The Elusive 1,4-Dioxy Biradical: Revised Mechanism for the Formation of Diol from 3,3-Dimethyldioxetane in Cyclohexadiene

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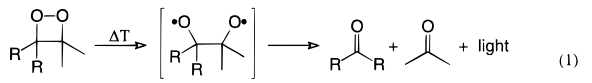
Abstract: We confirm a report that 3,3-dimethyldioxetane (**1a**) produces 2-methyl-1,2-propanediol (**5a**) when heated in 1,4-cyclohexadiene as solvent. Previously, the resulting diol was taken as evidence for a stepwise, biradical mechanism in which a 1,4-dioxy biradical is trapped by the H-atom donor solvent. To investigate this possibility in more detail, the decomposition rates and product yields were measured under various conditions. We have found that the diol is not formed by trapping of the 1,4-dioxy biradical, but rather from an initial attack by the double bond of 1,4-cyclohexadiene on the strained O−O bond of the dioxetane. Furthermore, we report that tetramethyldioxetane (**1b**) also produces 1.6 ± 1.0% of the corresponding diol, pinacol (**5b**), when heated in 1,4-cyclohexadiene. As the 1,4-dioxy biradical is not a likely intermediate in the thermal decomposition of dioxetanes, we support the previously proposed asynchronous, concerted mechanism for thermal decomposition of dioxetanes; the definitive evidence is formation of n−π^* *versus* π−π^* triplets.

Introduction

Dioxetanes are the best studied chemiluminescent molecules since authentic samples may be readily tailor-made for mechanistic investigations. In their direct thermal decomposition, enough energy (ca. 85 kcal/mol) is available to excite electronically one of the two carbonyl products that are generated (eq 1), first shown convincingly by Kopecky et al. in 1975.[1] The



(1)

1a, R = H
1b, R = CH_3

mechanism of this reaction has been extensively studied[2−4] in order to understand not only the significant yield of excited states from the reaction (typically 10−30%) but also the amazingly high ratio of triplets to singlets (often 100−1000). Yet, to this day, a controversy exists whether the 1,4-dioxy biradical is a *bona fide* intermediate or merely the transition state to the triplet-excited carbonyl product.

Traditionally, three mechanisms have been postulated for the thermal decomposition of dioxetanes. They are represented in Figure 1. The first was a synchronous, concerted mechanism (Figure 1A) put forth by both Kearns[5] and McCapra[6] when the experimental details were still sketchy. Since the O−O bond

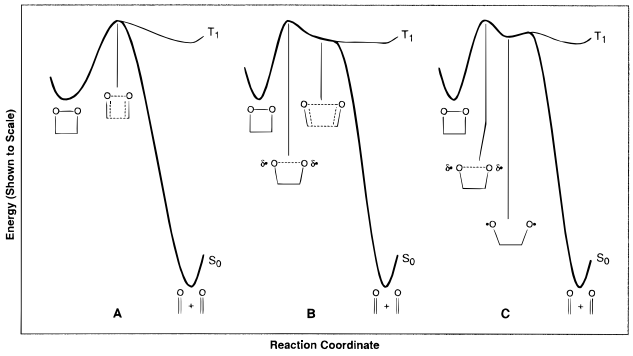


Figure 1. Postulated mechanisms for the thermal decomposition of dioxetanes: (A) synchronous, concerted mechanism, (B) asynchronous, concerted mechanism, and (C) stepwise, biradical mechanism. The singlet energy surface is not shown.

is weaker than the C−C bond, Turro and Lechtken[7] later proposed the asynchronous, concerted mechanism (Figure 1B) with an initial oxygen−oxygen bond cleavage. Adam and Baader[8] used this asynchronous, concerted mechanism (renamed the merged mechanism) to rationalize both the kinetics and the excitation yields in a series of methyl-substituted dioxetanes. Lastly, Richardson et al.[9] postulated a stepwise, biradical mechanism (Figure 1C), actually chronologically prior to the asynchronous, concerted mechanism, in which the oxygen−oxygen bond breaks completely before the carbon−carbon bond. As we will briefly review, a great deal of experimental work has been performed over the past 20 years to elucidate the mechanism of this intriguing process.

The evidence in favor of the stepwise, biradical mechanism has been most recently reviewed by Baumstark.[2] The bridged

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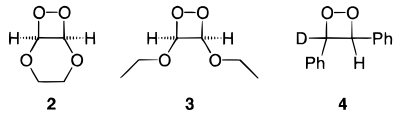
dioxetane **2** was compared with the unbridged diethoxydioxetane



2 **3** **4**

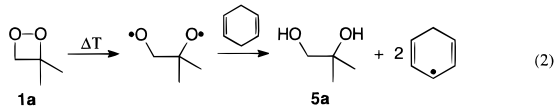
(**3**) by Wilson and co-workers.[10] If the synchronous, concerted mechanism operates, the bridged dioxetane **2** should have a smaller activation energy because the 3−4 kcal/mol strain energy in the dioxane ring is partially released in the transition state. However, the measured activation energies for **2** and **3** were the same within 0.2 kcal/mol, and this was taken as evidence for the stepwise mechanism. In another experiment by Schuster et al.,[11] an isotope effect was probed with dioxetane **4** by comparing the activation energy to the nondeuterated analog. No isotope effect was observed and this was also argued to support the stepwise mechanism. Many other structure/reactivity studies were conducted, and the general conclusion was that the stepwise mechanism most likely operates with the 1,4-dioxy biradical as a *bona fide* intermediate;[2−4] however, the concerted mechanism could not be ruled out entirely.

