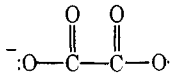
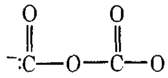
pears to be the reverse of reaction 7, the forms of $C_2O_4^{-}\cdot$ may be very different. Thus the species resulting from the oxidation of oxalate would have structure I, while that formed by the reaction of CO_2 and $CO_2^{-}\cdot$ could have structure II, thus accounting for the formation of CO and CO_3^{2-} as other reduction products.[26] Thus, conversion of I to II might require dissociation, rearrangement, and recombination, with $CO_2^{-}\cdot$ having a sufficiently long lifetime as an intermediate to transfer an electron to an acceptor.



$^{-}{:}O{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}O\cdot$

I



$^{-}{:}\overset{\overset{O}{\|}}{C}{-}O{-}\overset{\overset{O}{\|}}{C}{-}O\cdot$

II

The ecl which results on *oxidation* of oxalate and a suitable additive resembles the ecl which is produced by the *reduction* of a substance undergoing a dissociative decomposition [e.g., 9,10-dichloro-9,10-dihydro-9,10-diphenylanthracene ($DPACl_2$) and benzoyl peroxide] and a reducible additive.[12,27,28] For this latter case the production of a strong oxidant upon reduction was invoked as a necessary step to emission. The formation of a strong reductant ($CO_2^{-}\cdot$) upon oxidation, as proposed here, is an interesting parallel. The ecl intensity-time behavior found in this study resembles that observed during reduction of $DPACl_2$[12] and can be justified by the mechanism presented, i.e., a relatively slow rise time necessitated by the diffusion of $D^{+}\cdot$ away from the electrode and a buildup of sufficient concentrations of the needed intermediates and a decay to a steady state because of continual diffusion of oxalate toward the electrode and regeneration of D via reaction 6. Finally these results point to the usefulness and sensitivity of ecl in detecting short-lived electrogenerated reaction intermediates. Thus intermediates in the oxidation of oxalate and reduction of $DPACl_2$ give rise to easily observed emission, although they could not be detected by the sensitive RRDE method.

Acknowledgment. The support of this research by the U.S. Army Research Office, Durham, is gratefully acknowledged.

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Dioxetane Chemiluminescence. The Effect of Deuterium Substitution on the Thermal Decomposition of *trans*-3,4-Diphenyl-1,2-dioxetane

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Received January 21, 1977

Abstract: *trans*-Diphenyl-1,2-dioxetane was prepared by cyclization of the corresponding β-bromohydroperoxide. Thermal decomposition of this compound proceeds with an activation energy of 23.6 ± 1.6 kcal/mol to yield benzaldehyde, 10 ± 2% of which was in an excited triplet state. The effects of replacement of a dioxetane ring proton with a deuterium were investigated. No detectable partitioning between electronically excited protio- and deuteriobenzaldehyde was detected. The secondary deuterium isotope effect on the rate of thermal decomposition of this dioxetane was found to be 1.01 ± 0.02. We suggest that the absence of an isotope effect is consistent with a stepwise decomposition for 1,2-dioxetanes.

The discovery that 1,2-dioxetanes are isolable molecules that thermally decompose to produce high yields of electronically excited carbonyl compounds ushered in a new era of research into chemiluminescent processes.[1,2] Since the initial observations, investigators have probed the structural dependency of this remarkable reaction in an attempt to elucidate, in intimate detail, the conversion of ground state starting material to electronically excited states of the products.

Two fundamental mechanistic schemes have emerged for dioxetane decomposition. The first, originally considered by McCapra[3] and Kearns,[4] postulates simultaneous cleavage of both the oxygen to oxygen and the carbon to carbon bonds of the dioxetane in a concerted manner to directly generate electronically excited products. Later, Turro[5] expanded this picture by suggesting that a spin multiplicity change occurred coincidentally with bond cleavage thereby rationalizing the observation that carbonyl triplet states predominate from dioxetane reactions. MINDO/3 calculations have supported this sequence.[6] The second general mechanistic scheme was advanced by Richardson.[7] This approach favors a stepwise reaction passing through the intermediate 1,4-biradical formed by cleavage of the oxygen to oxygen bond of the strained four-membered ring peroxide. The intermediate thus formed is then postulated to partition between excited state carbonyl products of both singlet and triplet multiplicity and ground state carbonyl products.

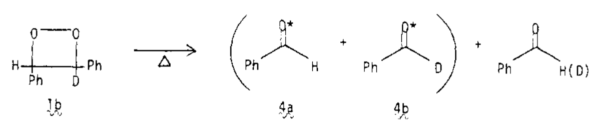
The concerted mechanism enjoys widespread appeal because it nicely rationalizes the formation of electronically excited products. Simple orbital symmetry correlation arguments predict that the geometrically permissible suprafacial retrocycloaddition mode would result in a crossing of ground state and lower excited state potential energy curves during the reaction.[4,8] However, experimental evidence is beginning to accumulate that favors the biradical mechanism.

