We believe that our data are uniquely consistent with the existence of the dimeric tetrakis(substituted-amino)phosphonium ions **10** and **11**. These dimeric cations are analogous to neutral dimeric tris(amino)boranes.[1] We attribute the dimerization in these phosphorus compounds to the same phenomenon as in the boron compounds—bond angle strain. The driving force for a distorted aminophosphonium ion to dimerize apparently is sufficient to overcome the repulsions of two cations forming a four-membered dicationic ring.

Chemiluminescence of Dioxetanone Investigated by Self-Consistent-Field Theory

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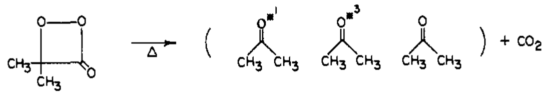
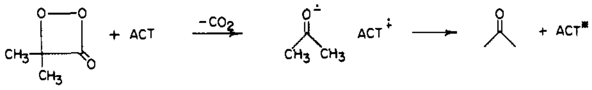
The unusual facility of the four-membered ring peroxides to generate electronically excited states by thermolysis has focused attention on their chemical behavior.[1] In recent reports we have described our findings on the chemical behavior of dimethyldioxetanone (**1**).[2-5] In particular we find that thermolysis of dioxetanone **1** in any one of a number of nonpolar solvents at 30 °C gives both excited singlet and triplet acetone in yields of 0.1% and 1.5% respectively (eq 1).[3] Also, we find that dioxetanone **1** is subject to catalytic decomposition by electron donors (activators, ACT) and excited-state generation by the path we have designated chemically initiated electron-exchange luminescence (CIEEL)[4,6] (eq 2).



(1)



(2)

Tetramethyldioxetane (**2**) also generates electronically excited acetone upon thermolysis.[7] However, in contrast to dioxetanone **1**, it does not react readily with electron donors, and the yield of excited acetone from **2** is nearly 20 times greater than from **1** despite the fact that the dioxetanone rearrangement is more exothermic by ca. 20 kcal/mol.[8] Herein we report the results of theoretical calculations on the parent unsubstituted dioxetanone. These calculations offer considerable insight into the structure and reactivity of this molecule and provide a basis for understanding the different properties of peroxides **1** and **2**.

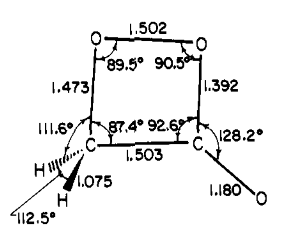


Figure 1. Optimized equilibrium structure of dioxetanone (bond distances are in ångstroms).

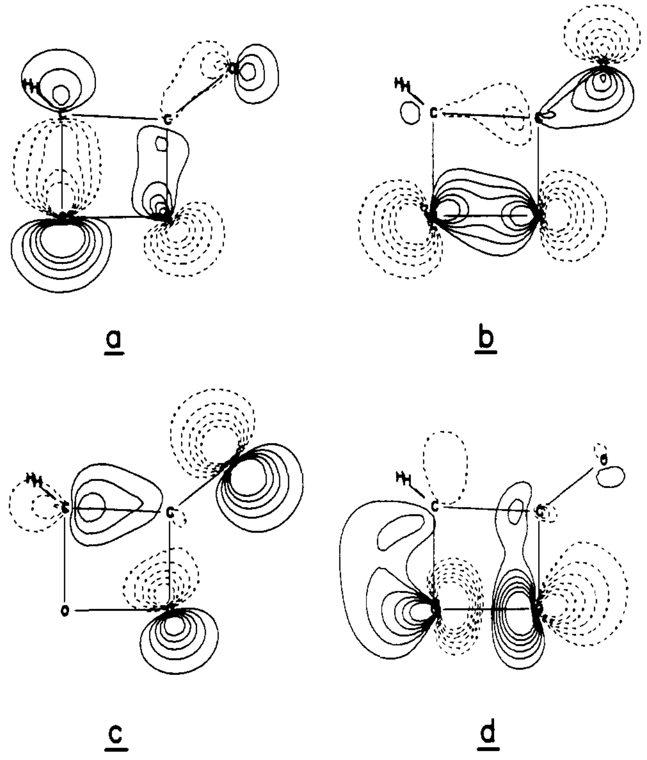


Figure 2. Molecular orbital contour plots[11] of the occupied or internal orbitals (a) 13a′, (b) 14a′, and (c) 15a′ and the virtual or external orbital (d) 16a′.

SCF calculations were performed on dioxetanone using a 4-31G basis set[9] of contracted Gaussian functions. The equilibrium structure, shown in Figure 1, was determined by using the gradient procedure of Pulay[10] and point-by-point searches. The energetics of stretching the oxygen–oxygen bond were investigated by fixing its length and then reoptimizing the two C–O–O ring angles, constraining the ring to be planar in these calculations. The effect of increasing the oxygen–oxygen bond length on the energy of the molecule and some orbital energies at these distorted structures are given in Table I. Plots of selected orbitals are given in Figure 2.[11] SCF energies of the $^2A'$ anion state, formed by adding an electron to the 16a′ orbital, were calculated at these optimized structures and are shown in Table I.