The above studies discount the synchronous, concerted mechanism (Figure 1A), but they are still consistent with the *asynchronous*, concerted pathway. Inspection of Figures 1B and 1C shows that for both the stepwise and asynchronous, concerted mechanisms the activation energy is determined primarily by the oxygen−oxygen bond cleavage. The crucial question is whether the carbon−carbon bond starts to break *before* or *after* the oxygen−oxygen bond scission. While this may appear to be difficult to test experimentally, evidence exists to support *both* possibilities, which we describe next.

Expanding upon theoretical work by Kearns[5] and others,[12] Turro and Devaquet[13] predicted that a concerted mechanism would favor the n−π* triplet carbonyl product over the π−π* one based on the favorable spin−orbit coupling in the former. They postulated that the ground state dioxetane surface intersects the various excited state surfaces and that the crossing probabilities, along with the energy levels, determine which path is ultimately taken. In order to cross onto the triplet-excited surface from the ground state surface, a change in electron spin must occur. This "spin flip" is 100−1000 times faster for the transition to the n−π* triplet than to the π−π* triplet because the former moves an electron from the O−O bond to an orbital *perpendicular* to the O−O bond. This change in orbital momentum couples with the electron spin momentum, and the transition becomes highly favored compared to the case in which there is little spin−orbit coupling (the π−π* transition in this case).

Most dioxetanes generate n−π* carbonyl fragments which are lower in energy than the corresponding π−π* states. Thus, any preference for n−π* could be explained by a Boltzmann-type distribution.[14] However, in aryl-substituted dioxetanes which yield a π−π* carbonyl product lower in energy than the n−π* state, the higher energy n−π* carbonyl fragment is still formed in large excess, as shown convincingly by Zimmerman et al.,[15] Richardson et al.,[16] and others.[17,18] These elegant studies provide strong evidence for the asynchronous, concerted mechanism because an intermediate biradical with appreciable lifetime would lose the memory of its orbital symmetry, and the n−π* triplet state would not be formed preferentially.

The stepwise mechanism (Figure 1C) is supported by two experiments in which the postulated biradical intermediate is either trapped or gives rearrangement products. The first such evidence for a 1,4-dioxy biradical was reported by Richardson et al.[19] in the decomposition of 3,3-dimethyldioxetane (**1a**) in 1,4-cyclohexadiene as solvent (eq 2). Up to 18% of diol **5a**



1a **5a** (2)

was observed. They proposed that a 1,4-dioxy biradical was trapped as shown in eq 2. A second study[20] also initially supported the involvement of a 1,4-dioxy biradical in the thermal decomposition of 3,3-dibenzyldioxetane in toluene. However, this claim was subsequently revised because on further investigation it was shown that the rearrangement products resulted from a complex radical-chain mechanism.[21]

Thus, a perplexing situation exists in regard to the mechanism of the thermal decomposition of dioxetanes. Namely, the high n−π* selectivity supports the asynchronous, concerted process while the diol formation from 3,3-dimethyldioxetane in 1,4-cyclohexadiene suggests a stepwise, biradical mechanism. Curiously, the thermolyses of trimethyldioxetane and tetramethyldioxetane yield no detectable trapping products in 1,4-cyclohexadiene.[19] These conflicting experiments led Richardson et al.[16] to suggest that for 3,3-dialkyl-substituted dioxetanes the decomposition is stepwise, but for higher- and aryl-substituted dioxetanes the asynchronous, concerted mechanism operates.

In light of the radical-chain mechanism for the 3,3-dibenzyldioxetane decomposition,[21] we decided to re-investigate the 3,3-dimethyldioxetane thermolysis. Since Richardson had already tested carefully for radical-induced decomposition,[19] we considered the possibility of a molecule-induced process, wherein either the solvent or an intermediary product attacks the dioxetane and promotes decomposition to afford the diol **5a**.

Results

3,3-Dimethyldioxetane (**1a**) and Tetramethyldioxetane (**1b**) were prepared from the corresponding bromo hydroperoxides according to the literature procedure.[1,22] All solvents and additives used in this study were carefully purified (see Experimental Section for details). Trace impurities in the solvents, especially 1,4-cyclohexadiene and cyclohexene, were found to have noticeable effects on the reaction products and decomposition rates. Therefore, rigorous purification of the solvents was crucial in obtaining consistent results.

