gas phase (cf. Table VI). Indeed, only form **11** is experimentally detectable in aqueous solutions of guanine.[1]

Conclusions

The results presented in this paper confirm our earlier observations about the validity of the AM1 SCRF method[9,32] for the quantitative prediction of relative stabilities of heterocycle tautomers in solution.

In a few cases, where the comparison is available, the predictions by AM1 are correct also for gas-phase tautomerization energies of nucleic acid bases. AM1 gives also a good representation of the charge distribution in molecules in terms of calculated dipole moments, enabling us to correctly account for the specific solvent polarity effects on the tautomer energies in the framework of the self-consistent reaction field model. Therefore, this method is promising for the study of base pairing and mispairing processes in DNA, which has great importance in the investigation of mutation frequency. Such an investigation is now in progress.

Registry No. Cytosine, 71-30-7; thymine, 65-71-4; uracil, 66-22-8; 1-methylcytosine, 1122-47-0; 1-methylthymine, 4160-72-9; 1-methyluracil, 615-77-0; adenine, 73-24-5; guanine, 73-40-5.

Supplementary Material Available: Tables of AM1 and MNDO/PM3 Z matrices for cytosine, uracil, thymine, 1-methylcytosine, 1-methyluracil, and 1-methylthymine tautomers, adenine, and guanine and listings of PM3 SCF and SCRF calculated relative heats of formation and dipole moments of cytosine, uracil, thymine, 1-methylcytosine, 1-methyluracil, and 1-methylthymine tautomers in different media (65 pages). Ordering information is given on any current masthead page.

Chemiluminescent Decomposition of 1,2-Dioxetanes: An MC-SCF/MP2 Study with VB Analysis

Mar Reguero,[1b] Fernando Bernardi,[1a] Andrea Bottoni,[1a] Massimo Olivucci,[1b] and Michael A. Robb*,[1b]

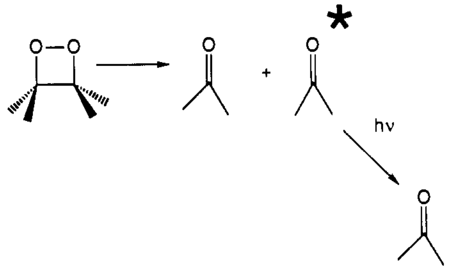
Contribution from the Dipartimento di Chimica "G. Ciamician" dell'Universita di Bologna, Via Selmi 2, 40126 Bologna, Italy, and the Department of Chemistry, King's College, London, Strand, London WC2R 2LS, U.K. *Received July 6, 1990*

Abstract: MC-SCF (at the 4-31G level) geometry optimizations and analytical hessian (frequencies) for ground-state (S_0) and excited state (T_1 and S_1) surfaces that are necessary in the description of the mechanism of the chemiluminescent decomposition of 1,2-dioxetane are reported. The energetics have been confirmed by multi-reference MP2 computations at selected critical points. The origin of the S_0/T_1 surface intersection and the different barrier heights in S_0/T_1 fragmentation are rationalized using a rigorous VB model. The computed results suggest a novel mechanism where the rate-determining step occurs on the excited T_1 surface. The computed activation energy is 25.3 kcal mol^{-1} at the MC-SCF/MP2/6-31G* level (21.3 kcal mol^{-1} with zero-point correction from 4-31G level MC-SCF) which is in acceptable agreement with the experimental activation energy of 22.1 ± 0.3 kcal mol^{-1}. Our computed value of $\Delta S^{\ddagger}$ is 5 cal mol^{-1} K^{-1} in agreement with the experimental result which is small or negative depending upon solvent. Our results suggest that the thermal S_0 ring opening of dioxetane to produce a biradical can occur almost without activation energy. The S_0–T_1 *avoided* crossing is shown to occur along an O–O bond rupture coordinate in the region just before the biradical minimum and is controlled by strong spin-orbit coupling. After passage (via C–C stretching) through a second *real* T_1–S_0 crossing immediately after the biradical minimum the rate-determining step involves a transition state for C–C fragmentation on the T_1 surface to produce triplet and ground-state formaldehyde.

Introduction

The chemiluminescence of 1,2-dioxetantes (Scheme I) is an electronically forbidden *nonadiabatic* (i.e. a change from one potential energy surface to another) reaction.[2] As a result of much experimental work, very accurate energetics and rate data are available;[3,4] however, the precise nature of the mechanism remains the subject of some controversy.[5] In this paper we shall show that theoretical computations can now provide a rationalization of the experimental data and a more detailed discussion of the mechanism.

Scheme I



Such reactions are difficult to study theoretically because not only must one treat synchronous and biradical paths on the ground-state surface with balanced accuracy but also one must treat the excited state and the ground state with equal accuracy since a surface crossing is involved. Further, in addition to the location of minima and transition structures on ground and excited states, one is interested in characterizing the regions where the ground- and excited-state surfaces intersect.

Let us begin with a summary of the mechanistic possibilities for these reactions. First, let us consider only the ground-state thermal decomposition of a 1,2-dioxetane to produce 2 mol of

---

(1) (a) Dipartimento di Chimica "G. Ciamician" dell'Universita di Bologna. (b) Department of Chemistry, King's College.

(2) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publishing Co.: Menlo Park, CA, 1978, pp 597–602.

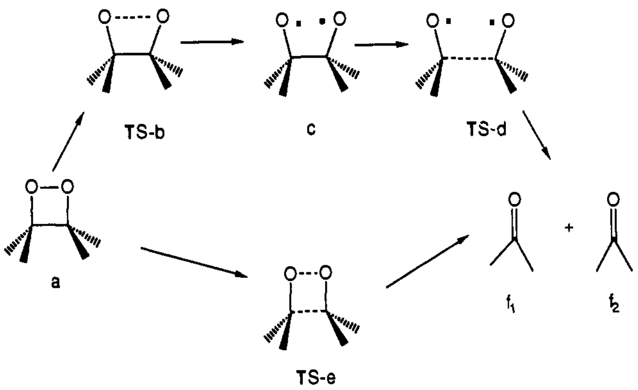
(3) Adam, W.; Baader, W. J. *J. Am. Chem. Soc.* **1985**, *107*, 410–416.

(4) (a) Bechara, E. J. H.; Wilson, T. *J. Org. Chem.* **1980**, *45*, 5261–5268. (b) Schmidt, S. P.; Schuster, G. B. *J. Am. Chem. Soc.* **1980**, *102*, 306–314. (c) Schmidt, S. P.; Schuster, G. B. *J. Am. Chem. Soc.* **1978**, *100*, 5559–5562. (d) Hass, Y.; Greenblatt, G. D.; Anner, O. *J. Am. Chem. Soc.* **1985**, *107*, 5068–5074. (e) Tolbert, M. A.; Huestis, D. L.; Rossi, M. J. *J. Phys. Chem.* **1982**, *92*, 4094–4099. (f) Cannon, B. D.; Crim, F. F. *J. Chem. Phys.* **1981**, *75*, 1752–1761.