Of the fundamental approaches available to probe the order of bond forming or breaking steps in a nonpolar cycloaddition process, substituent effects, identification of intermediate, and effects of isotopic substitution are applicable to dioxetanes. Two types of substituent effects have been employed to probe the dioxetane decomposition mechanism. In a well-planned series of experiments, Richardson[7] has examined the electronic effect of phenyl substituents on the stability of 1,2-dioxetanes. These results are interpreted as being consistent with a stepwise decomposition. The effect of the steric bulk of substituents was probed with the remarkably stable adamantylideneadamantanedioxetane.[9] These results may also be interpreted in terms of a biradical mechanism. In a recent report, differential quenching experiments have also been explained in terms of a biradical intermediate on the path to electronically excited states from dioxetanes.[10]

A key step, common to both the concerted and stepwise fragmentation of dioxetanes, is the conversion of an energetic transition state to an electronically excited state species. This fundamentally important step has been analyzed by Dougherty and others[11] in terms of the separability of nuclear and electronic motions (the Born-Oppenheimer approximation). In this analysis, a breakdown of the Born-Oppenheimer approximation is postulated to occur when the energy separating two electronic states becomes very small. One consequence of this breakdown is that the two nearly isoenergetic states are mixed together by vibrational motions of the nuclear skeleton. Of course, this mixing of states is just what is required to convert a transition state for dioxetane cleavage to an excited state of the carbonyl compound product.

If the vibrations of the nuclear framework are in fact important to excited state formation, it should be demonstrable with substituent effects. Experimental evidence of these special substituent effects was available at the outset of this work. A comparison of the chemiluminescent reaction of tetramethyldioxetane (**2**) with di-*n*-butyldimethyldioxetane (**3**) revealed some startling differences. First, the ratio of triplet to singlet excited states from **2** was reported to be ca. 50:1 while the multiplicity ratio from **3** was reported to be 1:3.[12] Subsequent to our initiation of this work, a report appeared revising the multiplicity ratio for dioxetane **3** so that it was consistent with tetramethyldioxetane **2**.[13] Second, the total yield of excited states from **2** is thought to be ca. 30%[14] while the yield of excited states from **3** is claimed to be ca. 3%. Such a dramatic difference between dioxetanes **2** and **3**, we felt, was too large to explain with the electronic and steric differences normally resulting from replacement of a methyl group with an aliphatic alkyl group. Therefore, this difference might be a manifestation of the predicted nuclear vibrational coupling effect. Our work (vide infra) has confirmed the value for the yield of excited states from **2**.

One aspect of the results reported herein concerns the investigation of the deuterium isotope effect on the rate of decomposition of *trans*-3,4-diphenyl-1,2-dioxetane (**1a**). The results of this investigation provide further convincing evidence for the biradical mechanism for retrocycloaddition of 1,2-dioxetanes. A second aspect concerns a test of Born-Oppenheimer breakdown prediction. Thermolysis of deuterated dioxetane **1b** was anticipated to form excited benzaldehydes (**4a,b**) with and without a deuterium (eq 1). Different efficiencies for formation of protio- and deuteriobenzaldehydes could then be taken as evidence that nuclear vibrations were important in controlling excited state production. Isotopic substitution is expected to vary the nuclear vibrations in a well-defined manner.

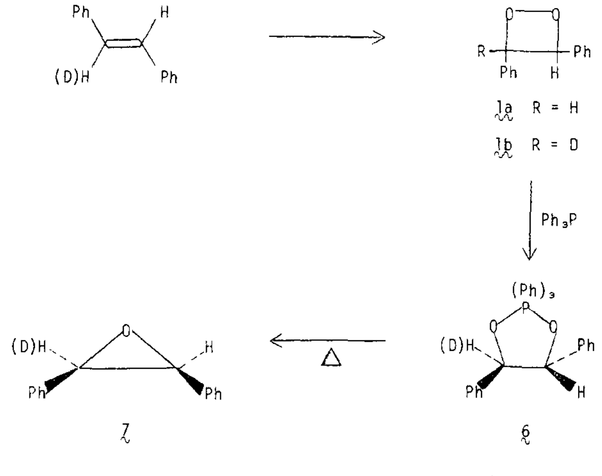


(1)

Results

Preparation and Analysis of Deuterated Dioxetane 1. The preparation of *trans*-3,4-diphenyldioxetane (**1a**) and *trans*-3,4-diphenyldioxetane-*3*-d_1 (**1b**) was accomplished by modification and application of known synthetic procedures. Reduction of deoxybenzoin with $LiAlD_4$ followed by acid-catalyzed dehydration of the alcohol resulted in *trans*-stilbene-d_1. NMR and mass spectral analysis indicated that the stilbene was of at least 98% isotopic purity. Formation of the β-bromohydroperoxide **5** was accomplished by the usual procedure of reaction of the olefin with dimethyldibromohydantoin and hydrogen peroxide.[15] Ring closure of **5** to dioxetane **1** was accomplished in ca. 70% yield by employing a two-phase base-promoted technique. This sequence of reactions is outlined in Scheme I and detailed in the Experimental Section.