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Table 1. First-Order Rate Constants for Dioxetane Decomposition

entry no.	dioxetane[a]	concn (M)	solvent/additive	$10^4 k_{dec}$ (s^{-1})[b]	relative k_{abst} (s^{-1})[c]
1	**1a**[d]	0.028	1,4-cyclohexadiene	16	230
2	**1a**	0.051	1,4-cyclohexadiene	16	
3	**1a**	0.066	1,4-cyclohexadiene	15	
4	**1a**	0.090	1,4-cyclohexadiene	24	
5	**1a**	0.029	1,4-cyclohexadiene/ 0.45 M BHT[e]	15	
6	**1a**	0.090	1,4-cyclohexadiene/ 0.52 M BHT	17	
7	**1a**	0.04−0.06	benzene	3.8	
8	**1a**	0.04	benzene/0.45 M BHT	4.0	
9	**1a**	0.04	toluene	5.3	1.0
10	**1a**	0.03	toluene/0.26 M peroxy oxalate[f]	(10)[g]	
11	**1a**	0.03	toluene/0.37 M BHT	3.7	
12	**1a**	0.04	indane	(15)[g]	29
13	**1a**	0.022	indane/0.44 M BHT	4.0	
14	**1a**	0.054	cyclohexene	8.4	25
15	**1a**	0.043	cyclohexene/0.41 M BHT	4.9	
16	**1a**	0.03	norbornadiene	26	
17	**1a**	0.03	norbornadiene/0.43 M BHT	26	
18	**1b**[h]	0.063	benzene	2.2	
19	**1b**	0.068	1,4-cyclohexadiene	3.0	
20	**1b**	0.052	1,4-cyclohexadiene/ 0.41 M BHT	2.4	

[a] 3,3-Dimethyldioxetane (**1a**), tetramethyldioxetane (**1b**). [b] Experimental error ±10% (2σ) determined from four runs in benzene. [c] Rate constant for hydrogen atom abstraction with *tert*-butoxy radicals relative to toluene for which the absolute rate constant is 2.3×10^5 M^{-1} s^{-1} (ref 35). [d] All dioxetane **1a** decompositions were run at ca. 48 °C. [e] 3,5-Di-*tert*-butyl-4-hydroxytoluene (BHT) as radical inhibitor. [f] Di-*tert*-butyl peroxy oxalate as radical source. [g] Non-first-order decay; the rate constant is for the best fit with a single exponential. [h] All dioxetane **1b** decompositions run at ca. 67 °C.

Table 1 shows the first-order rate constants (k_{dec}) for the decomposition of dioxetanes **1a** and **1b** in various solvents with and without additives. The rates were measured from the direct chemiluminescence of the singlet-excited carbonyl products. The decomposition profile was cleanly first order unless otherwise noted. The experimental error is estimated to be ±10%. To test for the presence of a radical chain process, 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT) was added as a radical inhibitor.[23] Alternatively, radical-chain processes were induced with di-*tert*-butyl peroxy oxalate, a low-temperature thermal source of *tert*-butoxy radicals.[24]

In benzene, the rate constant for 3,3-dimethyldioxetane (**1a**) is 3.8×10^{-4} s^{-1} (Table 1, entry 7), in agreement with the literature reported values.[8,14] The rate does not change within the experimental error when BHT inhibitor is added (Table 1, entry 8). In all solvents which contain easily abstracted allylic or benzylic hydrogen atoms, the rate constants increase from those observed in benzene in the order 1,4-cyclohexadiene > indane > cyclohexene > toluene (Table 1, entries 1−4, 12, 14, and 9). This order parallels the propensity of the solvent to donate a hydrogen atom (k_{abst}, Table 1). The decomposition kinetics in indane without BHT did not fit a first-order exponential decay, and the constant was estimated with the best fit. A similar non-first-order decay was found for dioxetane **1a** in toluene in the presence of di-*tert*-butyl peroxy oxalate as radical initiator (Table 1, entry 10), for which the estimated rate constant was also faster than that observed in pure toluene (Table 1, entry 9). Significantly, for the non-olefinic solvents toluene and indane, the addition of BHT decreases the rate constant to that observed in benzene (Table 1, entries 11 and 13).

1,4-Cyclohexadiene and cyclohexene possess both abstractable hydrogen atoms and olefinic bonds which may react with dioxetane. Indeed, in 1,4-cyclohexadiene (Table 1, entries 4 *versus* 6) and in cyclohexene (Table 1, entries 14 *versus* 15), the addition of the BHT inhibitor reduces the rate of decomposition, but not down to the level in benzene without BHT (Table 1, entry 7). In contrast, norbornadiene has double bonds but no easily abstracted hydrogen atoms. In this solvent the largest rate constant of 26×10^{-4} s^{-1} was observed, which is not reduced by the addition of BHT (Table 1, entries 16 and 17). For cyclohexadiene solutions of dioxetane **1a** below 0.07 M, the decomposition rates are faster than in benzene and are not reduced by BHT (Table 1, entries 1−3 and 5).

The decomposition rate of tetramethyldioxetane (**1b**) showed a small but significant increase in 1,4-cyclohexadiene compared to benzene (Table 1, entries 18 and 19). In contrast to the results of dioxetane **1a**, when BHT was added, the decomposition rate of **1b** was reduced to the level of that in benzene within the experimental error (Table 1, entries 18 and 20).

As previously reported,[19] the products of dioxetane **1a** decomposition in 1,4-cyclohexadiene are the usual carbonyl fragments formaldehyde and acetone as well as the diol **5a** and benzene. The diol was not detected in any of the other solvents used in this study. Decomposition of **1a** in cyclohexene and norbornadiene led to a complex product mixture as observed by GC analysis. All attempts to isolate and characterize the reaction products failed due to decomposition. The influence of reaction conditions on the yield of diol **5a** was examined, and the results are given in Table 2. A solution of dioxetane **1a** was heated for 5 h at 50 °C (as reported by Richardson et al.[19]) unless otherwise noted. The yield was determined by quantitative gas chromatography by employing the internal standard method. The response factor for diol **5a** was determined with an independently synthesized sample.

