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DIOXETANE DECOMPOSITION REVISITED: A SEMI-EMPIRICAL STUDY OF THE POTENTIAL ENERGY SURFACE

THÉRÈSE WILSON
Department of Molecular and Cellular Biology, Harvard University, Cambridge, Massachusetts 02138, U.S.A.

AND

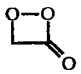
ARTHUR M. HALPERN
Department of Chemistry, Indiana State University, Terre Haute, Indiana 47809, U.S.A.

The potential energy surface describing the unimolecular thermolysis of 1,2-dioxetane into two formaldehydes is explored via semi-empirical calculations using the PM3 Hamiltonian with multi-electron configuration interaction. An active space of the four highest occupied orbitals and the two lowest virtual orbitals is used. Several reaction coordinates were examined, and the in-plane O—O distance was used most extensively. The results indicate that the activation barrier to fission is on the ground state surface and is about 18 kcal mol^{-1}, in good agreement with experimental results. Furthermore, calculations of the vertical triplet-state energies show that the ground and triplet states are nearly degenerate for O—O distances beyond that corresponding to the 18 kcal mol^{-1} barrier, until the molecule abruptly dissociates into two formaldehydes (at *ca* 2·55 Å). This picture is indicative of a diradical pathway, where the activation energy is associated with motion of the system on the ground-state surface, not the triplet surface, but where generation of a triplet product can be expected. Similar results were obtained for dimethyl- and tetramethyldioxetanes, which require higher E_a for dissociation, and for dimethyldioxetanone. Thermochemical calculations pertaining to these reactions and to the formation of triplet products are also presented.

INTRODUCTION

The unimolecular diabatic decomposition of 1,2-dioxetanes (D) into two carbonyl products has long attracted attention,[1] largely because the high exothermicity of the reaction [62 ± 7 kcal mol^{-1} (1 kcal = 4·184 kJ), depending on alkyl substitution] is quite efficiently channeled into electronic excitation energy of one of the fragments. Indeed, with one or more alkyl substituents, from 6 to 40% of one carbonyl compound is generated in its T_1 state, compared with <0·1% in its S_1 state.[1] Adding to the interest of four-membered ring peroxides, the less stable dioxetanone moiety is the energy-rich precursor of the bioluminescence of several organisms, such as that of fireflies.[2]


Dioxetane


Dioxetanone

A point which is critical to the understanding of dioxetane chemistry, but not always appreciated, is that there exists no 'dark' (i.e. adiabatic) pathway of low activation energy for decomposition on the ground-state surface. The activation energy, E_a, of D thermolysis can be determined in two ways:[1] (a) by measuring the slope of the Arrhenius plot of reaction rates (the decay rate of either D concentration or of light intensity, or the rate of product formation), or (b) by taking direct advantage of the chemiluminescence emission and measuring the intensities of light emission from the same solution at two or more temperatures, provided that these temperatures are low enough that the concentration of dioxetane can be considered to be constant during the measurements. The first method gives a value of E_a which reflects the decomposition of the dioxetane by *all* pathways, light or dark. The E_a value obtained by the second method is attached only to the light-emitting process. In the case of dioxetanes, these two activation energies have repeatedly been shown to be equal (unless impurities catalyze a dark pathway). Therefore, dioxetanes do not decompose rapidly to form ground-state products. In fact, even though they may explode, they are surprisingly stable peroxides considering the ring strain.

When methyl-substituted dioxetanes were first synthesized, they caused some surprise and posed a challenge to theorists, not only because of their unexpected stability, but also their capacity to generate high yields of excited-state products. Various semi-empirical (SE)[3] and *ab initio* (AI)[4] methods were applied to the

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problem. Qualitatively, the consensus was that intersystem crossing from the singlet ground-state surface to a triplet surface had to be an integral part of the dissociation process, and that the cross-over point should determine the value of the activation energy. Today, however, even the parent compound is still barely accessible to truly rigorous AI methods,[5] since the problem requires the evaluation of spin–orbit coupling at the intersecting regions of the potential surfaces.

Because reliable experimental information is available on the thermodynamic properties of many alkyl-substituted dioxetanes and their yields of excited-state products,[1] it seemed worthwhile to test the ability of contemporary semi-empirical calculations to 'second guess' these data, and in the process possibly to throw some light on the mechanism of these diabatic reactions. The objective of this paper is to report the results of such SE calculations. We show in our conclusion that if, 30 years ago, a chemist with no preconceived idea had drawn the structure of the then hypothetical dioxetane ring, and used an SE method such as AM1 or PM3 to calculate its molecular structure and explore its fate upon elongation of the O—O or C—C bond, he or she would have concluded that dioxetanes should be stable enough to be synthesized. Furthermore, there would have been reason to expect the formation of excited triplet-state products.

