

analysis. Table I summarizes the k_H/k_D results.

The first important conclusion is that epimers exhibit the same isotope effect (cf. entries 1 vs. 2; 3 vs. 4; 5 vs. 6). Therefore the alkoxy radicals from both epimers behave the same in the transition state for H-abstraction even though one of these radicals cannot be in an electronic or vibrational "excited" state because it has to survive an epimerization pathway before it can abstract.⁵ Because an "excited" (i.e., high energy) species is expected to show less isotopic discrimination than a ground-state species, this is the first direct evidence that ground state rather than excited alkoxy radicals perform the H-abstraction, even when these radicals are generated photochemically.¹¹

The second striking finding is that, whereas the primary isotope effect of 4.3 (at 80 °C) for the secondary alcohols (entries 1 and 2)¹² indicates appreciable C-H weakening¹³ in the cyclic transition state, the corresponding tertiary alcohols (entries 3 and 4) show almost no primary isotope effect (viz., ~1.1).¹⁴ Because of the locked skeleton in these tricyclic substrates, the C-O radical from the secondary and tertiary alcohols cannot differ much in spatial location, and so we conclude that even slight changes in molecular geometry can markedly alter the bonding situation in the transition state. In view of this sensitivity, the known^{2,15} remarkable regioselectivity of the Barton reaction (even for two competing six-membered transition states) is more understandable.

The third notable finding (entries 5 and 6) is the size (~1.7) of the secondary isotope effect, which appears to be one of the highest observed.¹⁶ The reasons for its magnitude are obscure especially since we don't know if the 2 α -D exerts any effect. (This 2 α bond should not interact strongly with C-3 via hyperconjugation if the transition state is truly radical-like and not ionic-like.¹⁷) Among other things, we are considering the possibility that slight differences in average (nonharmonic) vibrational amplitudes¹⁸ of C-D and C-H destroy the apparent skeletal symmetry of the labeled substrates. For intramolecular competition, any such slight distortion could, in effect, enhance (or diminish) an inherent isotope effect,¹⁶ when a transition state is very sensitive to geometry.

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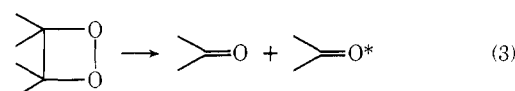
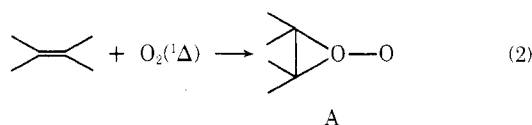
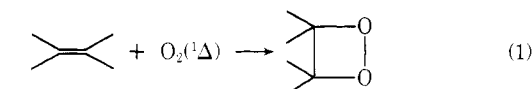
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Intermediates in the Chemiluminescent Reaction of Singlet Oxygen with Ethylene. Ab Initio Studies

Sir:

The excited singlet state of dioxygen molecule, ¹O₂, is thought to play an important role in such biologically important phenomena as "photodynamic action" (photosensitized oxidation),¹ photocarcinogenicity,² photochemical smog formation,³ and bioluminescent processes.⁴ However, despite numerous experimental studies^{5,6} of the chemistry of ¹O₂, there is yet a great deal of uncertainty concerning the mechanism involved in the reactions of ¹O₂ and in the chemiluminescence⁷ that often results. In this paper we will use the results of ab initio studies (large basis including polarization functions; generalized valence bond⁸ with extensive configuration interaction) to examine the processes 1, 2, and 3.