(5) For a general discussion on the chemistry of 1,2-dioxetanes, see: Adam, W. *Adv. Heterocycl. Chem.* **1977**, *21*, 437–481.

0002-7863/91/1513-1566$02.50/0

Scheme II



ketone (Scheme II). The ground-state reaction can be a 2-step process where the O–O bond is broken first (a → TS-b → c) and then the C–C bond is broken (c → TS-d → $f_1 + f_2$) or it can be concerted (forbidden: a → TS-e → $f_1 + f_2$). Unfortunately, there is almost no experimental information on the ground-state reaction except that dioxetanes are explosive[6a] so that one can presume that the barrier a → TS-b/e is quite small. The overall reaction is exothermic by approximately 60 kcal mol^{-1}. In the excited-state reaction, decomposition of a 1,2-dioxetane produces 1 mol of ketone in its ground state and 1 mol of ketone in a *triplet* $^3(n-\pi^*)$ excited state. Experimentally, the $^3(n-\pi^*)$ state is produced in preference to the *singlet* $^1(n-\pi^*)$ state. Two mechanisms have been proposed. We begin with the Turro[2,6] scheme (Figure 1a). In Turro's scheme the combined action of stretching the O–O bond and rotation about C–C is assumed[5] to lead to an anti biradical on S_0. The T_1 surface is assumed to cut the S_0 surface during this O–O bond rupture and there is very large spin–orbit coupling at point A leading to an *avoided* crossing. In contrast the spin–orbit coupling at B is small leading to the observed preference for the $^3(n-\pi^*)$ state. The other possibility is the biradical mechanism[7] (Figure 1b). This mechanism presupposes the existence of a biradical (c and c*) minima on S_0 and T_1, and the nature of the surface crossings at A and B (in Figure 1b) is assumed to be similar to the Turro mechanism[2,6] illustrated in Figure 1a.

The experimental data on this reaction are very extensive but do not completely resolve many questions about the mechanism. The activation energy for the *chemiluminescence reaction* has been shown[3] to be 22.7 kcal mol^{-1} for the parent system. A priori one cannot know if this activation energy corresponds to the energy difference between a and TS-b/e, or c and TS-d, or c* and TS-d* (see Figure 1b and Scheme II for the meaning of the notation). In addition, the $\Delta S^{\ddagger}$ is very small or negative.[6b] Since it is difficult to imagine a highly ordered transition structure this fact is very curious. The activation energy for the *dark ground state decomposition* does not seem to have been determined. In view of the fact that the compound explodes one is tempted to assume that the "dark" reaction path is much lower in energy; however, other factors such as exothermicity, energy transfer, and the competition between uni- and bimolecular reaction mechanisms are also involved.

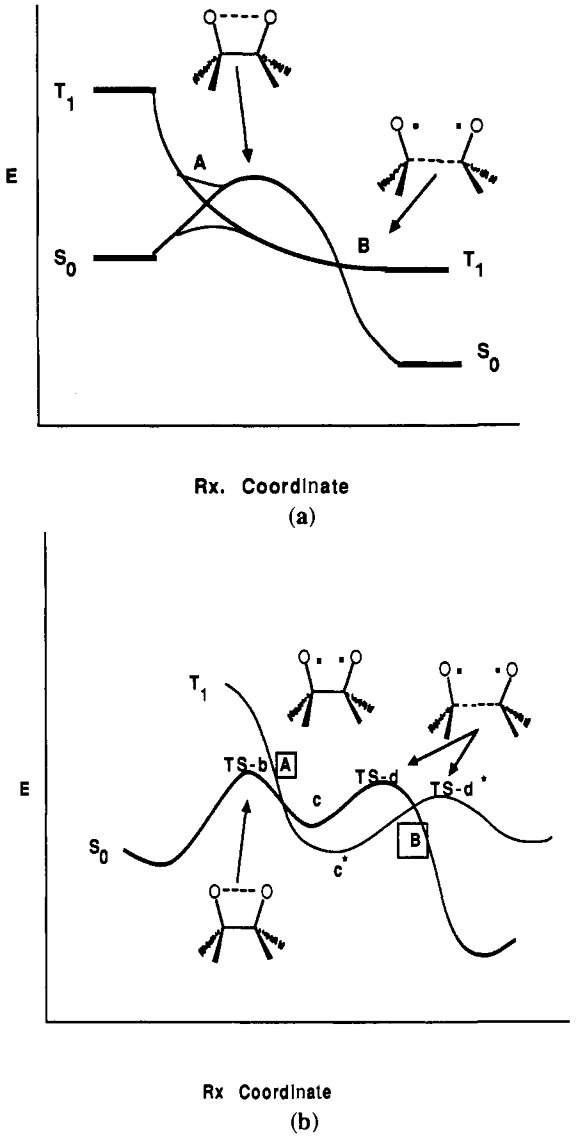


Figure 1. Schematic representation of (a) the Turro[2,6] mechanism for the fragmentation of dioxetanes and (b) the biradical mechanism.[7] The reaction coordinate in each case is assumed to involve O–O stretching leading to ring opening in the initial phase followed by C–C stretching leading to fragmentation. The points A and B indicate S_0/T_1 crossings. The symbols TS-b, c etc. refer to Scheme II.

There seem to have been only a few attempts at theoretical computations.[8-10] Goddard et al.[8] studied this reaction 13 years ago using VB methods. They reported that there are 8 nearly degenerate biradical states of the form of c/c* (see Figure 1b and Scheme II for the meaning of the notation) at an energy of 14 kcal mol^{-1} above the cyclic 1,2-dioxetane. This result is often taken as evidence for the biradical scheme of Figure 1b. However, Goddard et al. did not report detailed structures or transition states. Dewar's earlier calculations[9] gave support for the Turro mechanism. He found a biradical transition state corresponding to an activation energy of 45 kcal mol^{-1} ruling out the biradical mechanism. However, he has also characterized a singlet triplet crossing at 38 kcal mol^{-1} above dioxetane which he assumed to be the "transition state" for the reaction.

It would appear that the detailed answers to mechanistic questions can only be obtained by more accurate theoretical computation. One needs MC-SCF methods to get a balanced

---

(6) (a) Turro, N. J.; Lechtken, P.; Schore, N. E.; Schuster, G.; Steinmetzer, H. C.; Yekta, A. *Acc. Chem. Res.* **1974**, *7*, 97–105. (b) Turro, N. J.; Lechtken, P. *Pure Appl. Chem.* **1973**, *33*, 363–388. (c) Turro, N. J.; Lechtken, P.; Schuster; Orell, J.; Steinmetzer, H. C.; Adam, W. *J. Am. Chem. Soc.* **1974**, *96*, 1627–1629. (d) Turro, N. J.; Devaquet, A. *J. Am. Chem. Soc.* **1975**, *97*, 3859–3862. (e) Turro, N. J.; Ramaurthy, V. In *Rearrangements in ground and excited states.* De Mayo Ed.; Academic Press: New York, 1980; Vol. III, pp 1–23.