COMPUTATIONAL METHODS

All work was performed on an IBM RS/6000 Model 320 with 32 MB RAM and 2·7 GB of mass storage. *Ab initio* calculations were carried out on dioxetane (D) using the Gaussian 92 (Revision A) suite of programs.[6a] AM1 and PM3 calculations[6b] with the multi-electron configuration interaction (MECI) utility were run using MOPAC 93.[6c]

We utilized the PM3 Hamiltonian with multi-electron configuration interaction and chose as the active space the four highest-filled MOs and the two lowest virtual MOs; thus, there are eight active electrons populating six active orbitals (8/6). These levels correspond, in increasing energy, to $1a_2$, $5a_1$, $2b_1$, $2a_2$, $4b_2$ and $5b_2$ MOs in dioxetane. Calculations spanning the same space without the lowest energy filled MO ($1a_2$) (i.e. 6/5) gave nearly identical results.

SE calculations give O—O distances (1·60 Å from PM3 and 1·34 Å from AM1) in keeping with available x-ray data (average 1·5 Å), and with the result (1·521 Å) of *an ab* initio calculation using MP2/6–31G*, known to give geometries in good agreement with experimental structural data in the case of dioxirane.[7]

We compared the energies of ground state D obtained from both SE and AI methods (see Table 1). As a reference point, we used the result of an AI calculation using the MP2 method at the 6–31G* level, which is −228·2503147 h. Single-point MP2/6–31G* calculations were performed on the optimized D structures obtained from PM3 and AM1.[6] The results show that the optimized PM3 and AM1 structures are higher only by 3·11 and 12·93 kcal mol^{-1}, respectively. The closeness in energy between the PM3 structure and the fully optimized MP2/6–31G* geometry, and also the more realistic O—O bond length obtained with PM3, lend a degree of confidence to the use of PM3/MECI for exploring the reaction surface for the thermolysis of D into two formaldehydes (F).

The potential energy surface of ground-state D was scanned by incrementing a chosen coordinate while optimizing all other coordinates at each point. We explored several possibilities for the independent variable and found that the coordinate that appears to

Table 1. Structural and energetic properties of 1,2-dioxetane

Parameter	AM1	PM3	AI/MP2	Ref. 5	Expt 1[a]
r_{OO}/Å	1·339	1·599	1·521	1·74	1·47–1·58
r_{CC}/Å	1·541	1·526	1·509	1·54	1·49–1·58
r_{CO}/Å	1·48	1·436	1·459	1·47	1·44–1·49
Torsion angle/°	0·064	0·296	19·22	15·8[g]	0–22
E(diox)/kcal mol^{-1}	12·93[b]	3·11[b]	0·0[c,d]		
E(form)/kcal mol^{-1}	0·0717[b]	0·537[b]	0·0[e]		
$-\Delta H_r$[f]/kcal mol^{-1}	78·2	62·8	53·4	57·1	

[a] Ranges for substituted dioxetanes from x-ray data; see Ref. 1b.

[b] Single-point calculation (kcal mol^{-1}) at MP2/6–31G* level; energies are relative to those of the fully-optimized MP2/6–31G* values.

[c] MP2/6–31G* optimized energy is −228·2503147 h. The energy reported by Reguero *et al.*[5] for D (MC-SCF/4–31G) is −227·3771 h, which is substantially higher.

[d] The planar structure is higher by 0·68 kcal mol^{-1}.

[e] MP2/6–31G* optimized energy is −114·1677476 h.

[f] Defined here as E(diox) − 2E(form) obtained from the respective methods.

[g] The planar structure is only 0.1 kcal mol^{-1} higher.

provide the most realistic picture of the reaction surface is the (in-plane) stretching of the O—O bond.

RESULTS

Unsubstituted dioxetane

Both AM1 and PM3 calculations (with MECI) indicate that when the O—O bond is elongated (to *ca* 1·7 Å in the case of AM1/MECI and 2·0 Å for PM3/MECI), the dioxetane ring is ready to come apart very abruptly on the ground-state surface, with very little extra activation energy beyond that point. However, to obtain this bond length, considerable energy has to be spent, about 17–20 kcal mol^{-1}, in fair agreement with the experimental value of E_a.[8]

A scan of the globally relaxed potential energy surface shows that when the O—O bond distance is between 2·55 and 2·60 Å, the C—C bond breaks, and two F molecules are produced. A plot of the PM3/MECI (8/6) energy vs O—O distance is shown in Figure 1. There is a monotonic increase in energy up to about 2.0 Å, after which the energy fluctuates somewhat until the system dissociates when the O—O distance is *ca* 2·55 Å. In view of the fact that triplet formaldehyde is bent, its generation from activated dioxetane is presumably facilitated by increased Franck–Condon factors (see Figure 1).