Both the planar concerted addition of ethylene to O₂(¹Δ) and the concerted decomposition of dioxetane to ground-state formaldehydes are considered as orbital-symmetry-forbidden processes.⁹ Three alternative mechanisms have been proposed for the addition reaction: (1) a nonplanar [2_s + 2_a] concerted addition,^{9,10} (2) a stepwise addition involving an acyclic biradical or zwitterionic (CCOO) intermediate,¹¹ and (3) a stepwise addition through a peroxirane (B) intermediate.^{9,11,12}

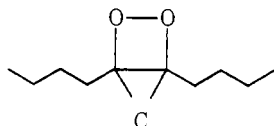
Table I. Comparison of GVB-CI, MINDO/3, and Experimental Heats of Formation

Reaction	Total energy change (kcal/mol)		
	GVB-CI ^a	Exptl ^b	MINDO/3 ^c
CH ₂ O → CH ₂ (³ B ₁) + O(³ P)	168.7 (174.6)	176.2	176.6
C ₂ H ₄ → 2CH ₂ (³ B ₁)	161.1 (171.6)	169.8	163.8
O ₂ (¹ Δ) → 2O(³ P)	96.0 (98.2)	95.4	94.6
CH ₃ CH ₃ → 2CH ₃	85.0 (93.4)	87.8	
CH ₃ OH → CH ₃ + OH	89.6 (98.0)	90.3	
HOOH → 2HO	53.6 (56.4)	49.4	
$\overline{\text{CH}_2\text{CH}_2\text{O}} \rightarrow \cdot\text{CH}_2\text{CH}_2\text{O}\cdot$	59.4 (62.2) ^d	57.4 ^e	~67.5 ^f
$\overline{\text{CH}_2\text{CH}_2\text{O}} \rightarrow \text{C}_2\text{H}_4 + \text{O}(\text{}^3\text{P})$	79.8 (84.0)	83.2	105.3

^aIn order to compare with experiment, the quantities in this table are D_0 's, that is, zero-point energy corrections have been included (using vibrational frequencies tabulated in ref 22 and estimated in ref 24). The uncorrected bond energies, D_e , are included in parentheses. ^bReference 22. ^cReferences 23 and 25. ^dAveraged over the four covalent diradical states. ^eExperimental activation energy for decomposition. ^fEstimated using the implied MINDO/3 ring strain energy of 14.2 kcal.



The decomposition (3) has generally been assumed to be either concerted¹³ or to involve a 1,4-OCCO biradical.¹⁴ An important feature of this decomposition, which has yet to be satisfactorily explained,¹⁵ is the observed production of excited state carbonyl products, both ¹($n \rightarrow \pi^*$) and ³($n \rightarrow \pi^*$). For the particular case of tetramethylidioxetane, the decomposition is thought to produce triplet products with a quantum yield of 0.5.¹⁶ Other dioxetanes, however, are found to produce much smaller yields of excited products. For example, C is observed to produce singlet and triplet excited products with quantum yields of 0.05 and 0.035, respectively.¹⁷



Analysis of the proposed mechanisms in these systems has been hindered by a lack of accurate thermochemical data on both dioxetanes¹⁸ and peroxiranes. It is the purpose of this letter to report ab initio calculations on key intermediates in these reactions and to analyze the implications of these results on the mechanism of the reactions.

We found (from numerous preliminary calculations) that, in order to obtain accurate bond energies for the processes as in 1–3, it is necessary (i) to use a flexible basis of “double zeta”²⁰ quality, including d polarization functions on each C and O and (ii) to incorporate correlation effects among all valence orbitals including O nonbonding pairs in addition to the CH, CO, OO, and CC bonding pairs. Generalized valence bond (GVB)⁸ calculations were carried out correlating all 12 valence pairs self-consistently (and including up to five natural orbitals for some bond pairs). Within the space of GVB orbitals we carried out extensive configuration interaction (CI) calculations allowing up to quadruple excitations. The geometries of the dioxetane and peroxirane intermediates were optimized at the GVB (4) level of calculation.²¹

Similar calculations on the bond energies of a variety of carbon and oxygen containing compounds were performed in order to ascertain the accuracy of the method. These results are shown in Table I. The errors in the GVB-CI single bond energies range from –3 kcal for ethane to +4.2 kcal for hy-