Scheme I



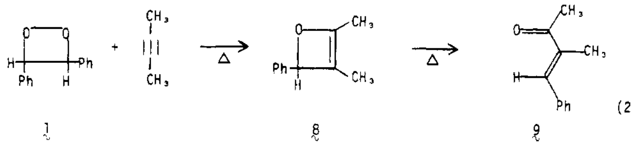
Dioxetane **1** was probed as to both its stereochemistry and the deuterium incorporation in **1b**. NMR analysis of CCl_4 solutions of dioxetane **1b** indicated that it was at least 98% monodeuterated. Reaction of **1b** with triphenylphosphine resulted in the isolation of the relatively stable phosphorane **6**.[16] NMR analysis of **6** indicated a deuterium incorporation of at least 98%. Thermolysis of **6** resulted in the predominant formation of *cis*-stilbene oxide[17] (**7**). This observation establishes that the phenyl groups of dioxetane **1** have a trans orientation. NMR spectral analysis of **7** confirmed the deuterium incorporation. This sequence of reactions is outlined in Scheme I.

Chemiluminescent Properties of Dioxetane 1. A thorough investigation of the properties of dioxetane **1** establishes that this dioxetane is typical of most that have been prepared and investigated.[18] Therefore only the results that are relevant to our isotopic analysis are reported here.

The activation energy (E_A) for the thermal decomposition of **1** in CCl_4 was determined by two different techniques. First, the total rate of disappearance of dioxetane **1** was determined at several temperatures by monitoring the chemiluminescent decay. Standard Arrhenius analysis of the derived rate constants (see Experimental Section) yielded an E_A of 23.6 ± 1.6 kcal/mol and a preexponential factor of $10^{12.9}$. Second, we employed the previously described step analysis[19] to obtain E_A specifically of the reaction producing electronically excited states. Correction for the temperature dependence of the luminescence efficiency of the 9,10-dibromoanthracene used in this analysis[20] gave an E_A of 22.3 ± 1.9 kcal/mol. An important implication of the identical E_A value from both methods of analysis is that both the path leading to excited state formation and the path leading to only ground-state products have the same rate-determining step.

The multiplicity of the excited state of benzaldehyde formed from thermolysis of **1** was assigned by both spectral comparison and lifetime determination. The observed chemiluminescent emission spectrum from **1** is shown in Figure 1. It is identical with the phosphorescence spectrum of photoexcited benzaldehyde. Furthermore, the emission could be quenched with low concentrations of acrylonitrile. All of the bands in the spectrum were quenched at the same rate indicating that there was no residual fluorescence. The lifetime of benzaldehyde excited state was determined using standard Stern-Volmer quenching techniques[21] to be ca. 0.1 μs at 29.5 °C in CCl_4 solution. This lifetime is inconsistent with the excited singlet state of benzaldehyde and establishes that the triplet state is responsible for the chemiluminescence.[22]

The important issue of the yield of benzaldehyde excited states from the decomposition of **1** was resolved by two independent techniques. First, the triplet benzaldehyde formed during the thermal reaction was chemically trapped with 2-butyne. The photochemical reaction of benzaldehyde and 2-butyne has been previously reported to proceed through the oxetene (**8**) formed via a [2 + 2] cycloaddition.[23] Thermal rearrangement of the oxetene at room temperature generated the (*E*)-enone (**9**) exclusively[24] (eq 2). This trapping reaction



(2)

is specific for benzaldehyde triplet; no other species would be capable of forming enone **9**. This observation eliminates considerable ambiguity present in other systems. The quantum yield of photochemical enone formation was determined to be 0.60 ± 0.05 under conditions where every benzaldehyde triplet was quenched by 2-butyne. The type II reaction of valerophenone in hexane/*tert*-butyl alcohol was used as the actinometer.[25] Quantitative trapping of the benzaldehyde excited states generated from decomposition of **1**, under conditions *identical* with the photochemical quantum yield experiment, indicated that the yield of benzaldehyde triplet from **1** was 10 ± 2%.

The second technique used for estimation of the yield of excited states from **1** was the comparison of luminescent intensity of **1** and tetramethyldioxetane (**2**). The yield of electronically excited acetone from **2** has previously been reported to be ca. 30%.[14] We compared dioxetanes **1** and **2** under conditions where energy transfer from the chemically formed carbonyl excited states to DBA is expected to occur. The sensitized DBA emission was electronically integrated for more than 5 half-lives for both dioxetanes. The integrated total luminescent intensity as a function of DBA concentration was determined and extrapolated to infinite DBA concentration for both dioxetanes. The total light emission from **2** was 3.0 ± 0.5 times the emission from **1** at infinite DBA concentration in both CCl_4 and benzene, consistent with our determination of the yield of **1** and the previous measurement for **2**.