Table 2. Diol Yield in the Decomposition of Dioxetanes[a]

entry no.	dioxetane[b]	concn (M)	conditions/additives	diol yield (%)
1	**1a**	0.0048		19 ± 2
2	**1a**	0.024		18 ± 2
3	**1a**	0.049		19 ± 2
4	**1a**	0.073		18 ± 2
5	**1a**	0.097		18 ± 2
6	**1a**	0.052	0.49 M biphenyl[c]	18 ± 2
7	**1a**	0.074	0.83 M BHT[d]	16 ± 1
8	**1a**	0.074	0.12 M peroxy oxylate[e]	39 ± 1
9	**1a**	0.052	0.057 M alcohol **6**	27 ± 2
10	**1a**	0.022	indane, 0.44 M BHT[d]	ND[f]
11	**1b**	0.091	60 °C, 6 h	1.6 ± 1.0

[a] All reactions were run at 50 °C for 5 h in 1,4-cyclohexadiene, unless otherwise noted. Acetone and benzene were also observed as products in the reaction but were not quantified by GC analysis. [b] 3,3-Dimethyldioxetane (**1a**), tetramethyldioxetane (**1b**). [c] Triplet acetone quencher. [d] 3,5-Di-*tert*-butyl-4-hydroxytoluene (BHT) radical chain inhibitor. [e] Di-*tert*-butyl peroxy oxalate as the source of *tert*-butoxy radicals. [f] Not detected; detection limit 0.5%.

The observed 18 ± 2% yield of diol showed no dependence on the initial concentration of dioxetane **1a** over a 20-fold increase from 0.0048 to 0.097 M (Table 2, entries 1−5).[25] The

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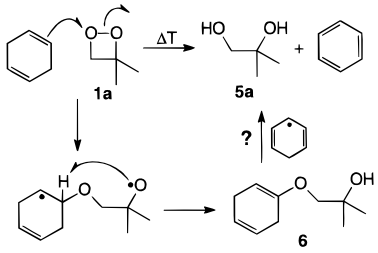
(25) Our results contrast those reported by Richardson et al. (ref 19), who observed a linear dependence of the diol **5a** yield on the initial dioxetane concentration over the same range. A constant diol yield *versus* dioxetane concentration was also found by Dr. W. J. Baader (University of São Paulo, Brazil) in an independent study.

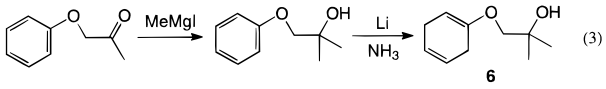
Scheme 1



addition of biphenyl as a triplet quencher (Table 2, entry 6) or BHT as a radical scavenger (Table 2, entry 7) had no significant effect on the yield of diol **5a**. The addition of the peroxy oxalate, a convenient low-temperature, thermal source of *tert*-butoxy radicals, increased the yield of diol **5a** to 39%.

In contrast to the literature reports,[19,26] pinacol **5b** was observed from dioxetane **1b**, but in a much smaller amount (Table 2, entry 11) than the diol **5a** from dioxetane **1a**. The yield of pinacol was determined by quantitative GC analysis by the same method as for diol **5a**.

To establish whether the proposed intermediary alcohol **6** (Scheme 1) is the precursor to the diol **5a** in the reaction of dioxetane **1a** with 1,4-cyclohexadiene, an authentic sample was prepared (eq 3). Phenoxyacetone was first treated with methylmagnesium iodide to form the phenoxy alcohol. This was then reduced under Birch reduction conditions to give selectively the alcohol **6** in high yield.

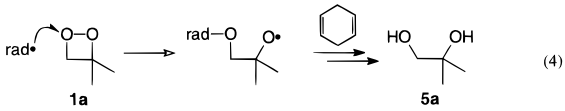


(3)

When the alcohol **6** was heated in a solution of dioxetane **1a** in 1,4-cyclohexadiene at 50 °C, the yield of diol was increased to 27% (Table 2, entry 9). Additionally, a cyclohexadiene solution of alcohol **6** was heated in the absence and presence of di-*tert*-butyl peroxy oxalate radical source. Only a trace (ca. 0.3%) of diol was observed without the radical source and 38% was observed with the maximum 6 equiv. The yield of the diol **5a** was found to increase linearly with increasing peroxy oxalate concentration (7 points, $r^2 = 1.00$).