Table II. Thermochemical Results on Proposed Intermediates

Reaction	ΔH_0°	
	GVB-CI ^a	MINDO/3 ^b
	+14.3 (15.9) ^c	
	53.4 (52.7)	49.4
	–36.9	–65.5
	+16.5	–16.1
	+9	
	–50.2	–27.5
	+21.9	+44.4
	+30.6	+50.5

^aThe first two reaction enthalpies come directly from GVB-CI calculations (the value before correcting for zero-point energies is in parentheses). The remaining reaction enthalpies were obtained using the estimated GVB-CI dioxetane heat of formation (see text) and experimental heats of formation from ref 22. ^bReferences 11, 23, and 25. ^cAveraged over all eight biradical states and corrected for the error (–4.2 kcal) in the hydrogen peroxide bond strength.

drogen peroxide. The GVB-CI double bond energies are less accurate, the largest error being –8.7 kcal for ethylene.

In order to establish the heat of formation of dioxetane, a GVB-CI calculation on the O–O bond energy of dioxetane was carried out (first line of Table II). The resulting bond energy of 14.3 kcal (corrected for the error in the GVB-CI hydrogen peroxide energy) is 23.8 kcal below that of the corresponding acyclic peroxide bond energy (38.1 kcal).²⁴ This then implies a strain energy for the dioxetane ring of 23.8 kcal (a previous estimate was 26 kcal^{14a}). Using the group additivity method of Benson²⁴ then yields

$$\Delta H_f(\text{dioxetane}) = -2.2 \text{ kcal}$$

Alternatively, we can estimate the heat of formation of the OCCO biradical directly using²⁷

$$\Delta H_f(\text{HOCH}_2 - \text{CH}_2\text{OH}) = -93.9 \text{ kcal}$$

and

$$D(\text{H} - \text{OC}_2\text{H}_5) = 104.3 \text{ kcal}$$

Correcting the experimental heat of formation of ethanediol for the extra stability due to the intramolecular hydrogen bond in this species (approximately 2.0 kcal²⁸) leads to

$$\begin{aligned} \Delta H_f(\cdot\text{OCH}_2\text{CH}_2\text{O}\cdot) &= -93.9 + 2.0 - 2(104.3) - 2(52.1) \\ &= 12.5 \text{ kcal} \end{aligned}$$

Using then the calculated O–O bond energy of dioxetane we obtain $\Delta H_f(\text{dioxetane}) = -1.8$, in good agreement with the above estimate. This result and those of Table II, together with the experimental heats of formation of oxygen, ethylene, and formaldehyde,²² lead to the heats of reaction shown in Table II.

Since the measured activation energies for the thermal decomposition of substituted dioxetanes are ~24 kcal,^{15,29} the open OCCO diradical (14 kcal above dioxetane) is a plausible intermediate in this reaction. Alkyl substitution on the dioxetane ring will have the effect of increasing the ring strain (the substituents are forced to be nearly eclipsed in the ring). By analogy to substituted cyclobutanes²⁶ we expect this effect to

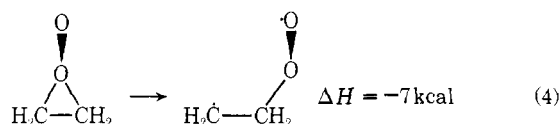
be 1–2 kcal/mol per eclipsed methyl pair. Therefore, the ring strain of, for example, tetramethyldioxetane may be up to 4 kcal larger than that of dioxetane. Thus we estimate that the ΔH_f for tetramethyl dioxetane is -36 kcal/mol.