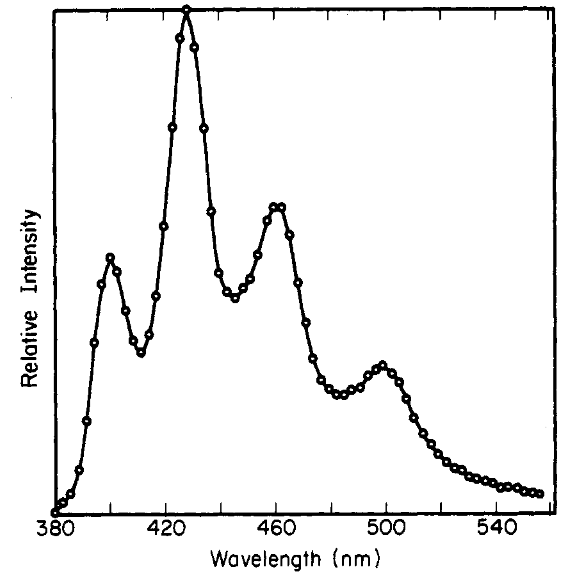
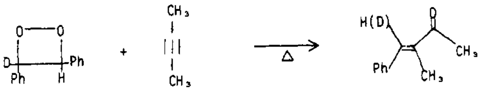


Figure 1. Chemiluminescence emission spectrum from thermal decomposition of dioxetane **1a**.

Effect of Isotopic Substitution on Dioxetane 1. As noted above, two distinct phenomena can be probed by the introduction of a deuterium into dioxetane **1**. We have investigated the effect of isotopic substitution on the rate of thermal decomposition of dioxetane **1** and have probed the influence of the deuterium in directing excited state formation.

The thermal decomposition of dilute solutions of **1a** and **1b** is strictly first order for more than 6 half-lives. Since the chemiluminescent intensity was found to be directly proportional to the dioxetane concentration, and the chemiluminescence could be continuously monitored, very precise first-order rate constants for reaction of **1a** and **1b** could be obtained. The results of this study are summarized in Table I. These data indicate that, within experimental error, the rate constants for unimolecular decomposition of dioxetanes **1a** and **1b** are identical. That is, the secondary deuterium isotope effect for unimolecular reaction of these dioxetanes (k_H/k_D) is 1.01 ± 0.02. Furthermore, comparison of the total integrated luminescent intensity from **1a** and **1b** revealed no isotopic dependency.

Investigation of isotopic selection of the location for the excitation energy was probed with a trapping reaction. Each deuterated dioxetane **1b** that fragments can form at most one electronically excited benzaldehyde. The excited benzaldehydes produced were quantitatively trapped with 2-butyne (vide supra). Any predilection toward protio or deuterio excited benzaldehyde formation would be reflected in the deuterium incorporation in the isolated enone **9** (eq 3).



(3)

It was shown that under the conditions of the experiment, the trapping reaction was equally efficient for both deuterated and undeuterated benzaldehyde. Mass spectral and NMR analysis of the enone formed from reaction of deuteriodioxe-

Table I. Determination of Secondary Deuterium Isotope Effect for Dioxetane **1**

	$k_H \times 10^4$, s^{-1}	$k_D \times 10^4$, s^{-1}	k_H/k_D	$\phi H/\phi D$[a]
Run 1, BA[b]	5.25 ± 0.01[c]	5.13 ± 0.01	1.023	0.93
Run 2, BA	5.80 ± 0.04	5.45 ± 0.02	1.063	0.94
Run 3, BA	4.60 ± 0.01	4.69 ± 0.01	0.981	1.01
Run 4, BA	5.42 ± 0.02	5.32 ± 0.01	1.019	
Run 5, BA	5.22 ± 0.01	5.39 ± 0.03	0.968	
Run 6[d]	4.14 ± 0.02	4.07 ± 0.01	1.016	1.00
			Mean 1.01 ± 0.02	0.97 ± 0.03

[a] Ratio of total light emission from **1a** and **1b**. [b] BA = biacetyl. Typical conditions: [**1**] = 5×10^{-7} M; [BA] = 5×10^{-3} M; in CCl_4; solutions were purged with N_2 for 3 min at 0 °C; temperature ca. 40 °C, variation between runs ca. 1.5 °C, within a run less than 0.1 °C. [c] All errors are standard deviations. [d] Determined by monitoring benzaldehyde phosphorescence. [**1**] = 2×10^{-4} M in CCl_4; aerated; temperature 40.0 ± 0.1 °C.

tane **1b** revealed a deuterium incorporation of 48%. Correction for the deuterium content of **1b** revealed that there was no preferential formation of either isotopic benzaldehyde. Thus, there was no isotopic influence on the selection of the location for the excitation energy at the transition state for excited state formation.