(7) (a) O'Neal, H. E.; Richardson, W. H. *J. Am. Chem. Soc.* **1970**, *92*, 6553–6557. (b) Richardson, W. H.; Hodge, V. F. *J. Am. Chem. Soc.* **1971**, *93*, 3996–4004. (c) Richardson, W. H.; Montgomery, F. C.; Yelvington, M. B.; O'Neal, H. E. *J. Am. Chem. Soc.* **1974**, *96*, 7252–7532.

(8) Harding, L. B.; Goddard, W. A. *J. Am. Chem. Soc.* **1977**, 4520–4523.

(9) Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1974**, *96*, 7578–7579.

(10) (a) Yamaguchi, K.; Yabushita, S.; Fueno, T. *Chem. Phys. Lett.* **1981**, *78*, 572–575. (b) Hilal, R. *Int. J. Quantum Chem.* **1981**, *19*, 805–819. (c) Lechtken, P. *Chem. Ber.* **1978**, *111*, 1413–1419. (d) Wilson, T.; Golam, D. E.; Harris, M. S.; Daumstark, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 1086–1090. (e) Koo, J. Y.; Schuster, G. B. *J. Am. Chem. Soc.* **1977**, *99*, 5403–5408.

Table I. MC-SCF Energies and Geometries (at the 4-31G Basis Level) for Various Points on the S_0, T_1, and S_1 Surfaces for the Fragmentation of 1,2-Dioxetane into Two Formaldehyde Molecules

no.	structure (Scheme II)	state (nature)	geometry					energy	
			r_{C-C}, Å	r_{O-O}, Å	r_{CO}, Å	r_{CO}, Å	θ	total (E_h)	relative (6-31G* MP2), kcal mol^{-1}
1	a	S_0 min	1.54	1.74	1.47	1.47	15.8	−227.3771	0.0
2	a	T_1	structure 1					−227.2954	51.3
3	a	S_1	structure 1					−227.2811	60.2
4	a	S_0 TS	1.54	1.72	1.47	1.47	0.0	−227.3769	0.1
5	a	S_1	structure 4					−227.2954	51.4
6	b	S_0 SOSP[a]	1.75	2.79	1.37	1.37	0.0	−227.3656	7.71
7	b	S_0 TS	1.53	2.15	1.46	1.46	32.7	−227.3739	2.0
8/9	A (Figure 1b)	S_0/T_1 crossing	1.54	2.50	1.44	1.44	53.0	−227.374[b]	1.9
10	c gauche	S_0 (4π) min	1.58	2.97	1.41	1.41	76.2	−227.3816	−2.0
11	c* gauche	T_3 (4π) min	1.55	2.87	1.43	1.43	68.6	−227.3794	−1.4
12	c* gauche	T_1 (3π) min	1.55	2.95	1.43	1.42	69.5	−227.3826	−3.3 (−1.4)
13	c* gauche	S_1 (3π) min	1.55	2.96	1.42	1.42	70.9	−227.3824	−3.3
14	c* gauche	S_2 (2π) min	1.54	3.01	1.43	1.43	70.7	−227.3856	−5.3
15	c* gauche	T_2 (2π) min	1.54	3.01	1.43	1.43	70.7	−227.3854	−5.2
16	d gauche	S_0 TS	1.73	3.03	1.35	1.35	81.9	−227.3793	−1.3
17	d* gauche	T_1 TS	2.11	3.48	1.28	1.38	100.2	−227.3440	20.7
18	d* gauche	S_1 TS	2.16	3.40	1.27	1.39	88.2	−227.3387	24.1
19	c anti	S_0 min	1.59		1.41	1.41	180.0	−227.3829	−3.6
20	d anti	S_0 TS	1.71		1.36	1.36	180.0	−227.3821	−3.1
21	d* anti	T_1 TS	2.11		1.28	1.38	180.0	−227.3464	19.3 (23.9)
22	d* anti	S_1 TS	2.15		1.27	1.39	180.0	−227.3412	22.5
23	f + f	S_0 min			1.23	1.23		−227.4681	−57.1 (−61.4)
24	f* + f	T_1 min			1.23	1.37		−227.3658	7.1 (13.4)
25	f* + f	S_1 min			1.23	1.39		−227.3570	12.6

[a] SOSP second-order saddle point. [b] Lagrange–Newton optimization converged only to low accuracy.

representation of concerted versus biradical pathways and excited versus ground state. In addition to the determination of transition structures and biradical minima on ground- and excited-state surfaces, one must determine the lowest energy points on the seam of intersection of the S_0 and T_1 surfaces (i.e. Dewar's transition state discussed above).

Computational Details

All computations were performed with the GAUSSIAN[11] suite of programs using the STO-3G and 4-31G basis sets. In particular, the MC-SCF programs used[12] are those of GAUSSIAN 90.[13] The location of singlet–triplet crossings was performed[14] by using the Newton–Lagrange method introduced into quantum chemistry by Morokuma.[15] All structures were characterized with use of an analytical MC-SCF hessian.[16] The energetics (activation barriers etc.) were computed more accurately by performing MP2 computations using the 6-31G* basis at the 4-31G MC-SCF geometries. For closed-shell species we used RHF/MP2, and for transition structures or biradicaloid regions of the surface an MP2 method designed to work with MC-SCF was used.[17]

In MC-SCF computations the only element that is a somewhat subjective is the choice of active orbital space (i.e. those orbitals that may have variable occupancy). The orbital occupancy of those structures that correspond to the biradicaloid region of the potential surface (structure c/c* in Figure 1b) is illustrated in Figure 2. Thus one requires 6 active orbitals and 8 active electrons to describe the competition between c (a 4 π electron system) and c* (a 3 π electron system). Of course, if the occupancy of an orbital begins to approach 2.0 then the orbital becomes inactive and the active space can be reduced in dimension without changing the energy. In the limit where we have all orbitals doubly occupied then we have an SCF wave function. In fact if one attempts to perform an MC-SCF computation with a doubly occupied orbital in the active space then the computation will not converge. Thus in all our calculations we carried out computations with the smallest possible active space (4 active orbitals, either 4 σ orbitals or 3 σ orbitals and 1 π orbital) and then confirmed the result with a CI or MC-SCF in the full 6 active orbitals and 8 active electrons space.

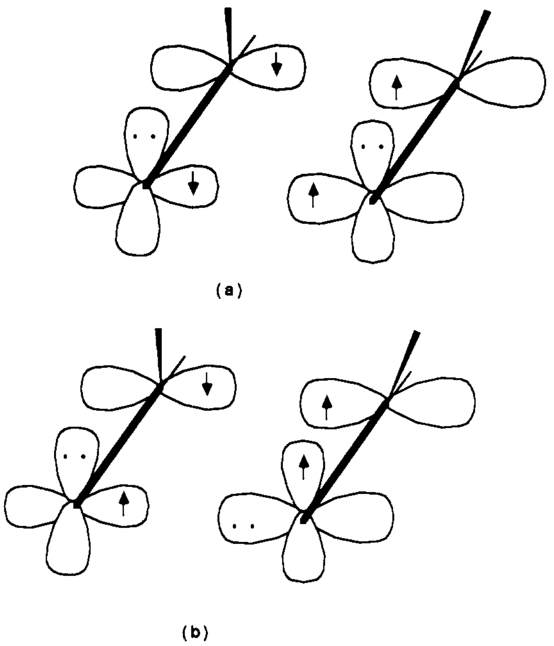


Figure 2. Active orbitals (i.e. those involved in bond breaking/making): (a) S_0 (4π electrons), (b) T_1/S_1 (3π electrons).