We also calculated the vertical energies of the lowest triplet state of the system corresponding to each structure along the O—O dissociation coordinate. Figure 1 shows that the triplet-state and the thermally 'activated' ground-state surfaces coincide for O—O distances between 2·00 and 2·55 Å, at which point cleavage abruptly occurs. However, the point to be emphasized here is that the *ca* 18 kcal mol^{-1} activation barrier to the dissociation process is associated with the ground-state surface, in keeping with experiment (see Introduction).

This result is at odds with the conclusion of a recent AI analysis,[5] which reported that there is only a very small energy barrier (*ca* 2 kcal mol^{-1}) to dioxetane decomposition on the ground state surface, calculated to intersect a triplet (T_1) surface at very low excess energy. Unrealistically efficient intersystem crossing at that cross-over point is then assumed to cause the system to move on to the triplet surface, where a calculated barrier of *ca* 25 kcal mol^{-1} is met to complete the dioxetane cleavage. This conclusion, which may be the consequence of a questionable ground-state starting geometry (with a 1·74 Å O—O bond length), is simply not tenable.

Our calculations show that, consistent with the sudden drop in energy at an O—O distance of 2·55 Å, the C—C distance, as expected, suddenly increases (to 2·7–3·0 Å), indicating the rupture of this bond; likewise, the C—O bond length decreases (from an initial value of 1·44 Å for D to 1·22 Å) as the carbonyl is formed in the F product. The calculation also reveals changes in the O—C—C—O torsional angle, *d*, as the O—O bond is elongated. This angle increases from 0·33° in the equilibrium configuration to about 12° (at O—O ≈ 2·2 Å), and then fluctuates until dissociation occurs at C—C = 2·55 Å, at which point $d \approx 9°$. The fully optimized lowest triplet-state structure of D [using PM3/MECI (8/6)] has a calculated O—O distance of 1·94 Å and an energy of 19·0 kcal mol^{-1}. This structure is close to the point along the O—O coordinate where the singlet and triplet surfaces first intersect.

An often debated question is whether dioxetane decomposition is a concerted, semi-concerted (an unclear concept) or stepwise process, via the intermediacy of a diradical. The PM3 surfaces of Figure 1 suggest the last process, since the abrupt rupture of the C—C bond occurs only after considerable elongation of the O—O bond. For the sake of completeness, we also explored the potential energy surface for the concerted cleavage of D using PM3/MECI (8/6). The O—O and C—C bonds were stretched in equal increments of 0·01 Å; thus the two OCH_2 fragments were separated from each other while keeping the C—O axes parallel. The activation barrier in this calculation is 35 kcal mol^{-1}, and occurs at an O—O (C—C) distance of *ca* 1·9 Å; the dioxetane cleaves abruptly at that point.

Figure 1 shows that ground and lowest triplet states are isoenergetic over a wide range of (relaxed) O—O distances. In this region of degeneracy, favorable conditions for intersystem crossing should obtain, as proposed by Turro and Devaquet,[9] resulting in triplet formaldehyde. We also calculated the overall thermochemistry of the fission reaction D→2F. These exothermicities, $-\Delta H_r$, may be compared with the thermochemical estimate[10] and with the adiabatic (i.e. 0-0) excitation energy, E_T, of the lowest triplet state of F (Table 1). Using SE and AI methods, we find E_T from PM3/MECI and CIS/6–31G* to be 54·4 and 79·4 kcal mol^{-1}, respectively, which bracket the experimental value of 72·0 kcal mol^{-1}. It is known that excitation energies are systematically underestimated by SE methods.[11] In any case, the sum $-\Delta H_r + E_a$ is sufficient to allow the thermal generation of triplet formaldehyde.

Methyl derivatives

SE methods remain easily applicable to the case of methyl-substituted dioxetanes. We applied the PM3/MECI method and the approach described above to the calculations of the potential energy surfaces of four dioxetane derivatives: 3,3-dimethyldioxetane (33DMD), *cis*-3,4-dimethyldioxetane (CDMD), *trans*-3,4-dimethyldioxetane (TDMD) and 3,3,4,4-tetramethyldioxetane (TMD). In each case, we employed the O—O distance as the reaction

