configuration as reported by Lightner is in error. Thus the molecule as represented by Lightner in his figure has the configuration (1*R*) and not (1*S*) as stated in the text.

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Kinetics and Mechanisms of the Thermal Decomposition of Triphenyl-1,2-dioxetane

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Triphenyl-1,2-dioxethane (**1**) was prepared and the kinetics of thermolysis in benzene and methanol were studied in order to more clearly define stepwise vs. concerted reaction paths in dioxethane decompositions. Activation parameters in benzene are $E_a = 23.3 \pm 0.3$ kcal/mol, $\log A = 12.04 \pm 0.19$, $\Delta H^{\ddagger} = 22.6 \pm .3$ kcal/mol, $\Delta S^{\ddagger} = -5.6 \pm 0.9$ eu, and in methanol $E_a = 23.3 \pm 0.5$ kcal/mol, $\log A = 12.07 \pm 0.34$, $\Delta H^{\ddagger} = 22.6 \pm 0.5$ kcal/mol, $\Delta S^{\ddagger} = -5.5 \pm 1.5$ eu. Activation parameters were calculated for **1**, based on stepwise O–O and C–C initiated bond ruptures of the dioxetane ring. The calculated values for the O–O process are $E_a = 25.1$ kcal/mol, $\log A = 12.8$, $\Delta H^{\ddagger} = 24.4$ kcal/mol, $\Delta S^{\ddagger} = -1.86$ eu, and for the C–C process $E_a = 35.2$ kcal/mol, $\log A = 13.9$, $\Delta H^{\ddagger} = 34.5$ kcal/mol, $\Delta S^{\ddagger} = +3.2$ eu. Considering the experimental activation parameters for **1** in comparison to calculated activation parameters, based on the O–O stepwise process and in comparison to experimental activation parameters for other dioxetanes, the O–O stepwise process appears most reasonable for **1**. The lack of any significant solvent effect in proceeding from benzene to methanol is also consistent with a stepwise thermolysis of **1**.

The formation of excited state molecules in the thermolysis of dioxetanes has attracted the interest of chemists in recent years.[1] Two mechanisms have been suggested for the thermolysis of these four-ring peroxides, namely, a concerted mechanism and a stepwise process initiated with peroxide bond rupture. These two mechanisms may represent the two ends of a mechanistic sequence, where the stepwise process merges into the concerted mode as the lifetimes of the stepwise biradical species decrease.

Of the simply substituted dioxetanes that we have studied to date, it appears that the kinetic data could be most readily accommodated by a stepwise thermolysis mechanism.[2] For example, observed experimental activation parameters are in good agreement with those calculated based on a stepwise process. The progressive replacement of methyl groups by up to two phenyl groups caused little or no change in the activation parameters. In addition, the predominance of triplet excited state carbonyl products relative to excited state singlets can be explained in a conventional manner without violating spin conservation.[2b]

These data suggest that we have been viewing dioxetanes that undergo decomposition at the stepwise end of the mechanistic spectrum. Dioxetanes of this type, with simple alkyl substitution or with up to two phenyl substituents,

produce predominantly triplets in low to moderate efficiency.[2d] We are now interested to proceed toward the concerted end of this potential mechanistic spectrum. Some of the questions that arise in this survey are: (i) what type of substitution on the dioxetane ring is required to promote a concerted process; (ii) how large a change in activation parameters will be observed over the entire stepwise to concerted reaction spectrum; (iii) and how will efficiencies and electronic states of the carbonyl products vary over the mechanistic spectrum?

One of our approaches in an attempt to proceed to the concerted end of the mechanistic spectrum is to progressively place phenyl substituents on the dioxetane ring.[2] We now report our kinetic results with the most highly phenyl substituted dioxetane prepared to date, i.e., triphenyl-1,2-dioxetane. Kinetic studies were made in benzene and methanol solvent. The latter solvent was used to provide the most favorable conditions for a concerted process.[2a]

Results

Triphenyl-1,2-dioxetane (**1**) was prepared by standard procedures from triphenylethylene. Numerous attempts were made to purify **1** by recrystallization and chromatography. Occasionally, **1** would partially survive silica gel column

Table I. First-Order Dependence in Triphenyl-1,2-dioxetane and the Effect of Triphenylethylene on the Rate[a]

10^4[1], M	Added $[(C_6H_5)_2C{=}CHC_6H_5]$, M	$10^4 k,$[b] s^{-1}
1.60	0	5.60 ± 0.03
16.0	0	5.30 ± 0.02
1.60	1.20×10^{-2}	5.60 ± 0.05

[a] In benzene at 59.90 °C with 5.40×10^{-4} M DBA. [b] By least squares with standard error.