MC-SCF Study of the Ground- and Excited-State Fragmentation Mechanism of Oxetane

In Table I we summarize the most important structural and energetic data computed at the MC-SCF/4-31G level for the S_0, T_1, and S_1 states. The various structures can be identified with the possible mechanisms via column 2 and Scheme II (or Figure 1). The MP2 relative energetics at the 6-31G* level for some selected points are given in brackets where appropriate. Notice that gauche and anti fragmentation channels differ by less than

---

[11] Gaussian 86: Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. E.; Martin, R. L.; Stewart, J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R.; Fox, D. J.; Fluder, E. M.; Pople, J. A. Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA.

[12] (a) Eade, R. H. A.; Robb, M. A. *Chem. Phys. Lett.* **1981**, *83*, 362. (b) Schlegel, H. B.; Robb, M. A. *Chem. Phys. Lett.* **1982**, *93*, 43.

[13] Gaussian 90: Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R. A.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA.

[14] McDouall, J. J. W.; Robb, M. A.; Bernardi, F. *Chem. Phys. Lett.* **1986**, *129*, 595–602.

[15] Morokuma, K.; Koga, N. *Chem. Phys. Lett.* **1985**, *119*, 371.

[16] Bernardi, F.; Bottoni, A.; Olivucci, M.; Robb, M. A.; Schlegel, H. B.; Tonachini, G. *J. Am. Chem. Soc.* **1988**, *110*, 5993–5995.

[17] McDouall, J. J.; Peasley, K.; Robb, M. A. *Chem. Phys. Lett.* **1988**, *148*, 183.

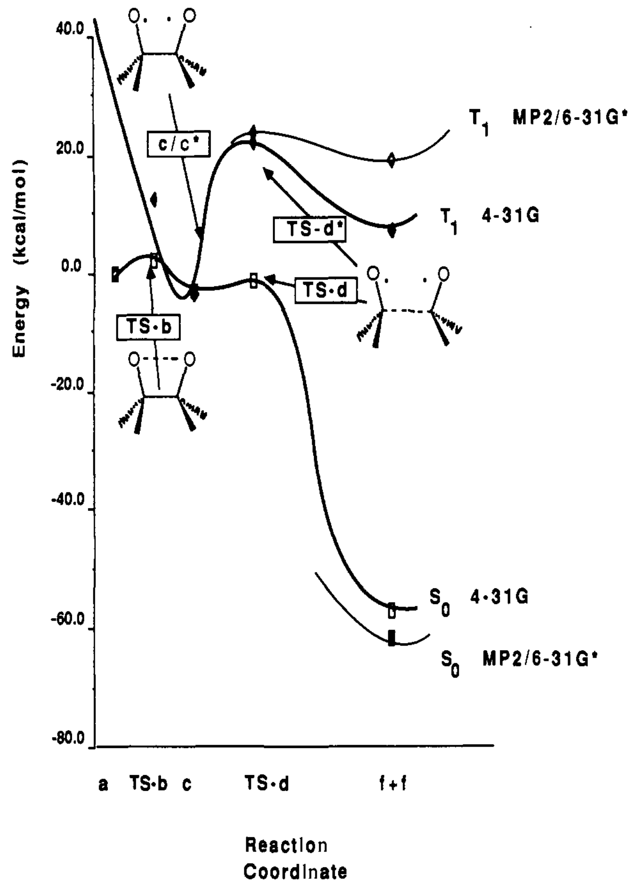


Figure 3. Summary of energetics at the MC-SCF and MP2 levels for the fragmentation of 1,2-dioxetane. The notation for labeling the critical points refers to Scheme II. The biradical structures c and d exist in gauche and anti conformations that differ in energy by 1-2 kcal mol^{-1}.

2 kcal mol^{-1} so for the biradical mechanism we will concentrate on the gauche channel. Further, notice that the equilibrium cyclic geometry of 1,2-dioxetane is not planar (structure 1, Table I) but rather there is a dihedral angle of 16°. The planar structure (structure 4, Table I) lies 0.1 kcal mol^{-1} higher and is a transition state.

We begin with an overall summary of our results concerning the behavior of the ground and excited triplet surfaces. The concerted path (Scheme II: a $\rightarrow$ TS-e $\rightarrow$ $f_1 + f_2$) does not appear to exist for the ground-state reaction. We found only a second-order saddle point (Table I, structure 6 which has 2 imaginary frequencies) when searching for a quasisynchronous pathway for S_0 fragmentation (Scheme II: TS-e). For this reason, the quasisynchronous path was not explored further. In contrast, we have located all the minima and transition states for the S_0 (4π), S_1 (3π), and T_1 (3π) biradical pathways (Scheme II) and the energies for S_0 and T_1 are summarized in Figure 3.

The most important observations are the following: (1) The T_1 crosses the S_0 state twice in the region of the biradical minimum in agreement with the biradical mechanism.[7] (2) In the region of the biradical minimum c we find $^1(4\pi)$, $^3(4\pi)$, $^1(3\pi)$, $^3(3\pi)$, $^1(2\pi)$, and $^3(2\pi)$ states whose energies lie within 4 kcal mol^{-1} of each other. The S_0 (4π), and S_1/T_1 (3π) states are the ones that are assumed to be relevant experimentally. (3) For the *dark ground state decomposition*, the rate-determining step involves O–O bond breaking (Scheme II: a $\rightarrow$ TS-b $\rightarrow$ c) with a very low activation energy (4-31G level) of 2.0 kcal mol^{-1}. The transition structure for C–C bond rupture (Scheme II: c $\rightarrow$ TS-d $\rightarrow$ $f_1 + f_2$, structure in 16 Table I) lies 3.3 kcal mol^{-1} below the transition state for O–O bond breaking. Experimentally, oxetanes are very unstable and explode! This is presumably a consequence not only of the low activation energy but also involving other factors such as exothermicity, energy transfer, and the competition between uni- and bimolecular reaction mechanisms. (4) The highest energy transition state for the *chemiluminescent reaction* involves the C–C bond rupture in the triplet biradical (Scheme II: TS-d*, Table I, structure 17) on the T_1 (3π) surface. *Thus the rate-determining step is on the excited-state surface* (Scheme II, c* $\rightarrow$ TS-d* $\rightarrow$ $f_1^* + f_2$).