Discussion

Revised Mechanism for Diol Formation. We identify three modes for dioxetane decomposition according to the kinetic data. First, the normal unimolecular O−O cleavage is observed in benzene, which serves as a reference to detect any molecule-induced decomposition. The second mode is a radical-induced pathway (eq 4) and can be observed in all solvents with easily

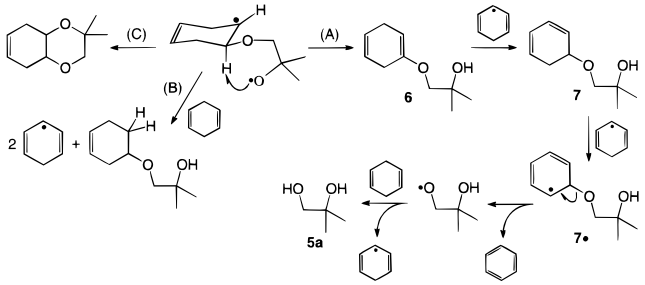


(4)

abstracted H atoms. The last mode is an olefin-induced decomposition seen in norbornadiene, cyclohexene, and 1,4-cyclohexadiene. We will show that the diol forms from the olefin-induced mode and possibly from the radical-induced mode. All of the evidence speaks against the involvement of an intermediary 1,4-dioxy biradical.

A radical-induced process accounts for the rate enhancement observed in both toluene and indane (Table 1, entries 9 and 12). These solvents are free of double bonds but have easily abstractable H atoms. Solvent radicals form from the excited

Scheme 2



state carbonyl products of dioxetanes by H abstraction; however, we rule out the direct involvement of carbonyl triplets because addition of the acetone triplet quencher, biphenyl, does not affect the diol yield (Table 2, entry 6). Such solvent radicals may then attack the O−O bond of the dioxetane[21] as shown in eq 4. Fortunately, this process can be inhibited by BHT and the decomposition rate decreases to the slower rate observed in benzene (Table 1, entries 11 and 13). The radical-induced decomposition can also be enhanced as shown by the greater decomposition rate when a radical producer is added to the toluene reaction (Table 1, entry 10). Solvent-radical-induced decomposition should also occur in cyclohexadiene and cyclohexene. The addition of BHT allows us to inhibit this process and measure the enhanced rates of the olefin-induced decomposition.

The rates of decomposition for olefinic solvents with BHT increase in the order cyclohexene < 1,4-cyclohexadiene < norbornadiene. Molecular modeling (Sybyl; MM2 force field) shows that the methylene hydrogens block the π system more so in the puckered cyclohexene than in the essentially planar 1,4-cyclohexadiene. This accounts for why cyclohexene shows less than half the rate enhancement of 1,4-cyclohexadiene, i.e. one *versus* two olefin bonds. The π system of norbornadiene is even less hindered and shows the fastest rate of dioxetane decomposition.

The addition of BHT quenches the radical-chain reaction but does not reduce the formation of diol[27] (Table 2, entry 7). We conclude from this that the initial step in the formation of diol is olefin-induced decomposition by cyclohexadiene. This type of mechanism was first described more than 40 years ago[28] and subsequently examined in detail by Greene et al.[29] A similar mechanism with a dipolar intermediate has recently been postulated for the reaction of 3,3-disubstituted dioxetanes with electron-rich olefins.[30]

The intermediate 1,6-biradical[31] may then react as shown in Scheme 2. The competition between H atom abstraction to yield an alkene (path A) and radical coupling to afford cyclization products (path C) has been studied for 1,5- and 1,6-biradicals by Wagner and co-workers.[32] They concluded that the selectivity was controlled mainly by steric effects. For our proposed biradical intermediate, the alkoxy moiety on the cyclohexene

(26) Bartlett, P. D.; Baumstark, A. L.; Landis, M. E. *Recl. Trav. Chim. Pays-Bas* **1979**, *98*, 104−108.

(27) The high concentration of BHT reduces the concentration of cyclohexadiene so the expected yield of diol is reduced from 18% to 17%.

(28) McElvain, S. M.; Stammer, C. H. *J. Am. Chem. Soc.* **1953**, *75*, 2154−2158.

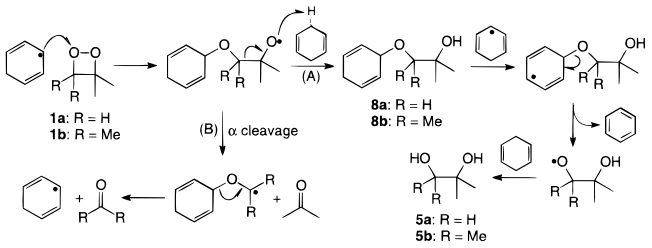
(29) Greene, F. D.; Rees, W. W. *J. Am. Chem. Soc.* **1958**, *80*, 3432−3437. Greene, F. D.; Adam, W.; Cantrill, J. E. *J. Am. Chem. Soc.* **1961**, *83*, 3461−3468.

(30) Adam, W.; Andler, S.; Heil, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1365−1366.

(31) The adduct biradical was calculated by using VAMP 5.00 with an AM1 force field. The relative energies of the singlet, triplet, and zwitterionic states were determined with configuration interaction. The biradical was calculated to be 70 kcal/mol more stable than the zwitterion in benzene as solvent.

(32) Wagner, P. J. *Acc. Chem. Res.* **1989**, *22*, 83−91. Zhou, B.; Wagner, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 6796−6799. Wagner, P. J.; Meador, M. A.; Zhou, B.; Park, B. *J. Am. Chem. Soc.* **1991**, *113*, 9630−9639.