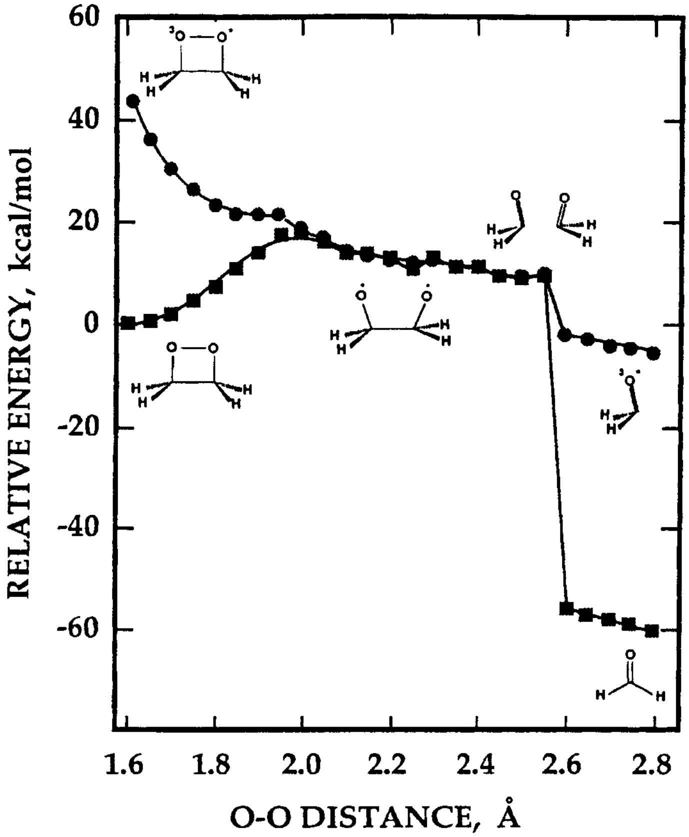

Figure 1. Potential energy surface (PM3/MECI) for dioxetane thermolysis. For the ground-state surface (■), the in-plane O—O distance was incremented in 0·05 Å steps, the geometry was reoptimized at each point, and the potential energy recalculated. (●) Corresponding vertical triplet-state energy values. The triplet and singlet surfaces are nearly isoenergetic in the region between *ca* 2·0 and 2·5 Å where the energy artefactually fluctuates. The detailed characteristics of the PE surface, e.g. the energy values and cleavage point, for O—O distances ≥2·0 Å depend on the active space used and the O—O step size, but in this region the qualitative picture remains basically unchanged

coordinate, and found that the C—C bond abruptly ruptures when the O—O separation is between 2·3 and 2·4 Å, depending on the compound. Also as in the case of D, the vertical triplet state energies of the species along this reaction path became nearly degenerate with the ground state for an appreciable distance after an energy barrier is passed on the ground-state surface. Thus the energies of the ground and (lowest) triplet state as a function of O—O distance resembled the data shown in Figure 1 for D. Table 2 summarizes the results for substituted dioxetanes. The activation barriers of dimethyldioxetanes are calculated to be between those of D and TMD, but very close to each other, in accord with the trend observed experimentally (see Table 2).[1b,8,14] However, the range of calculated values (14 kcal mol^{-1} from D to TMD) exceeds the experimental range of *ca* 8 kcal mol^{-1}. Likewise, the ΔH_r values calculated for the dimethyldioxetanes are intermediate between those for D and TMD.

Dimethyldioxetanone

PM3/MECI calculations performed on dimethyldioxetanone give a similar picture. When the O—O separation is *ca* 2·1 Å, an energy plateau about 19 kcal mol^{-1} above the ground state is reached, where the energy of the vertical triplet state and that of the ground state converge. Cleavage into acetone and CO_2 occurs at an O—O separation of *ca* 2·9 Å. The exothermicity of this process is calculated to be 86 kcal mol^{-1}.

Table 2. Structural and energetic properties of methyl-substituted dioxetanes and dimethyldioxetanone obtained with PM3/MECI

Compound[a]	E_a (kcal mol^{-1})[b]	$-\Delta H_r$ (kcal mol^{-1})[c]
33DMD	26 (24 ± 1)	66 (61)
CDMD	27 (24·4 ± 0·5)	68 (63)
TDMD	26 (23·8 ± 0·5)	67 (62)
TMD	33 (27 ± 1)	74 (81)
DMDO	19 (21 ± 1)	86 (81)[d]

[a] Abbreviations: 33DMD = 3,3-dimethyldioxetane; CDMD = *cis*-3,4-dimethyldioxetane; TDMD = *trans*-3,4-dimethyldioxetane; TMD = tetramethyldioxetane; DMDO = dimethyldioxetanone.

[b] In parentheses, experimental values (Refs 1b, 8, 12).

[c] In parentheses, thermochemical estimates of $-\Delta H_r$ by Benson's method for the same compounds (Ref. 10). Calorimetric measurements for TMD give 65 ± 1 kcal mol^{-1}, see Ref. 13.

[d] An *ab initio* calculation at the HF/6–31G* level gave $-\Delta H_r = 82{\cdot}3$ kcal mol^{-1}. The TMD energy is −383·7932466 h.

CONCLUSIONS

Our results indicate that SE methods such as AM1 and PM3, readily available to chemists, are capable of providing a description of the potential surfaces pertinent to dioxetane decomposition; perhaps surprisingly, this description is consistent with experimental data. Until an appropriately high level of theory can be successfully applied to this problem, SE methods can serve as useful tools.

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