Table II. Effect of Temperature on the Rate of Decomposition of Triphenyl-1,2-dioxetane (1) in Benzene[a,b]

Temp, °C	$10^4 k,$[c] s^{-1}	Temp, °C	$10^4 k,$[c] s^{-1}
40.10	0.550 ± 0.004	59.90	5.58 ± 0.02
50.05	1.88 ± 0.07	59.90	5.65 ± 0.03
50.30	2.08 ± 0.03	70.00	14.4 ± 0.1
59.82	5.35 ± 0.11	70.00	14.5 ± 0.1
59.90	5.28 ± 0.03	77.85	33.7 ± 0.5
59.90	5.30 ± 0.05	77.90	32.7 ± 0.5

[a] [1] = 4.20×10^{-5} M. [b] Rates determined by following the decay of emission from DPA, with [DPA] = 5.40×10^{-4} M. All measurements were made with aerated solutions. [c] Rate coefficients were obtained by a least-squares fit and they are reported with standard error within a given measurement. The values were determined with a Hewlett-Packard 65 calculator, using Stat-Pac 1-22A.

chromatography. On most occasions, decomposition of 1 would occur on the column, even though the column was treated with EDTA and operated at low temperatures.[3] No significant improvement in purity was found with our attempts to recrystallize 1. Due to these problems, we were usually forced to use samples of 1 for kinetic studies without chromatographic purification. However, similar rate coefficients were obtained from samples that were purified by chromatography or unpurified. Purified samples were employed for the product studies. By GLC analysis it appears that the major impurity in samples of 1 was triphenylethylene. For example, a sample with 7.40×10^{-3} M 1 contained 5.39 $\times 10^{-3}$ M of this olefin. Similar attempts to purify the bromohydroperoxide precursor to 1 met with failure. In fact, the bromohydroperoxide appeared even more susceptible to decomposition on the silica gel column than did 1.

The only products that were identified from the thermolysis of 1 were benzaldehyde and benzophenone. With an initial dioxetane concentration of 7.40×10^{-3} M in benzene–carbon tetrachloride (3:1), thermolysis at 45 °C to completion gave apparent yields of benzaldehyde and benzophenone by GLC of 110 and 111%, respectively. Apparently, some decomposition of 1 occurred prior to the thermolysis, which was undetected, and gave yields in excess of 100%.

Kinetic Data. Rates of decomposition of 1 were measured by monitoring light emission from added 9,10-diphenylanthracene (DPA) or 9,10-dibromoanthracene (DBA). Good first-order plots were obtained and the first-order rates were confirmed by varying the initial concentration of 1 by tenfold (cf., Table I). In addition, it was shown that the major contaminant in the sample of 1, i.e., triphenylethylene, did not alter the rate when this olefin was added at 1.20×10^{-2} M (cf., Table I). Activation parameters were determined from the kinetic data presented in Table II for thermolysis in benzene solvent. Similar rate data as a function of temperature for the thermolysis of 1 in methanol containing EDTA are given in Table III. The activation parameters, which result from the data of Tables II and III, are given in Table IV.

Table III. Effect of Temperature on the Rate of Decomposition of Triphenyl-1,2-dioxetane (1) in Methanol Containing EDTA[a]

Temp, °C	$10^4 k,$[b] s^{-1}	Temp, °C	$10^4 k,$[b] s^{-1}
37.08	0.487 ± 0.009	55.10	3.56 ± 0.03
37.08	0.511 ± 0.003	55.01	3.59 ± 0.06
45.10	1.09 ± 0.007	59.98	7.20 ± 0.10
50.20	2.19 ± 0.02	59.95	6.60 ± 0.11
50.20	2.31 ± 0.02	59.87	6.42 ± 0.07
52.99	2.60 ± 0.02	62.42	7.95 ± 0.05
52.99	2.77 ± 0.02	62.42	8.42 ± 0.20

[a] [1] = 6.14×10^{-4} M, [DPA] = 4.70×10^{-4} M (45–62 °C) and 1.25×10^{-3} M (37 °C). All measurements were made with aerated solutions. [b] Least-squares fit with standard error.