An interesting feature of dioxetane decomposition is the production of excited state carbonyls [both $^1(n \rightarrow \pi^*)$ and $^3(n \rightarrow \pi^*)$]. Assuming the reaction to be nonconcerted (vide supra) with a short-lived OCCO biradical intermediate, the ordering of the states of the biradical is of importance in determining the products states. GVB calculations indicate the relative ordering of these states to be $^3(4\pi) > ^1(4\pi) > ^1(3\pi) > ^3(3\pi) > ^3(2\pi) > ^1(2\pi)$ with the total energy difference, $^3(4\pi) - ^1(2\pi)$, being 3.1 kcal. Thus the $^1(4\pi)$ state (which correlates with both ground-state dioxetane and ground-state products) is the highest of the four singlet states. Therefore the reaction path to ground-state products necessarily crosses six other potential surfaces, four of which [the two $^1(3\pi)$ states and the two $^3(3\pi)$ states] correlate with one excited-state and one ground-state carbonyl product. In general, a transition between the two singlet surfaces at a potential surface crossing is expected to occur much more efficiently than crossings between two surfaces of differing spin multiplicities. However, the excited singlet product is an additional 16 kcal uphill from the biradical, whereas the triplet state is only 8 kcal uphill. Therefore the excited singlet product is energetically disfavored unless (i) the dioxetane has a large excess of vibrational energy (as in the gas phase addition of ethylene and $O_2(^1\Delta)$)⁷ or (ii) the substituents lower the energy of the singlet excited products relative to the biradical. In either of these two latter cases, singlet products should be preferred. If these singlet pathways to decomposition are not available (too endothermic), the intermediate biradical may be sufficiently long-lived to undergo intersystem crossing to a triplet state which would then decompose to triplet carbonyl. More detailed calculations on the states in the region of the surface crossing are presently in progress.

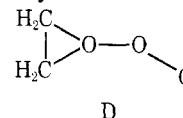
GVB-CI calculations (Table II) place the proposed peroxirane intermediate (A) 53 kcal above dioxetane and 16 kcal above the reactants, ethylene and $O_2(^1\Delta)$. The calculated geometry of A is close to that of epoxide, with a second oxygen atom placed at an angle of 60° with respect to the epoxide CCO plane and a O–O bond length of 1.51 Å. The GVB orbitals indicate that the terminal oxygen atom should be thought of as a singlet oxygen with two doubly occupied p orbitals (p_x and p_y) perpendicular to the O–O bond and an empty p orbital along this bond. This empty p orbital is aligned with the doubly occupied (nonbonding) $p\pi$ orbital of the epoxide (p_z) to form the bond.

One important feature of this mode of bonding should be stressed, the character of the end oxygen is very much that of a singlet oxygen atom, which is quite different from what is found in the low-lying states of O_2 ($^3\Sigma_g^-$ and $^1\Delta$).³⁰ As a result of this change in orbital character (from that of the reactants), we expect a sizable barrier to formation of peroxirane in process 2.

We find peroxirane to lie 53 kcal/mol above dioxetane, whereas we predict the CCOO biradical to be 46 kcal/mol above dioxetane³¹ (or 7 kcal below peroxirane).³² The reason for this instability of peroxirane is that the terminal oxygen is forced to have the character of a singlet state. Upon breaking a CO bond of peroxirane, one lone pair of the terminal oxygen can delocalize onto the ring oxygen leading directly to the 1,4 biradical structure shown in eq. 4. Because of this stability it



seems highly unlikely that peroxiranes play any role in the mechanism of $O_2(^1\Delta)$ reactions. Similar considerations argue against the intermediacy of D in ozonolysis reactions.



Two theoretical studies, both semiempirical, have recently been reported on the processes 1–3. Dewar and co-workers¹¹ carried out MINDO/3 studies and concluded that addition of 1O_2 to ethylene passes through a peroxirane intermediate (A). In addition, in the decomposition of dioxetane they found³³ that decomposition to singlet products required an activation energy >45 kcal and concluded that the decomposition involves intersystem crossing to a triplet state. We disagree with both conclusions. It is well known²⁵ that MINDO/3 leads to errors of ~ 20 kcal for compounds involving small rings or adjacent heteroatoms (e.g., in Table I the ΔH for $C_2H_4 + O \rightarrow$ epoxide is 22 kcal too large). We find that MINDO/3 puts dioxetane and peroxirane 29 and 33 kcal too stable with respect to products, reactants, and the decomposition intermediates. For example, MINDO/3 calculations predict a dioxetane ring strain energy of only 1.5 kcal, well below that of any known four-membered ring. (Typically, four-membered ring strain energies range from 25 to 27 kcal.) These errors result in an incorrect interpretation of the reaction sequence.