Scheme 3



ring will assume an equatorial position, and the axial H atom will be abstracted to yield intermediate **6** (path A). The cyclization reaction, in contrast, is sterically crowded and requires several rotations of the chain to adopt a suitable conformation. We, therefore, predict that H atom abstraction (path A) will be favored over cyclization (path C). H atom abstraction from solvent (path B) is also expected to be fast.

The alcohol **6** then isomerizes to **7** by reacting with cyclohexadienyl radicals produced from path B. Further reaction yields the labile radical **7•**. This intermediate forms benzene by elimination of the dioxetane-derived alkoxy radical. This unusual radical elimination is expected to be ca. 12 kcal/mol exothermic due to the aromatic stabilization energy gained. The resulting alkoxy radical then abstracts a hydrogen atom from 1,4-cyclohexadiene to produce diol **5a**.

The proposed mechanism is supported by the substantial increase in diol yield when the diol **6** is added to the reaction of dioxetane **1a** in 1,4-cyclohexadiene (Table 2, entry 9). The formation of diol in the reaction of **6** in 1,4-cyclohexadiene with added di-*tert*-butyl peroxy oxalate shows that the reaction of intermediate **6** to diol **5a** is mediated by radicals. We expect cyclohexadienyl radicals to be the reacting species because the majority (≥98%)[33] of the *tert*-butoxy radicals should react first with the solvent rather than the dioxetane. Note that the yield of diol increases *linearly* with the amount of *tert*-butoxy radicals provided. This implies that while a chain reaction is possible, it does not operate under the experimental conditions. This happenstance also explains why BHT—which halts radical chain reactions—does not inhibit diol formation to any appreciable extent (Table 2, entry 7).

The above mechanism accounts for the diol formed at low concentrations (<0.07 M) of initial dioxetane **1a**. At high dioxetane concentrations, the yield of diol remains the same within experimental error while the dioxetane decomposition rate is increased (Table 1, entries 1−4 and Table 2, entries 1−5). Since an additional decomposition mode appears to intervene, less dioxetane will decompose by the olefin-attack pathway (Scheme 1), and, thus, less diol will be formed by that pathway. To reconcile the observed constant diol yield, an additional mechanism of diol formation must make up the difference. We propose diol formation from a radical-induced decomposition (Scheme 3, R = H). The mechanism is similar to Path A in Scheme 2, and the resulting alcohol **8a** is an isomer of alcohols **6** and **7**. The abstraction of a hydrogen atom from alcohol **8a** and subsequent elimination of benzene leads to the dioxetane-derived alkoxy radical, which finally affords diol **5a** by H atom transfer from 1,4-cyclohexadiene. This additional mechanism is supported by the observed large increase in diol yield when a source of radicals is added to the reaction mixture (Table 2, entry 8).

1,4-Cyclohexadiene has as solvent three attributes which make the formation of diol possible: (1) it initiates molecule-induced dioxetane decomposition with its reactive, unhindered π bonds, (2) it donates H atoms to generate the necessary solvent-derived radicals (Scheme 2, path B) for the completion of the reaction, and (3) it supplies two hydrogen atoms to reduce the dioxetane to the diol and forms benzene in a crucial elimination made possible by the aromatic stabilization gained.

The Elusive 1,4-Dioxy Biradical. We have assumed above that the diol is formed from the fraction of dioxetane which is attacked by cyclohexadiene. From kinetics we calculate that 25% cleaves thermally (for the time being let us suppose through a 1,4-dioxy biradical!) and the rest, 75%, reacts by the olefin-induced mechanism.[34] Could the observed 18% diol result from the thermally decomposed dioxetane, i.e. the fraction (25%) which does not involve induced reactions? If the 18% diol were to result from the 25% of the dioxetane which was thermally cleaved, the percentage of 1,4-dioxy biradicals trapped would be very high. Namely, 18 out of 25 dioxetane molecules would be trapped, or 72%. We tested for such a high trapping efficiency by using indane as solvent.

We reacted dioxetane **1a** in indane with added BHT to inhibit radical-chain reactions. In this non-olefinic solvent, kinetics established negligible molecule-induced decomposition of the dioxetane. Thus, 100% of the dioxetane should proceed through the supposed 1,4-dioxy biradical, which would have to be trapped by indane, a less efficient H atom donor. After correction for the differences in molarity and in H-atom-donating ability[35,36] between indane and 1,4-cyclohexadiene (CHD), the yield of diol in indane should be [72% × 7.3 M (indane)/10.6 M (CHD) × 8.3 × 10^6 s^{-1} M^{-1} (indane)/68 × 10^6 s^{-1} M^{-1} (CHD)] = 6%; however, no trace of diol was observed in this reaction, for which the detection limit was estimated at 0.5% (Table 2, entry 10). This shows convincingly that the diol does not derive from biradical trapping in the thermal decomposition. Rather, it is a product of the olefin-induced decomposition of the dioxetane, as proposed initially in Scheme 1.

As to the lifetime of the dioxy biradical, should it intervene as a *bona fide* intermediate, we estimate τ < 10 ps from the upper limit of 0.5% diol (estimated detection limit) in the indane experiment; were it longer lived traces of diol would have been detected. Since this lifetime is still maximally ca. 100 times longer than a vibrational period (ca. 0.1 ps), our present results merely imply that if the dioxy biradical indeed exists, it cannot be trapped by H atom abstraction under the usual chemical conditions.