Table IV. Experimental Activation Parameters for the Thermolysis of Triphenyl-1,2-dioxetane (1) in Benzene and in Methanol[a]

Solvent	E_a[b]	$\log A$	$\Delta H^{\ddagger}$[b,c]	$\Delta S^{\ddagger}$[d]
Benzene	23.3 ± 0.3	12.04 ± 0.19	22.6 ± 0.3	-5.6 ± 0.9
MeOH	23.3 ± 0.5	12.07 ± 0.34	22.6 ± 0.5	-5.5 ± 1.6

[a] Activation parameters are obtained by a least-squares fit and they are given with standard error. [b] kcal/mol. [c] At 60 °C. [d] eu.

Scheme I

$$\xrightarrow{fast} (C_6H_5)_2CO + C_6H_5CHO$$

Scheme II

$$\xrightarrow{fast} (C_6H_5)_2CO + C_6H_5CHO$$
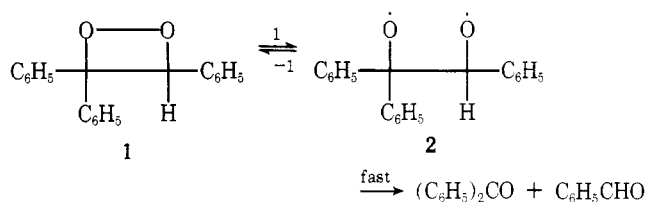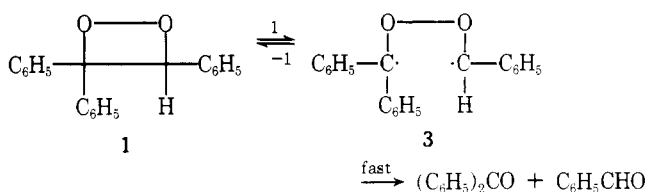
Calculation of Activation Parameters. Previously we showed that activation parameters for the thermolysis of dioxetanes could be well estimated by use of the hypothetical two-step O–O bond initiation process shown in Scheme I for 1.[2] Although this simple scheme can be used to estimate the activation parameters, a more detailed mechanism which involved singlet and triplet biradicals was required to explain the known photoemission or stimulated emission properties of dioxetane thermolyses.[2b] However, in both this extended biradical mechanism and the simple two-step scheme, the rate-determining step is O–O bond homolysis. Thus, Scheme I is an adequate model from which to calculate activation parameters.

In addition to calculating activation parameters based on Scheme I, it was necessary to consider the thermolysis of 1 proceeding by a C–C initiated homolysis process as shown in Scheme II. The necessity for considering Scheme II is due to the resonance stabilized biradical 3, which when reflected to the transition state in the first step could sufficiently alter the activation parameters to make them competitive with Scheme I.

Activation energies based on Schemes I and II are calculated from eq 1.[4] The value of $\Delta H^{\circ}_{1,-1}$ in eq 1 is determined

$$E_a = \Delta H°_{1,-1} + E_{-1} \qquad (1)$$

by the difference of heats of formation between the product and reactant. The heats of formation may be estimated by group additivity methods[4] or by a combination of the latter method and bond dissociation energies. Some group, gauche, and cis contributions that are required to estimate $\Delta H_f°$ for **1**, **2**, and **3** are not reported. For example, corrections were made to reported group contributions where bonding was to aliphatic carbon (C), whereas bonding was required to benzene carbon (C_B). These corrections were made by noting comparable changes from replacing C_B with C in reported groups and the corrections are usually small. A satisfactory method for estimating gauche interactions, based on using one-half cyclohexane *A* values, was previously reported and is used here.[2b] With **2** in its most stable conformation as shown below,