Hinze and co-workers³⁴ carried out CNDO-MCSCF calculations for the decomposition of dioxetane using additional empirical corrections to compensate for the well-known errors in bond dissociation energies for CNDO. They concluded that the transition state has $R_{CC} = 3.27$ Å with $R_{OO} = 1.88$ Å; that is, the C–C bond is essentially broken in the transition state! This is contrary to our results (and to generally accepted thermochemistry). The problem here is that the semiempirical CNDO-MCSCF method³⁵ leads to C–C bond strengths ~ 31 kcal too small (for C_2H_6) and O–O bond strengths ~ 100 kcal too large (for H_2O_2).³⁶

From our studies we conclude that the addition of 1O_2 and ethylene leads to dioxetane with $\Delta H_f = -37$ kcal (calculated $\Delta H_f^{298^\circ}$ (dioxetane) = -2 kcal; the strain energy is calculated to be 24 kcal). We find that peroxirane should play no role in this process. In the decomposition of dioxetane, it requires only 14 kcal to break the O–O bond (to form the trans or gauche biradical); since experimental activation energies are ~ 23 kcal, we need not assume the decomposition to be concerted. We find that the ground state of dioxetane crosses three triplet states in opening up to the biradical intermediate and it is suggested that these crossings play an important role in the processes leading to chemiluminescence.

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 (36) Since only heats of atomization using CNDO-MCSCF were reported, the estimates of bond strengths were necessarily approximate. For the C-C bond bond strength of C_2H_6 , we assumed the error in each C-H bond strength to be equal to the average error in the CH_4 atomization energy. The remaining error was then assumed to be in the C-C bond strength. A similar analysis of the heats of atomization of H_2O_2 and H_2O gave the estimated error in O-O bond strengths.

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Hydroxide Ion as a "Non-Innocent" Quencher of the Photoaquation Reaction of Chromium(III) Complexes

Sir:

Several Cr(III) complexes are known to exhibit appreciable phosphorescence under experimental conditions (fluid solutions near room temperature) in which photochemistry is usually observed.¹ For these complexes the comparison of the phosphorescence and photolysis quenching²⁻¹⁰ or sensitization¹¹⁻¹³ has led to important progress in the understanding of the excited-state behavior. Quenching and sensitization processes involve an intimate interaction between the excited molecule and the quencher.¹⁴ Such an interaction may result in physical events (e.g., electronic energy transfer, spin-catalyzed deactivation, etc.) or in some kind of chemical reaction between the excited state and the quencher (e.g., electron transfer, hy-

Table I. Quenching of the t -Cr(en)₂(NCS)₂⁺ Phosphorescence Emission^a

Quencher ^b (kK)	k_q , ^c M ⁻¹ s ⁻¹	Quenching mechanism
Ni(gly) ₂ ^d (10) ^e	7.5×10^7	Energy transfer
Co(NH ₃) ₅ Cl ²⁺ (11.4) ^e	1.8×10^8	Energy transfer
Cr(CN) ₆ ³⁻ f (12.3) ^g	2.3×10^9	Energy transfer
Co(CN) ₆ ³⁻ (~ 18) ^h	$< 1 \times 10^5$	
I ⁻ (44) ⁱ	$< 1 \times 10^5$	
OH ⁻ j (54) ⁱ	1.3×10^8	Chemical reaction ^k

