triplet excited products.

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