The Mechanism for Tetramethyldioxetane. The lower yield of 1.6 ± 1.0% pinacol (**5b**) from tetramethyldioxetane (**1b**) in 1,4-cyclohexadiene (Table 2, entry 11) must be due, in part, to the greater steric hindrance around the O−O bond.[30] As expected, the decomposition rate in 1,4-cyclohexadiene is enhanced less from that in benzene, only a 40% increase whereas for **1a** it increased by 310%.[37]

(33) Calculated from the H atom abstraction rate for *tert*-butoxy radicals of 6.79 × 10^7 s^{-1} M^{-1} (ref 19) and a very generous 10-fold faster rate constant for reaction of *tert*-butoxy radicals with dioxetane.

(34) The fractions of **1a** which go through the non-induced (Φ_{ni}) and induced (Φ_i) pathways in 1,4-cyclohexadiene may be calculated from the decomposition rate constants in benzene and 1,4-cyclohexadiene. The rate constant (k_{ni}) for the non-induced pathway is taken as that in benzene which is 3.8 × 10^{-4} s^{-1}, while the rate constant in 1,4-cyclohexadiene (1.6 × 10^{-3} s^{-1}) is equal to the sum of k_{ni} and k_i (the induced rate constant); thus, k_i = 1.6 × 10^{-3} s^{-1} − k_{ni} = 1.2 × 10^{-3} s^{-1}. The percent of non-induced decomposition of **1a** is given by $\Phi_{ni} = k_{ni}/(k_{ni} + k_i)$ = 25%, while for the induced pathway it is $\Phi_i = k_i/(k_{ni} + k_i)$ = 75%.

(35) H atom donor ability estimated from the rates of reaction with *tert*-butoxy radicals. Paul, H.: Small, R. D.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520−4527. Hendry, D. G.; Mill, T.; Piszkiewicz, L.; Howard, J. A.; Eigenmann, H. K. *J. Phys. Chem. Ref. Data* **1974**, *3*, 937−978.

(36) The absolute rate for 1,4-cyclohexadiene was given by Richardson et al. (ref 19). The rate for indane was assumed to be the same as that for tetralin. This assumption is supported by the similarity of rates for cyclopentene and cyclohexene, which are 1.14 × 10^6 and 1.09 × 10^6 M^{-1} s^{-1}. To compute an absolute rate for tetralin, the ratio of rates for tetralin to toluene was taken from Hendry et al. (ref 35) and the ratio of toluene to 1,4-cyclohexadiene was taken from Paul *et al*. (ref 35).

In order to distinguish between the olefin- and radical-induced mechanisms for dioxetane **1b**, it should be noted that the rate in 1,4-cyclohexadiene with added BHT is the same as in benzene within experimental error. This suggests that there is no olefin-induced opening, and the diol is proposed to form from the solvent radical-induced pathway (Scheme 3, R = Me), analogous to the proposal for high concentrations of the disubstituted dioxetane **1a**. This is in accord with our previous observation on the much larger steric effects for tetrasubstituted *versus* disubstituted dioxetanes toward nucleophilic substitution.[30]

In Scheme 3, α cleavage of the intermediary adduct radical is expected to occur (path B) because a stabilized tertiary radical results. Thus, the lower diol yield may also be due to the greater chance of α cleavage which competes with H atom abstraction from cyclohexadiene.

Conclusion

The mechanism for the formation of diol **5a** from dioxetane **1a** in 1,4-cyclohexadiene has been probed by a combination of detailed product and kinetic studies. Our experimental data demonstrate that the 1,4-dioxy biradical mechanism does not operate; instead, we propose that the olefin functionality of the 1,4-cyclohexadiene first attacks the O−O bond of the dioxetane and that such molecule-induced decomposition leads to the observed diol. We contend that there is no longer any direct evidence for an intermediary 1,4-dioxy biradical in the decomposition of dioxetanes. The asynchronous, concerted—or merged—mechanism supported by the pronounced n−π^* selectivity is consistent with all of the experimental data available to date.

Experimental Section

General Aspects. ^{1}H and ^{13}C NMR spectra were run on a Bruker AC 200 (200 and 50 MHz) and are referenced to TMS. Elemental analyses were performed by the Analytical Division of the Institute of Inorganic Chemistry (Universität Würzburg). The UV/vis spectra were taken with a Hitachi U-3200 spectrophotometer. The chemiluminescence was monitored by using a Mitchell-Hastings photometer previously described.[8] Gas chromatographic analysis was performed on a Carlo Erba HRGC 5160 with an OV-1 capillary column (60 m, ϕ = 0.25 mm), FID detector, and nitrogen gas as carrier at an initial pressure of 0.8 kg/m^2. Retention times stated below were run with the following temperature program: 20 min at 40 °C; increase to 150 °C at 15 °C/min. Pinacol was synthesized according to the method of Adams[38] and recrystallized from water to give the hexahydrate. Di-*tert*-butyl peroxy oxalate was made by the method of Bartlett et al.[24] 3,5-Di-*tert*-butyl-4-hydroxytoluene was obtained commercially and recrystallized from cyclohexane. 3,3-Dimethyldioxetane and tetramethyldioxetane were synthesized from the bromohydroperoxides according to literature procedures.[22]