^a Air equilibrated aqueous solution, 15 °C, complex concentration 1×10^{-2} M, pH 3, unless otherwise stated. ^b The energy of the lowest excited state is given in brackets. ^c Bimolecular quenching constant obtained from the Stern-Volmer plot $I^0/I = 1 + k_q\tau[Q]$; $\tau = 10.5 \mu\text{s}$. ^d Natural pH. ^e C. K. Jørgensen, *Adv. Chem. Phys.*, **5**, 33 (1963). ^f Lifetime quenching measurements showed that static quenching is negligible. ^g From ref 12. ^h J. N. Demas and J. W. Addington, *J. Am. Chem. Soc.*, **98**, 5800 (1976). ⁱ M. Fox, in "Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Ed., Wiley, New York, N.Y., 1975, p 333. ^j Phosphate buffer, 0.05 M. ^k See text.

drogen transfer, etc.). In the latter case new chemical species are formed which exhibit their own chemical reactivity. This may cause complications in the analysis of the experiment and may also lead to erroneous mechanistic conclusions.

We have studied the phosphorescence and photoreaction (NCS⁻ release)¹⁵ quenching of $trans$ -Cr(en)₂(NCS)₂⁺ (en, ethylenediamine) and have found that OH⁻, which is currently used in investigations of this kind,^{5,9} causes anomalous results for the quenching of the photoreaction.

Phosphorescence and photolysis studies were carried out in air equilibrated aqueous solutions at 15 °C with 508-nm excitation using apparatus and techniques previously described.¹⁸ The species Ni(gly)₂ (gly, glycinate ion), Co(NH₃)₅Cl²⁺, Cr(CN)₆³⁻, Co(CN)₆³⁻, I⁻, and OH⁻ were used as potential quenchers. The results obtained in the quenching of the $trans$ -Cr(en)₂(NCS)₂⁺ phosphorescence are summarized in Table I. As the energy level of the ²E emitting state of $trans$ -Cr(en)₂(NCS)₂⁺ is 13.8 kK above the ground state,¹ quenching via electronic energy transfer is thermodynamically allowed for Ni(gly)₂, Co(NH₃)₅Cl²⁺, and Cr(CN)₆³⁻, whereas it is forbidden for Co(CN)₆³⁻, I⁻, and OH⁻. Nevertheless, OH⁻ does quench the $trans$ -Cr(en)₂(NCS)₂⁺ phosphorescence with a relatively high rate constant. In parallel experiments the quenching of the NCS⁻ photoaquation reaction was investigated¹⁹ and it was found that a fraction of the photoreaction quantum yield (Φ_{NCS^-}) was unquenchable under conditions of total phosphorescence quenching. Plots of $\Phi_{NCS^-}/\Phi_{NCS^-}^0$ against I/I^0 ⁷ revealed that the data obtained for Ni(gly)₂, Co(NH₃)₅Cl²⁺, and Cr(CN)₆³⁻ fall on the same straight line, whereas those concerning OH⁻ fall on a different straight line (Figure 1). Specifically, the results obtained with Ni(gly)₂, Co(NH₃)₅Cl²⁺, and Cr(CN)₆³⁻ show that the unquenchable part of the photoreaction is $\sim 20\%$, whereas the results obtained with OH⁻ would indicate that the unquenchable part is $\sim 55\%$. Since the fraction of unquenchable photoreaction has important mechanistic implications as a measure of the "prompt" quartet reaction,^{2-10,14} it is necessary to know which of the two values is the right one. There seems to be little doubt that the right value is that obtained with Ni(gly)₂, Co(NH₃)₅Cl²⁺, and Cr(CN)₆³⁻, which are expected to quench by a chemically "innocent" mechanism, i.e., electronic energy transfer. The quenching by OH⁻, on the contrary, has to take place by means of some kind of chemical reaction.

For the quenching of (²E)Cr(NH₃)₆³⁺ by OH⁻, Langford and Tipping⁵ suggested the involvement of an amine-hydrogen deprotonation step. This mechanism was also considered likely for hydroxide quenching of (²E)Cr(en)₃³⁺,⁹ but it seems to be less probable in our case owing to the lower positive charge of