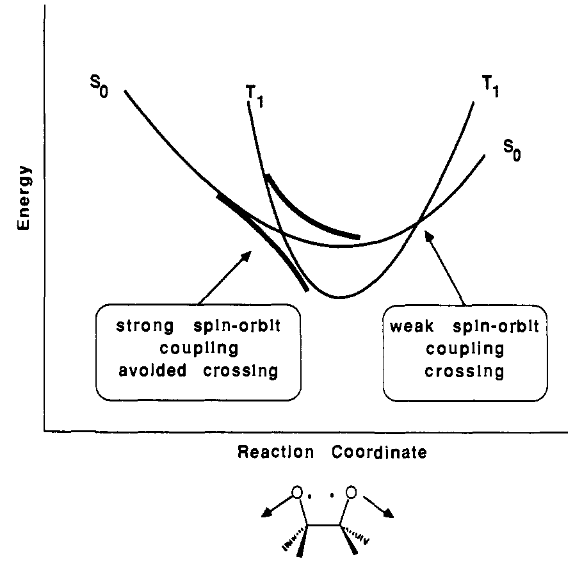


Figure 4. Model for the spin-orbit interaction proposed by Turro.[6c]

These observations though novel are consistent with the experimental data. The experimental[3] $\Delta H^{\ddagger}$ is 22.1 ± 0.3 kcal mol^{-1}. Our value for E(TS-d*) − E(c*) is 25.3 kcal mol^{-1} at the MC-SCF/MP2/6-31G* or 21.3 kcal mol^{-1} if we add a correction due to zero-point energies computed at the 4-31G level. Our value of $\Delta S^{\ddagger}$ is 5.0 cal mol^{-1} K^{-1} (computed as the difference of S for the reactant c* and TS-d*) whereas the experimental value is −3.9 cal mol^{-1} K^{-1} and we will return to discuss this point subsequently. Finally, our best theoretical value (MC-SCF/MP2/6-31G*) for the exothermicity, $E(f_1+f_2) - E(a)$, is −61.4 kcal mol^{-1} which compares well with the value of 63 kcal mol^{-1} for tetramethyl-1,2-dioxetane given by Turro.[2]

Clearly the surface of S_0–T_1 intersection and the role of spin–orbit coupling is a central element in the reaction mechanism. The situation, as discussed by Turro[6c] but adapted to a biradical mechanism, is illustrated schematically in Figure 4. Turro argued that the spin–orbit coupling would be particularly strong at the first crossing because the S_0 and T_1 states differed by two perpendicular π orbitals but that the spin–orbit coupling at the second crossing would be much smaller because of the orbital delocalization associated with the C–C bond breaking.

The general problem of the S_0/T_1 intersystem crossing has two facets. First, the S_0 and T_1 potential energy surfaces must intersect and the S_0/T_1 intersystem crossing must take place without additional energy of activation. Second, the spin–orbit coupling needs to be large enough so that the crossing is avoided as in the first crossing shown in Figure 4. From the mechanistic point of view we are particularly interested in the first aspect: we need to find the geometry and the energy of the lowest point on the $n - 1$ dimensional surface of intersection of S_0 and T_1. This is the analogue of a *transition structure* and the "extra" direction (the normal to the surface of intersection) is the "transition vector" that connects the S_0 and T_1 states. These critical points on the $n - 1$ dimensional surface of intersection of S_0 and T_1 can be located by using MC-SCF gradient methods as discussed elsewhere.[14,15]

Clearly we must characterize the S_0/T_1 intersections in the O–O bond-breaking region and in the C–C bond-breaking region. Let us begin with the O–O bond-breaking region. From the energy profile given in Figure 3 we expect to find a S_0/T_1 crossing between TS-b and the biradical minimum c/c*. By performing a geometry optimization on the $n - 1$ dimensional S_0/T_1 surface of intersection, starting at a point midway between TS-b and the biradical minimum c, we do in fact find the analogue of the *transition state*

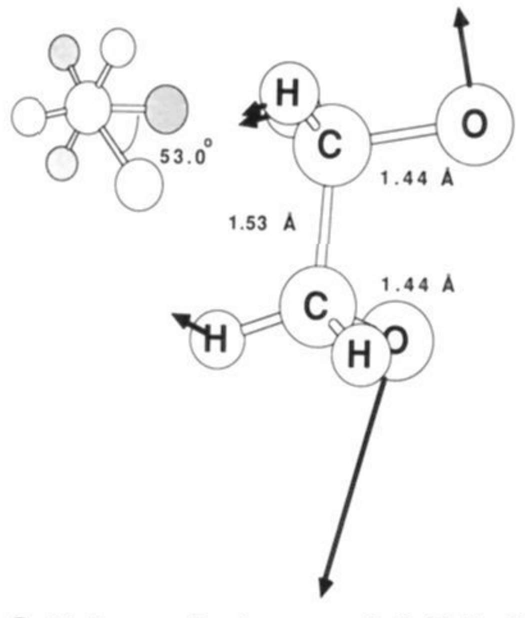


Figure 5. The S_0/T_1 intersection (structure 8/9, Table I). The arrows indicate the *normal to the seam of intersection*. This direction is the analogue of the transition vector/reaction path for a transition state.

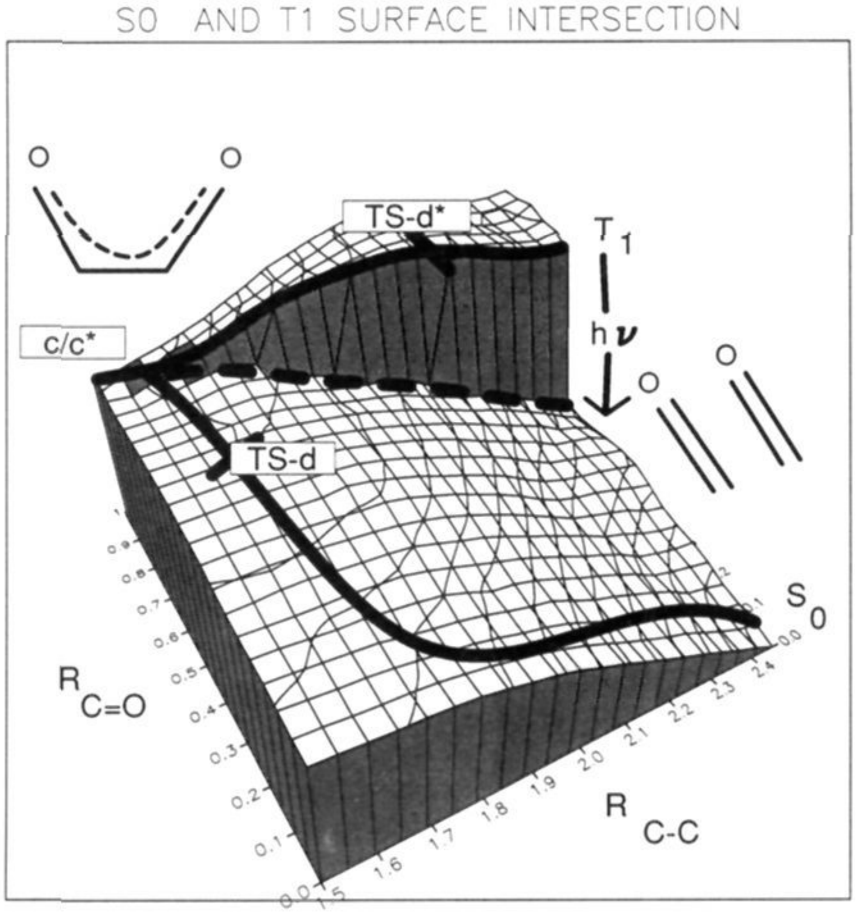


Figure 6. The T_1 and S_0 reaction paths (solid lines). The S_0 energies evaluated at points on the T_1 reaction path are shown as a fault (dashed line).