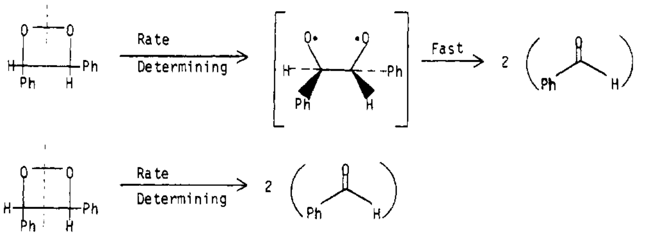
Discussion

The study of the chemistry of dioxetane **1** and the effect of deuterium substitution on it has revealed several important features about dioxetane chemiluminescence. First, the observed absence of a measurable secondary deuterium isotope effect on the rate of formation of benzaldehyde from **1** places some important constraints on the nature of the rate-determining step for this reaction.

Secondary deuterium isotope effects have been analyzed by Streitwieser and co-workers by statistical mechanics.[26] They conclude that the major influence of the isotopic substitution on the rate of reaction is through a change in an "out-of-plane" C-H bending vibration. They observed that this vibrational mode was very sensitive to the hybridization of the isotopically substituted carbon. This model predicts that a change from sp^3 to sp^2 hybridization of the isotopically substituted carbon should give rise to a secondary deuterium isotope effect of ca. 1.38. Experimental verification of this prediction has been forthcoming. Investigation of the deuterium isotope effects in solvolytic substitution at saturated carbons has routinely revealed isotope effects of about 12% per deuterium atom.[27] A study of the secondary deuterium isotope effects on the radical polymerization of styrene indicated that the magnitude of the effect was the same in nonpolar reactions as for the polar solvolyses.[28] Perhaps of more relevance to the current investigation are reports of the effect of deuterium substitution on the rate of [2 + 2] cycloaddition reactions. Baldwin[29] studied the effect of deuterium substitution on the rate of the cycloaddition reaction of diphenylketene with styrene. A secondary deuterium isotope effect (k_H/k_D) of 0.91 was observed when the styrene was substituted with a deuterium at the β position. This observation was interpreted to imply that the β carbon of styrene progressed from sp^2 toward sp^3 hybridization as the transition state for this reaction was approached. Similar effects of isotopic substitution were observed by Dolbier[30] during an investigation of allene [2 + 2] cycloaddition reactions.

Consider the two mechanisms advanced for the thermal fragmentation of dioxetanes to carbonyl compounds (Scheme II). For the concerted mechanism, the isotopically substituted carbon of dioxetane **1b** undergoes a change in hybridization from sp^3 toward sp^2 as the reaction approaches the transition state. Theory predicts, and experiments confirm, that this change in hybridization should lead to an observable normal secondary deuterium isotope effect. On the other hand, for the stepwise mechanism in which cleavage of the oxygen-oxygen bond of the dioxetane is the rate-determining step, no change in hybridization at the isotopically substituted carbon is anticipated. Thus, this sequence for bond breaking is not expected to give rise to an observable α secondary deuterium isotope effect. Our results are consistent only with the stepwise mechanism for fragmentation of 1,2-dioxetanes.

Scheme II



The lifetime of carbonyl triplet excited states in rigid media at low temperature has been found to be dependent upon isotopic substitution.[31] The lifetime of benzaldehyde triplet in EPA at 77 K was found to depend upon isotopic substitution at the aldehyde carbon.[32] Furthermore, spectroscopic investigation of benzaldehyde has revealed that the aldehydic hydrogen plays an important, if not dominant, role in the radiationless deactivation of the electronically excited triplet state.[33] The effect of deuterium substitution on the lifetime of triplet excited states has been attributed to the difference in the Franck-Condon overlap factors for the hydrogen and deuterium substituted compounds.[34] That is, at constant vibrational excitation energy, the deuterium substituted compound would be at a considerably higher vibrational quantum number than the hydrogen substituted compound. The vibrational quantum number is postulated to influence the overlap between the wave functions describing the ground and electronically excited state of the chromophore[35] and hence the rates of interconversion between these states. A chemiluminescent reaction is a conversion between electronic states. Furthermore, the model for this conversion proposed by Dougherty (vide supra) takes specific account of vibrations of the nuclear skeleton. Monodeuterated dioxetane **1b** provides an ideal system for examining these ideas.

According to the model described above, the formation of electronically excited states during dioxetane decomposition can be thought of as a radiationless transition from the postulated biradical intermediate to the excited carbonyl group. As such we anticipated that **1b** might decompose to yield unequal portions of protio- and deuteriobenzaldehyde. In fact, no such selection for the excited state location was observed. This result may be due to the expected small energy gap and strong coupling between the biradical intermediate and the excited state. For such a circumstance theory predicts that the controlling nuclear vibration may be low-frequency skeletal modes.[34] Thus, the lack of an observed isotopic dependency does not rule out vibrational coupling as the perturbation that results in excited state formation.