Caution! *Dioxetanes, bromohydroperoxides, and peroxy oxalates tend to decompose spontaneously and violently at room temperature. All safety precautions must be strictly observed.*

Purification of Solvents. Benzene, toluene, 1,4-cyclohexadiene, and norbornadiene were fractionally distilled from calcium hydride through a 15-cm Vigreux column. Indane (100 mL) was washed with concentrated sulfuric acid to remove indene (3 × 10 mL) and with water (1 × 100 mL), dried over $MgSO_4$, and fractionally distilled. Cyclohexene (100 mL) was washed with 10% aqueous $Na_2S_2O_5$ (5 × 100 mL) to remove peroxides and with water (1 × 100 mL), dried over $CaSO_4$, and fractionally distilled. The cyclohexene was slightly colored and before each run it was passed through a small column (7 mm × 0.5 mm diameter) of 63−200 μm neutral alumina (activity I, Merck). All solvents were stored under an atmosphere of argon gas. 1,4-Cyclohexadiene was kept at ca. −50 °C and after a few runs it was either redistilled from calcium hydride or passed through a column of neutral alumina to ensure adequate purity.

Thermal Decomposition of the Dioxetanes. 3,3-Dimethyldioxetane (**1a**) was stored as a methylene chloride solution. A small portion (1−2 mL) of the solution was concentrated in vacuo (ca. 15 torr and 0 °C) to give a yellow oil. The oil was then added quickly to the reaction vessel and weighed. The remainder of the oil was dissolved in $CDCl_3$ and the relative amounts of dioxetane and methylene chloride were determined by ^{1}H NMR. In this manner accurate concentrations were obtained. The solid tetramethyldioxetane (**1b**) was weighed directly into the reaction vessel. For the product yield determinations, a 60 mm × 10 mm diameter Fiolax-glass test tube closed with a rubber stopper was used as reaction vessel. The tube was then immersed into a 50 °C water bath and protected from light. For the kinetic measurements, the reaction vessel was a low-potassium chemiluminescence vial (50 mm × 25 mm diameter) and the reaction chamber was heated with an external water bath set at 50 (**1a**) and 70 °C (**1b**) which provided a reaction temperature of 48 and 67 °C.

2-Methyl-1,2-propanediol (5a). The diol was obtained in 30% yield by acid hydrolysis of the corresponding epoxide as described by Meerwein et al.[39] The required 1,1-dimethyloxirane was prepared from isobutylene in 32% yield by MCPBA oxidation.[40] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.42 (s, 2 H), 2.2 (s, 2 H), 1.22 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 71.0, 70.9, 25.7.

1-Phenoxy-2-methyl-2-propanol was obtained in 76% yield by the addition of methylmagnesium iodide to phenoxyacetone as described by Hurd and Perletz.[41] ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.3 (m, 2 H), 6.9 (m, 3 H), 3.79 (s, 2 H), 2.3 (s, 1 H), 1.35 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 158.55, 129.34, 120.85, 114.38, 75.64, 69.92, 25.98.

1-Cyclohexa-1,4-dienyl 2-Hydroxy-2-methylpropyl Ether (6). The procedure for the reduction of anisole reported by Birch and Chamberlain[42] was followed. Into a 250 mL flask equipped with a mechanical stirrer, dry ice condenser and drying tube was placed 10 mL of dried tetrahydrofuran, 10 mL of absolute ethanol, and 5.08 g (31 mmol) of 1-phenoxy-2-methyl-2-propanol. Approximately 100 mL of liquid ammonia was condensed into the flask and to the vigorously stirred solution was cautiously added 1.2 g (170 mmol) of lithium metal cut into small pieces. After the addition was complete (ca. 2 h), the stirring was continued for 30 min while keeping the dry ice in the condenser. To the reaction mixture was carefully added dropwise 50 mL of water and the flask was allowed to warm to room temperature and sit overnight to evaporate the ammonia. Water (30 mL) was added to dissolve the lithium salts and the product was extracted with ether (3 × 25 mL). The combined organic extracts were washed with saturated aqueous NaCl solution (1 × 50 mL), dried over $MgSO_4$, and concentrated at reduced pressure (20 °C at 20 Torr) to yield 4.19 g (81.5%) of hydroxy ether **6** as a clear liquid. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.63 (m, 2 H), 4.58 (t, 1 H), 3.46 (s, 2 H), 2.7 (m, 4 H), 2.47 (s, 1 H), 1.21 (s, 6 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 151.67, 124.37, 122.91, 91.63, 74.05, 69.58, 28.30, 26.13, 26.00. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 70.94; H, 9.21.

Reaction of Alcohol 6 in 1,4-Cyclohexadiene with *tert*-Butyl Peroxy Oxalate. Seven solutions containing 0.020 M alcohol **6** and 0, 0.010, 0.020, 0.030, 0.040, 0.050, or 0.060 M di-*tert*-butyl peroxy oxalate were heated for 5 h at 50 °C. The amount of diol **5a** was then measured by GC analysis and the following yields were found for conversion of the alcohol: 0.3, 6.3, 13, 19, 26, 32, and 38%.

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(37) This analysis is only qualitative since the reactions with dioxetanes **1a** and **1b** were run at different temperatures and have different activation energies.

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