between the S_0T_1 surfaces. The geometry of this *transition state* for singlet–triplet crossing is illustrated in Figure 5 along with displacement vectors indicating the normal to the seam of intersection (i.e. the analogue of a *transition vector*). Remarkably, this first S_0/T_1 crossing lies very close to the minimum energy path between TS-b and c in Scheme II and has an energy almost identical with the energy of TS-b.

The situation for S_0/T_1 crossing along the C–C bond-breaking coordinate (leading to fragmentation) is more complicated because the reaction paths for S_0 fragmentation and T_1 fragmentation as determined by the intrinsic reaction coordinate method[13,18] are very different. This situation arises because of the different asymtotes of the S_0 and T_1 fragmentation intrinsic reaction coordinates. (The C=O bond length ($\cong$1.4 Å) in the $H_2C{=}O$ (n–π^*) T_1 state is longer than that in the $H_2C{=}O$ S_0 state ($\cong$1.2 Å).) Thus as fragmentation takes place in the S_0 state both the C=O bond lengths shrink from the value of 1.41 Å at the biradical minimum to values of 1.23 Å in ground-state formaldehyde. In contrast, for the T_1 fragmentation, the $H_2C{=}O$ (n–π^*) T_1 bond length contracts only slightly to 1.37 Å from its value of 1.43 Å at the biradical minimum. Thus in order to understand the S_0/T_1 surface intersection we must look at a 3-dimensional energy diagram in the variables C—C and C=O as shown in Figure 6. In this figure we show (a) the T_1 fragmentation reaction profile (solid line) computed using the IRC method,[18] (b) the energy of S_0 along this same T_1 fragmentation reaction profile (dashed line), and (c) the S_0 fragmentation profile (other solid line) computed using the IRC method. The plots of (a)/(b) are illustrated as a *fault* in Figure 6 so that the way in which the S_0 surface slices the T_1 surface can be seen. As suggested by Turro,[6c] one presumes that there is no spin–orbit coupling in this region because the orbitals become delocalized as fragmentation takes place.

The energetic data and the S_0/T_1 surface crossings can be seen to be in good general agreement with the available experimental data. Thus one is now left with a new proposal for the mechanism which involves the following steps: (1) ground-state (S_0) ring opening (a → TS-b → c) to produce a biradical that occurs almost without activation energy; (2) passage through a S_0–T_1 *avoided* crossing in the region (via O–O change, Figure 5) just before the biradical minimum (controlled by strong spin-orbit coupling[6c] (Figure 4)); (3) passage through a second *real* T_1–S_0 crossing immediately after the biradical minimum (Figure 6); (4) passage over a transition state (TS-d* on the T_1 surface) for C–C fragmentation (rate-determining step) to produce triplet and ground-state formaldehyde.

In previous work[3,5,6,7] it has always been assumed that the rate-determining step involved the O–O bond rupture (Scheme II: a → TS-b → c) with an activation energy of approximately 23 kcal mol^{-1}. In contrast, our results suggest that the rate of the chemiluminescent reaction is controlled by the height of the transition state for C–C fragmentation on the T_1 surface ($\Delta H^{\ddagger}$). We are thus left with the question of the experimental $\Delta S^{\ddagger}$. In a variety of solvents $\Delta S^{\ddagger}$ was found to be negative or quite small (−5 to +11 cal mol^{-1} K^{-1}).[3,5,6b] Our computed value of 5 cal mol^{-1} K^{-1} is in satisfactory agreement with this trend. Since the barrier is on the excited surface *after* the surface crossing, one must interpret the negative or small value for $\Delta S^{\ddagger}$ in terms of an *order* or *stiffness of the bonds* in the transition state. In fact, while the S_0 transition state has two equal C=O bond lengths, in the T_1 transition state one of the C=O bonds is only slightly longer than in formaldehyde itself. Because of the large C=O force constant, the value of $S^{\ddagger}$ is thus smaller than one might have expected and gives rise to the small value for $\Delta S^{\ddagger}$.

Finally, we must comment on the S_1 fragmentation. The geometry of the S_1 biradical minimum c* is virtually identical with the T_1 biradical minimum and the energy difference is less than 0.1 kcal mol^{-1}. Thus the surface crossing between S_0 and S_1 will be very similar to the one between S_0 and T_1. The transition state for S_1 fragmentation is some 3.5 kcal mol^{-1} higher than that for T_1 fragmentation and the geometrical parameters differ by most 0.05 Å in C–C. This is in general agreement with the experimental fact that the triplet is favored by a factor of 100–1000.

Rationalization of the Mechanism Using a VB Model

Our objective in this section is to provide answers to the following two questions: (a) *Why do S_0 and T_1 surfaces have the same energy in the region of the biradical minimum yet their energies are very different in the region of the oxetane minimum or in the region of the fragmentation transition state*? (b) *Why is the barrier for T_1 fragmentation higher than that for S_0 fragmentation*?

In order to answer such questions we shall analyze our MC-SCF wave functions using a VB model that has the important feature that it is completely rigorous. Using the techniques discussed in detail in ref 19 one can construct a valence bond hamiltonian that reproduces the MC-SCF energies exactly. Using this hamiltonian

---

(18) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1989**, *90*, 2154.

(19) (a) Robb, M. A.; Bernardi, F. In *New Theoretical Concepts for Understanding Organic Reactions*; Bertran, J., Csizmadia, I. G., Eds.; Kluwer Academic Publishers: Lancaster, UK, 1989; pp 101–146. (b) Bernardi, F.; Olivucci, M.; McDouall, J. J.; Robb, M. A. *J. Chem. Phys.* **1988**, *89*, 6365–6375.