Conclusions

The mechanism of thermal decomposition of 1,2-dioxetanes to form electronically excited carbonyl compounds is central to an understanding of chemiluminescent phenomena. If indeed a prerequisite to efficient chemical formation of excited states is a concerted "forbidden" pericyclic process, then the number of potential chemiluminescent systems is clearly limited. Our work, and the work of others,[7,9,10,13,14] strongly suggests that an intermediate chemical species precedes formation of the triplet excited carbonyl compounds characteristic of dioxetane thermolysis. In particular, the absence of a measurable secondary deuterium isotope effect reported herein convincingly demonstrates that the hybridization at carbon is not changing during the rate-determining step of this reaction. This result is clearly consistent only with a stepwise reaction. The implication of this to the chemical formation of electronically excited states in general is apparent. The search for new efficient chemiluminescent processes should not be limited to reactions predicted to be "forbidden" by conservation of orbital symmetry considerations.

Experimental Section

General. All melting points were corrected according to the melting point (80.1 °C) of sublimed naphthalene. NMR spectra were recorded on a Varian Associates A-60A instrument with tetramethylsilane internal standard. IR spectra were obtained with a Beckman IR-12 spectrometer. Mass spectra were recorded using a Varian MAT CH-5 mass spectrometer. Elemental analyses were performed by the Analyses Laboratory, Department of Chemistry, University of Illinois, Urbana, Ill.

2-Bromo-1,2-diphenylethyl Hydroperoxide. A solution of *trans*-stilbene (2.70 g, 0.015 mol) in 40 mL of dry THF was poured into a solution of 90% H_2O_2 (28 g, 0.72 mol) in 140 mL of THF which had been dried with anhydrous Na_2SO_4 overnight at −20 °C. 1,3-Dibromo-5,5-dimethylhydantoin (2.5 g, 0.0090 mol, Matheson Coleman and Bell) was added in several portions to the stilbene solution over a period of 1 h, at room temperature under nitrogen. The resulting yellow solution was stirred for an additional 1 h at room temperature under nitrogen. The yellow solution was poured into 500 mL of a cold, saturated aqueous solution of Na_2CO_3. The resulting mixture was extracted with diethyl ether (3 × 100 mL). The combined extracts were washed with water and brine, and then dried over anhydrous Na_2SO_4 at 0 °C. The volume of the solution was reduced to about 50 mL and any precipitate formed was removed. The hydroperoxide was purified as its Dabco salt using the procedure of Kopecky[15] to give 2.53 g of white solid (57% yield), the NMR spectrum of which indicated the presence of about 95% pure β-bromohydroperoxide. An analytically pure sample was obtained by recrystallization in CH_2Cl_2: mp 116–118 °C; NMR ($CDCl_3$) δ 5.22 (d, J = 7 Hz, 1 H), 5.38 (d, J = 7 Hz, 1 H), 7.22–7.43 (m, 5 H), and 7.90 (broad s, 1 H); IR (KBr) 3498, 1497, 1455, 1343, 1202, 760, and 700 cm^{-1}.

Anal. Calcd for $C_{14}H_{13}O_2Br$: C, 57.36; H, 4.47. Found: C, 57.39; H, 4.40.

Diphenyldioxetane (1a). To a suspension of 2-bromo-1,2-diphenylethyl hydroperoxide (252 mg, 0.861 mmol) in 40 mL of CCl_4 at 0 °C was added, with vigorous stirring, an aqueous solution (20 mL) of KOH (600 mg, 11 mmol). The resulting mixture was stirred vigorously for 1.5 h at 0 °C in the dark. The CCl_4 layer was separated and dried over anhydrous K_2CO_3 at 0 °C for 20 min. The light yellow solution was transferred to a 50-mL volumetric flask. The concentration of the dioxetane in this solution was determined by NMR spectroscopy and iodometric titration to be 1.25 ± 0.05 × 10^{-2} M (73% yield). The only other compound in the solution was benzaldehyde with an approximate ratio of 7:1, dioxetane to benzaldehyde: NMR (CCl_4) δ 6.37 (s, 2 H) and 7.36–7.83 (m, 10 H).

1-Deuterio-1,2-diphenylethanol. A solution of deoxybenzoin (3.92 g, 0.020 mol, Aldrich) in 40 mL of dry THF was added dropwise to a suspension of $LiAlD_4$ (0.42 g, 0.010 mol, deuterium analysis 18.7%, from Alfa) in 120 mL of dry THF at room temperature with stirring under nitrogen. After the completion of the addition, the temperature of the reaction mixture was raised to 50 °C for 4 h. The usual workup gave crude product weighing 3.5 g (90% yield). The NMR spectrum showed only the presence of 1-deuterio-1,2-diphenylethanol. The crude product was used without further purification for the synthesis of α-deuteriostilbene. Further purification was achieved by recrystallization in *n*-hexane: mp 64–65 °C (lit. 64.4–65.4 °C);[36] NMR ($CDCl_3$) δ 2.16 (s, 1 H) (OH), 2.93 (s, 2 H) (CH_2), and 7.00–7.43 (m, 10 H).