The equilibrium ground-state structure of dioxetanone that is predicted by these calculations has two noteworthy aspects. The oxygen–oxygen bond length is somewhat longer than that determined by X-ray crystallography for adamantylideneadamantane-1,2-dioxetane (**3**) by Wynberg and co-workers.[12] However, the most surprising feature of the predicted structure of dioxetanone is that the atoms of the four-membered ring are found to be essentially coplanar. This finding is in contrast to the structure of dioxetane **3** in which one oxygen atom of the

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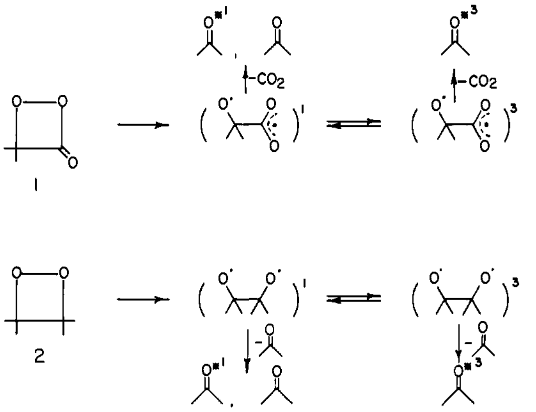
Table I. Dioxetanone Structures and Relative Energies

R_{O-O}, Å	R_{C-C}, Å	∠COO[a]	∠COO[b]	E, au	ΔE, kcal/mol	highest occupied orbital 4a″, au	virtual 16a′, au[c]	anion energy ΔE, kcal/mol
1.503	1.502	89.5	90.5	−300.8921	0.0	−0.483	0.138	0.0
1.525	1.502	89.0	90.0	−300.8919	0.2	−0.486	0.127	−8.5
1.55	1.502	88.5	89.5	−300.8910	0.7	−0.489	0.114	−17.0
1.60	1.501	87.7	88.4	−300.8877	2.8	−0.493	0.090	−31.2
1.70	1.501	85.5	86.5	−300.8765	9.8	−0.501	0.046	−51.9

[a] The methylene carbon atom is referred to. [b] The carbonyl carbon atom is referred to. [c] The 16a′ orbital is not the lowest virtual at the equilibrium geometry. This orbital crosses the 5a″ between R_{O-O} equals 1.525 and 1.55 Å.

Scheme I



peroxide is lifted ca. 21° from the plane defined by the remaining ring atoms.

Of significance to the understanding of the thermal chemistry of dioxetanone is the prediction that stretching the oxygen–oxygen bond does not cause a concomitant increase in the length of the ring carbon–carbon bond (Table I). Although we have not carried the calculations all the way through to the transition state, progress along the reaction coordinate is significant since the energy increase obtained is a substantial fraction of the experimentally determined activation enthalpy for dioxetanone **1**.[13] The implication of these findings is that the thermolysis of dioxetanone may proceed through the biradical state formed by crossing of the 14a′ and 16a′ orbitals as a result of cleavage of the oxygen–oxygen bond. A similar conclusion was reached by Goddard and Harding[14] for dioxetane by using GVB calculations. This conclusion is supported by extensive experimental evidence.[15]

These findings suggest an explanation for the difference in excited-state yields obtained from thermolysis of dioxetanone **1** and dioxetane **2**. Cleavage of the oxygen–oxygen bond in both cases leads to a biradical presumably initially in a singlet state. Intersystem crossing to the triplet biradical is therefore in competition with cleavage of the ring carbon–carbon bond (Scheme I). For the case of dioxetanone the loss of CO_2 competes with intersystem crossing; for dioxetane it is the loss of a simple carbonyl compound that is in competition with intersystem crossing. The former is more exothermic and, therefore, is probably more rapid, giving the biradical less opportunity to cross to the triplet manifold. Consistent with this postulate is the experimental observation that the yield of excited singlet acetone from thermolysis of **1** and **2** is quite similar, but the yield of triplet acetone from **1** is considerably reduced from that of **2**.[3]

Our formulation of the CIEEL mechanism has as a key tenet the activated transfer of an electron from an electron donor to the peroxide.[16] We postulate further that the oxygen–oxygen bond of the peroxide cleaves either simultaneously with the transfer of the electron or very rapidly following its arrival. Several of the results of the calculation bear on this mechanism. First, transfer of an electron from an activator (perylene, for example) to dimethyldioxetanone is estimated from electrochemical data to be endothermic at the equilibrium ground-state geometry.[19] Indeed, we have measured the activation energy for this process and find it to be 16 kcal/mol. The calculations show that stretching the oxygen–oxygen bond of dioxetanone results in a large decrease in the energy of the unoccupied 16a′ orbital (Table I), thereby facilitating the electron transfer. Thus, as we have previously suggested, the activating process for the electron transfer in the CIEEL mechanism is most likely stretching of the oxygen–oxygen bond.

The second result of the calculation that aids in the description of the CIEEL mechanism concerns the energy of the radical anion obtained by placing an electron in the 16a′ orbital. This orbital is antibonding between the peroxide oxygens (Figure 2d). Table I contains the change in energy of the anion as a function of oxygen–oxygen bond distances. The striking result is that on increasing this bond distance 0.2 Å from its equilibrium value, the energy of the anion drops by ca. 52 kcal/mol. We take this result to indicate that the oxygen–oxygen bond of the radical anion of dioxetanone is dissociative and irreversible cleavage follows immediately the receipt of the electron. This conclusion is entirely consistent with our experimental observations on the dioxetanone system.

In sum, these calculations provide new insight into the detailed chemistry of dioxetanone, though highly quantitative predictions will require more extensive calculations. They substantiate a reasonable rationalization of the different yields observed from dioxetanone **1** and dioxetane **2** and provide some confirmation of the major postulates of the CIEEL mechanism.

Acknowledgment. We thank Peter Dardi and Suketu Gandhi for assistance in generating the MO plots. This work was supported in part by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Office of Naval Research and the National Science Foundation.

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C-20 Stereospecific Introduction of a Steroid Side Chain

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The development of sterochemically controlled syntheses of steroid side chains in recent years has been spurred by the bio-