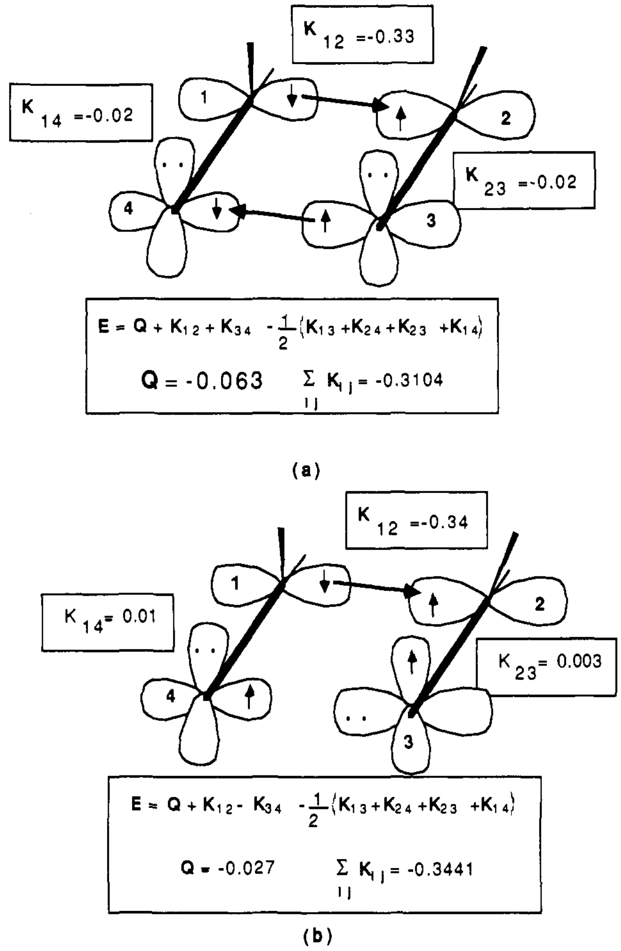


Figure 7. Coulomb ($Q = Q + [-227.0]E_h$) and exchange energies ($\sum_{ij}K_{ij}$) evaluated at the geometry of S_0/T_1 crossing. The symbol $\sum_{ij}K_{ij}$ means the total exchange energy evaluated from the formula above.

on can diabatize the potential energy surface into contributions from reactant and product-like bonding situations. One's objective is to attempt to understand the MC-SCF energetics in terms of the simple two center coulomb (Q_{ij}) and exchange (K_{ij}) parameters that are familiar from the Heitler–London treatment of H_2:

$$Q_{ij} = Q_C + [ii|jj] + \langle i|h|i\rangle + \langle j|h|j\rangle \qquad (1a)$$

$$K_{ij} = [ij|ij] + 2s_{ij}\langle i|h|j\rangle \qquad (1b)$$

Here i,j are active orbitals, $[ii|jj]$ and $[ij|ij]$ are the usual two-electron repulsion integrals (negligible until the distance between the sites of orbitals i and j becomes small), $\langle i|h|i\rangle/\langle i|h|j\rangle$ are the usual one-electron integrals (which will be dominated by the nuclear electron attraction term and are thus negative), and s_{ij} are overlaps between the nonorthogonal AO. The term Q_C contains the effect of the closed shell "core" and the effects due to nonbonded repulsions and steric effects.

We begin by explaining why the T_1 (3π) and S_0 (4π) surfaces have very similar energies in the region of the biradical minimum. Naively, one might suppose that the problem must involve only the O–O interaction since the C–C bond is fully singlet coupled. Since the O–O distance is very large the spin coupling (K_{ij}) between the unpaired electrons on the O atoms should be very small. Thus if the system contained only the 2 O-atom unpaired electrons the origin of the S_0/T_1 intersection would be obvious. However, this two-electron model is completely inadequate since it cannot explain why the T_1 fragmentation transition structure is much higher in energy than the S_0. In fact it turns out that the crossing region is controlled by a balance between the O—O lone pair repulsions and the C=O spin coupling.

The Q and K_{ij} computed (from the MC-SCF wave function[19]) at the minimum energy point of the surface of S_0/T_1 intersection are shown in Figure 7 along with the VB formula for the energy in each case. In Figure 7, the relative value of Q ($Q = Q + [-227]$) and the individual values of the K_{ij} are given beside the corresponding orbitals. The symbol $\sum_{ij}K_{ij}$ denotes the total of exchange terms. The exchange integral K_{34} between the two diradical centers is negligible in each case. One can see that there are two opposing effects that cancel at the S_0/T_1 crossing: (1) *S_0 stability due to smaller lone pair repulsions* ($Q(S_0) < Q(T_1)$ because of the greater lone pair–inner-shell repulsion in the T_1 state); and (2) *T_1 stability due to smaller nonbonded C=O exchange interactions* ($K_{23}(S_0) \ll K_{23}(T_1)$ (note $K_{23}(T_1)$ is positive) because orbitals 2 and 3 cannot overlap in the T_1 state; since K_{23} enters the energy formula with a negative sign (electrons 2 and 3 are uncoupled), the effect of K_{23} is destabilizing for S_0 and stabilizing for T_1). In the region of cyclic dioxetane, K_{34} is large and $Q(T_1)$ is strongly repulsive, so T_1 is of very high energy. As the O–O bond becomes lengthened $Q(T_1)$ decreases rapidly as K_{34} becomes small.

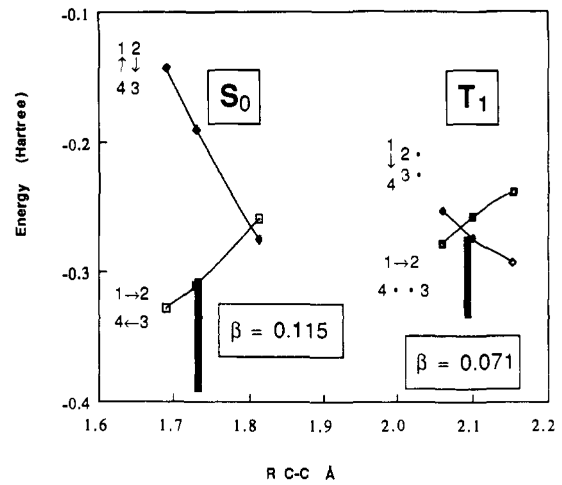


Figure 8. Diabatic energies evaluated along the S_0 and T_1 reaction paths for fragmentation.

Now let us turn to the second question which relates to the barriers to the fragmentation process in the S_0 and T_1 processes. In order to understand this process we must examine each of the S_0 and T_1 process using two diabatic wave functions,[19] a reactant diabat $|R\rangle$ corresponding to the spin coupling in the reactant and a product diabat $|P\rangle$ corresponding to the spin coupling in the product. In Figure 8 we show the diabatic curves that give rise to the transition states for S_0 and T_1 fragmentation. The X axis is r_{C-C} along the computed IRC. The vertical bar (at the geometry of the transition structure) gives the magnitude of the resonance energy β. The energy difference between the S_0 and T_1 fragmentation transition structures (TS-d and TS-d*) is 22.1 kcal mol^{-1} while the difference between S_0 and S_1 is 25.4 kcal mol^{-1}. The difference in β in Figure 8 is 27.6 kcal mol^{-1} so that the S_0 fragmentation transition structure is apparently strongly stabilized by resonance between the two diabatics. Further, we note that the diabatic crossing and the transition structure occur at larger C–C distances in the T_1 state.