***trans*-α-Deuteriostilbene.** 1-Deuterio-1,2-diphenylethanol (3.5 g, 0.018 mol) was dissolved in 45 mL of ethanol, 25 mL of concentrated HCl, and 0.5 mL of concentrated H_2SO_4. The mixture was refluxed for 4 h and the white flake precipitate that formed (2.64 g, 83% yield) was collected. The NMR spectrum of the white solid indicated that it was pure *trans*-α-deuteriostilbene, mp 123–124 °C (lit. 124 °C).[37] No depression upon mixture with an authentic sample of undeuterated *trans*-stilbene was observed. Deuterium content was determined by mass spectrometry (98 ± 1%) and by NMR assay (98 ± 2%).

Deuteriodiphenyldioxetane (1b). A mixture of 2-bromo-1-deuterio-1,2-diphenylethyl and 2-bromo-2-deuterio-1,2-diphenylethyl hydroperoxide was obtained in 51% yield from the reaction of *trans*-α-deuteriostilbene with 1,3-dibromo-5,5-dimethylhydantoin in dry THF in the presence of excess H_2O_2 following the same procedure as employed in preparing undeuterated 2-bromo-1,2-diphenylethyl hydroperoxide: NMR ($CDCl_3$) δ 5.23 (s, 1 H), 5.36 (s, 1 H), 7.20–7.47 (m, 10 H), and 8.0 (broad s, 1 H).

The deuteriodiphenyldioxetane was obtained in ca. 70% yield using the same procedure employed in the synthesis of the undeuterated dioxetane: NMR (CCl_4) δ 6.34 (s, 1 H) and 7.41–7.80 (m, 10 H). The NMR spectrum of deuteriodiphenyldioxetane showed 98 ± 2% deuterium content.

4-Deuterio-4,5-diphenyl-2,2,2-triphenyl-1,3,2-dioxaphospholane (6). A solution of triphenylphosphine (165 mg, 0.63 mmol) in 5 mL of CCl_4 was rapidly added to 30 mL of 2.1 × 10^{-2} M deuteriodiphenyldioxetane (0.63 mmol) in CCl_4 cooled in an ice bath. After 20 min the solvent was evaporated and the resulting residue was extracted with 2 mL of cold *n*-hexane, leaving a white solid (280 mg, 93% yield). An analytically pure sample was obtained from recrystallization in ether and *n*-hexane (1:3). NMR analysis of the recrystallized phosphorane indicated the presence of the phosphorane and diethyl ether in a ratio of 2:1. The ether could not be removed under high vacuum (0.2 mmHg): mp 85–96 °C; NMR (CCl_4) δ 4.44 (broad s, 1 H) and 6.90–7.95 (m, 25 H); deuterium content was 98 ± 2% by NMR assay; IR (KBr) 3070 (w), 1436 (m), 1100–1085 (m), 1044 (m), 1022 (m), 810–796 (m), 754 (m), 720 (m), 700 (s), 600 (m), and 557 cm^{-1} (s).

Anal. Calcd for $C_{32}H_{26}DO_2P \cdot 0.5C_4H_{10}O$: C, 79.82; H, 6.31; P, 6.05. Found: C, 79.79; H, 6.25; P, 5.94.

Undeuterated phosphorane was similarly prepared from the reaction of diphenyldioxetane with triphenylphosphine: NMR ($CDCl_3$) δ 4.56 (d, J = 1 Hz, 2 H) and 7.0–8.0 (m, 25 H).

Pyrolysis of 4,5-Diphenyl-2,2,2-triphenyl-1,3,2-dioxaphospholane. A solution of the phosphorane (161 mg, 0.34 mmol) in 10 mL of CCl_4 was refluxed for 7 h under nitrogen. Removal of the solvent and extraction of the residue with 10 mL of *n*-hexane precipitated triphenylphosphine oxide, 90 mg (95% yield), mp 154.5–156 °C (lit. 155–156 °C).[16] The filtrate was concentrated to give an oily residue (60 mg, 90% yield), the NMR spectrum of which indicated the presence of *cis*-stilbene oxide, *trans*-stilbene oxide, and deoxybenzoin in a ratio of 74:14:12.

A solution of the deuterated phosphorane (280 mg, 0.59 mmol) was refluxed in a mixture of benzene (7 mL) and dioxane (7 mL) for 7 h under nitrogen. Following the above procedure gave *cis*-α-deuteriostilbene oxide, *trans*-α-deuteriostilbene oxide, and α-deuteriodeoxybenzoin in a ratio of 72:20:9. Deuterium content of the isomers was determined to be at least 98% from NMR assay using mesitylene as internal standard.

Trap of Excited Benzaldehyde and Benzaldehyde-d_1 with 2-Butyne. A solution of deuteriodiphenyldioxetane (30 mL of 0.032 M in CH_2Cl_2, 0.96 mmol) and excess 2-butyne (0.8 mL, 10 mmol, Chemical Samples Co.) was reacted at room temperature for 20 h. Evaporation of the solvent gave benzaldehyde and a small amount of (*E*)-3-methyl-4-phenyl-3-buten-2-one, which was purified by gas chromatography (SE-30 8.4%, 4 ft, at 167 °C). The ratio of protio (*E*)-enone to deuterio (*E*)-enone was determined to be 52:48 by mass spectrometry. Analysis of deuterium content was done on the M − 15 fragment. Control experiments showed that the trapping efficiency for the deuterated and undeuterated benzaldehyde was the same.

Yield of Excited Benzaldehyde from Thermal Decomposition of Diphenyldioxetane. The quantum efficiency of the addition of benzaldehyde triplet to 2-butyne was determined using standard photochemical techniques. Simultaneous (merry-go-round) low conversion (ca. 1%) irradiation of optically dense degassed solutions of benzaldehyde with 2-butyne and valerophenone in hexane/*tert*-butyl alcohol with potassium chromate filtered (313 nm) light indicated a quantum efficiency for enone formation of 0.60 ± 0.05. Quantitative thermal decomposition of dioxetane **1** (0.012 M in CCl_4) with 2-butyne (0.125 M) under conditions identical with the photochemical quantum yield determination indicated the yield of triplet benzaldehyde from **1** to be 10 ± 2%.

Table II. Rate of Thermal Decomposition of Dioxetane **1a**

Temp, °C	$k \times 10^4$, s^{-1}	Temp, °C	$k \times 10^4$, s^{-1}
36.0	2.44^{a}	57.6	28.3
40.5	4.63	59.9	37.1
51.0	14.0	63.1	54.9
54.3	20.2	65.3	74.8
$E_A = 23.6 \pm 1.6$ kcal/mol			
Log $A = 12.9 \pm 0.9$			

Determination of the Activation Energy for Thermal Decomposition of 1. The rate constants for thermolysis of diphenyldioxetane **1a** were determined in CCl_4 solution over a 20 °C range (Table II). The emission intensity of sensitized DBA (1×10^{-3} M) was followed with time. The initial concentration of **1** was 1×10^{-5} M.

Acknowledgment. This work was supported by the Office of Naval Research.

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"Hydrophobic Interaction" and Solvation Energies: Discrepancies between Theory and Experimental Data

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Abstract: Prevailing descriptions of the "hydrophobic interaction" or "hydrophobic effect" are incompatible with relationships found between the structures of various nonpolar solutes and their solvation energies by water and 1-octanol. Previously reported linear relationships between partition coefficient and molecular volume actually result from compensation between relatively irregular solvation energies in water and lipid. In the partitioning of a $-CH_2-$ moiety from water into octanol, $\Delta G_{298} = -0.54$ (± 0.01) kcal/mol for favorable solvation by octanol and only $+0.18$ (± 0.01) kcal/mol for disfavorable solvation by water, whereas in the partitioning of a "CH_2-equivalent incremental molecular volume" of a rare gas, $\Delta G_{298} = -1.58$ (± 0.14) kcal/mol for favorable octanol solvation and -0.81 (± 0.03) kcal/mol for *favorable* water solvation. These two distinct linear relationships between molecular volume and solvation energy require two bulk-related modes of solute/solvent interaction. Such results appear more consistent with cavity-based models of solvation, such as the general "scaled-particle" theory. Other arguments in support of the "hydrophobic effect" are refuted.

Perhaps the most characteristic of the many physicochemical phenomena operative in a biological organism are partitioning processes, that is, the tendencies for nonpolar solutes and nonpolar portions of solutes to segregate themselves from aqueous media. For example, cell walls and internal membranes comprise highly structured lipoidal phases whose existence depends almost exclusively on partitioning. At a lower level of structural complexity, enzymes probably owe most of their affinity for substrates and their secondary structure itself to the same kinds of molecular interactions that are responsible for partitioning.[1] Consequently, it is not surprising to find that the partitioning behavior of a molecule is a major determinant of its pharmacological properties.[2]

In describing the molecular or mechanistic basis for these partitioning processes, biologically oriented chemists almost always invoke the "hydrophobic interaction", "hydrophobic effect", or "hydrophobic bond".[3] The theory of the "hydrophobic interaction" originates from the anomalously large loss of entropy which accompanies dissolution of nonpolar substances in water. From this observation, Frank, Kauzmann, Scheraga, Tanford, Ben-Naim, and others[4] have elaborated various highly ordered, entropically unfavorable arrangements