The rationalization of these effects is easily accomplished. Let us consider the C–C distance first. The diabatic crossing will occur for that geometry where the exchange energy of the reactant spin coupling is approximately equal to the exchange energy for the product spin coupling (provided Q is not changing too rapidly in the region of the transition state[19]). With the orbital labels of Figure 7 this implies

$$K_{12} + K_{34} \approx K_{14} + K_{23} \qquad (2)$$

but K_{34} is almost zero since the O–O distance is large. Further K_{14} (the exchange energy of the C=O bond that becomes the π bond in ground-state formaldehyde) is the same for both singlet and triplet fragmentation. Thus the position of the diabatic crossing is determined roughly by

$$K_{12} \approx \text{constant} + K_{23} \qquad (3)$$

Remember that K_{12} is the exchange energy of the C–C bond. In the S_0 fragmentation, K_{23} is the exchange energy of the C=O bond that becomes the π bond in ground-state formaldehyde while in the T_1 fragmentation K_{23} is the exchange energy of the C=O π bond that becomes the n–π^* spin coupled pair in T_1 excited-state formaldehyde and is almost zero. Thus at any point along the reaction path $|K_{23}|$ for S_0 will always be greater than $|K_{23}|$ for T_1 (since $K_{23} \cong 0$ in T_1). Since $|K_{12}|$ is a simple function of C–C distance, the condition of eq 3 can only be met for the triplet at a smaller value of $|K_{12}|$ and thus at a larger value of R_{C-C}. This last observation also gives some insight into the origin of the larger resonance in the S_0 transition structure. The resonance energy represents the balance between bonded and uncoupled (nonbonded) exchange (see the general eqs 79–81 in ref 19a). In the region of the transition state the resonance energy is dominated by K_{12}. In fact K_{12} is an order of magnitude larger than the other K_{ij}. Since K_{ij} is a function of C–C distance, the larger resonance in the S_0 transition state is merely a result of the shorter C–C distance and larger K_{12}.

Conclusions

In this paper we have reported 4-31G MC-SCF geometry optimizations and analytical hessian (frequencies) computations for S_0, T_1, and S_1 states that are necessary in the description of the mechanism of the chemiluminescent decomposition of 1,2-dioxetane. The energetics have been confirmed by multireference MP2 computation at selected critical points. The origin of the S_0/T_1 surface degeneracy in the region of the biradical minimum and the different barrier heights in S_0/T_1 fragmentation are rationalized using a rigorous VB model.

Our results suggest a mechanism which involves (1) thermal (S_0) ring opening of dioxetane to produce a biradical almost without activation energy; (2) passage (via O–O bond breaking) though a S_0–T_1 *avoided* crossing in the region just before the biradical minimum controlled by strong spin–orbit coupling;[6a] (3) passage (in T_1 via C–C stretching) through a second *real* T_1–S_0 crossing immediately after the biradical minimum; (4) passage (in T_1 via C–C bond breaking) over a transition state for C–C fragmentation to produce triplet and ground-state formaldehyde. In contrast to previous suggestions,[3,5-7] the rate-determining step occurs on the T_1 surface. Our estimate of the activation energy at the MC-SCF/MP2/6-31G* level with a zero-point correction computed at the 4-31G level is 21.3 kcal mol^{-1} which is to be compared with the experimental activation energy of[3] 22.1 ± 0.3 kcal mol^{-1}. The experimental value for $\Delta S^{\ddagger}$ is small or negative. Since the rate-determining step occurs on T_1 and not on S_0, our results show that this negative or small experimental value for $\Delta S^{\ddagger}$ could be consistent with the short C=O bond length (and large force constant of the double bond) in one of the C=O bonds.

Finally the rationalization of the computed results using a rigorous VB model gives a simple explanation of the origin of the S_0/T_1 crossing and the barrier heights for fragmentation that lends additional credence to the results. The S_0/T_1 crossing is seen to arise from a competition between the fact that the lone pair closed shell repulsions are different in S_0 and T_1 and the fact that one of the destabilizing π orbital exchange integrals is zero in the triplet. The differing activation energies for S_0 and T_1 fragmentation arise from the difference in resonance energy between the two diabatic surface intersections.

The reason for the broad acceptance of the biradical mechanisms[7] (where the O–O bond rupture was the rate-determining step) was the realization that the activation energy (21 kcal mol^{-1}) could be understood in terms of the bond strength of the peroxy bond (~36 kcal mol^{-1}) and the strain energy of a 4-membered ring. The results presented in this work indicate that the rationalization of the O–O bond rupture and the subsequent C–C bond rupture cannot be made using simple two-center/two-orbital models. For example, the barrier in the passage from a to c via TS-b results from avoided crossing of the electronic configuration in Figure 7a and the electronic configuration in Figure 7b (but with singlet spin coupling) which becomes S_1 at c. Thus energetics must be rationalized in terms of different closed shell/lone pair repulsions and different destabilizing C–O π orbital exchange integrals in addition to the C–O bond exchange.

Finally, we should note that the nature and magnitude of the spin–orbit coupling has only been discussed qualitatively in this work. A more detailed study of the mechanism of this reaction must address the nature of the spin coupling quantitatively.

Acknowledgment. The support of the SERC (UK) under Grant No. GR/F 48029 and GR/F 46452 is gratefully acknowledged. Mar Reguero is pleased to acknowledge support from a NATO postdoctoral fellowship.

Registry No. Dioxetane, 6788-84-7; formaldehyde, 50-00-0.

Alcohol Size as a Factor in the Ternary Complexes Formed with Pyrene and β-Cyclodextrin

A. Muñoz de la Peña,[†] **T. T. Ndou, J. B. Zung, K. L. Greene, D. H. Live, and I. M. Warner***

Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322.

Received August 2, 1990. Revised Manuscript Received October 29, 1990

Abstract: The effect of alcohols on the β-cyclodextrin (CD)/pyrene complex has been examined by using steady-state fluorescence measurements. A 1:1 stoichiometric ratio has been found between the alcohol and β-CD. As the stoichiometry of the binary β-CD/pyrene complex is 2:1, a ternary complex of stoichiometry of 2:1:2 β-CD/pyrene/alcohol is proposed. Apparent formation constants in the presence of different alcohols have been determined by using the variation of the I/III vibronic band ratio of pyrene with increasing cyclodextrin concentration. The 2:1 β-CD/pyrene stoichiometry for the binary complex has also been confirmed. The present study demonstrates that proper size matching among the pyrene, the cyclodextrin, and the alcohol leads to substantially larger equilibrium constants for the ternary complexes.

Introduction

Hydrophobic interaction of cyclodextrins (CDs) in aqueous solution is one of the primary forces involved in the formation of inclusion complexes between these cyclic oligosaccharides and different guest molecules. The size of the guest relative to that of the CD cavity is also a critical parameter.

Upon inclusion of a fluorophore, CDs offer a more protective microenvironment and generally enhance the luminescence of the guest molecule by shielding the excited species from quenching and nonradiative decay processes that occur in bulk solution. In

---

* Author to whom correspondence should be addressed.

[†] On leave from the Department of Analytical Chemistry, University of Extremadura, Badajoz 06071, Spain.