2
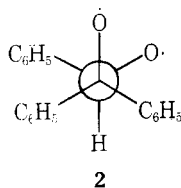
there are the following gauche corrections along with their estimates: [gauche $\dot{O},\dot{O}$] = 0.35 kcal/mol, 2 [gauche Ph,$\dot{O}$] = 2 × 1.55 = 3.1 kcal/mol, and [gauche Ph,Ph] = 1.55 kcal/mol.[5] The first two gauche interactions were estimated as one-half the cyclohexane *A* value for hydroxy and for phenyl, respectively. The [gauche Ph,Ph] interaction was also estimated as one-half the phenyl *A* value. This may somewhat underestimate this interaction, but it appears to be the best estimate that can be made. The cis O,O interaction in **1** was estimated as before by using one-half of the phenyl *A* value.[2b] The previously employed strain energy of 25 kcal/mol for dioxetanes was used here.[2b] Due to the lack of appropriate group additivity values, a combination of bond dissociation energy and group additivity methods were employed to estimated $\Delta H_f°$ for the carbon biradical **3**.[7] Briefly, the method was based on eq 2, where $\Delta H_f°$ of **4** was calculated by the group additivity
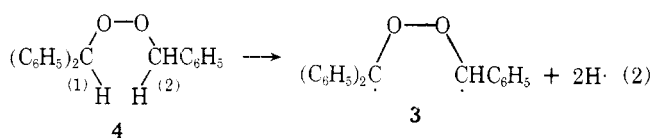
method, $\Delta H_f°$ for the hydrogen atom was obtained from tables,[4] and the heat of reaction ($\Delta H_r°_{4,3}$) was obtained as the sum of the estimated bond dissociation energies. From these values, $\Delta H_f°$ of **3** was calculated ($\Delta H_f°_3 = \Delta H_r°_{4,3} + \Delta H_f°_4 - 2\Delta H_f°_H$). The C_2–H bond dissociation energy was estimated as $D_{C_2-H} = D_{(CH_3)_2CH-H} + E_{Ph}$resonance + $E_{\alpha-O}$resonance, where $D_{(CH_3)_2CH-H}$ = 95 kcal/mol,[4] E_{Ph}resonance is the benzyl resonance energy (−10 kcal/mol),[8] and $E_{\alpha-O}$resonance is the resonance energy of an α-oxy radical (−1.3 kcal/mol).[10] The C_1–H bond dissociation energy was estimated as $D_{C_1-H} = D_{(CH_3)_3C-H} + E_{Ph_2}$resonance + $E_{\alpha-O}$resonance, where $D_{(CH_3)_3C-H}$ = 92 kcal/mol. Unfortunately, we were unable to find reliable data to estimate E_{Ph_2}resonance. This value is taken as an average of the benzyl (−10 kcal/mol)[8] and trityl (−14.2 kcal/mol)[11] resonance energies on a per phenyl group ([−10 + (−14.2/3)]/2 = −7.4 kcal/mol) basis. Thus, E_{Ph_2}resonance is estimated to be −14.8 kcal/mol (=2 × (−7.4)).

Activation entropies and *A* factors for initial (O–O) bond rupture (Scheme I) and for intital (C–C) bond rupture (Scheme II) are estimated as follows. Intrinsic entropies of **1**, **4**, and **5** are obtained directly from group additivity values, equating C_B carbons to ordinary C carbons, and using an $S°$ ring correction of 26.0 eu/mol for the dioxetane.[4] The entropy losses in proceeding from the acyclic peroxide **4** to the carbon

5
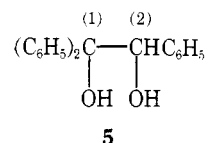
biradical **3** and from **5** to the oxy biradical **2** are then estimated. Comprising $\Delta S°_{4\to3}$ is the entropy loss due to the six vibrational motions of the two hydrogen atoms removed in going from **4** to **3** (mainly two HCO bends), and the entropy losses produced when the sixfold (therefore low rotational barrier) internal rotations of the three phenyl groups in **4** are restricted to torsional or highly hindered rotational motions (due to the development of radical resonance stabilizations) in **3**. Rotational barriers of the phenyl groups in **4** and **3** are estimated to be 1.5 (C-1), 1.5 (C-1), and 1.0 (C-2) kcal/mol and 13.0 (C-1), 5.0 (C-1), and 13.0 (C-2) kcal/mol, respectively. Treating the latter restricted rotors as torsions, the corresponding frequencies can be calculated to be 59, 37, and 59 cm⁻¹, respectively.[13] Therefore, $\Delta S°_{4\to3} = -2S°(Ph\overset{\rightarrow}{?}\infty)_{V_0}$ = 1.5 kcal − $S°(Ph\overset{\rightarrow}{?}\infty)_{V_0}$ = 1.0 kcal − 2(HCO)₁₁₅₀cm⁻¹ + 2S(59 cm⁻¹ torsion) + S(37 cm⁻¹ torsion) = −2(8.3) − 8.6 − (0.1) + 2(4.5) + 5.5 = −10.8 eu/mol. The back activation entropy for ring closure of **3** to **1** ($\Delta S^{\ddagger}_{-1}$) is equated to minus the entropy of the internal rotation about the O–O bond in **3**. This is the reaction coordinate for the (−1) reaction in

$$4 \overset{1}{\underset{-1}{\rightleftharpoons}} 3$$

An estimated reduced moment of about 335 amu Å² for this internal rotation gives a free rotor partition function of Q_f = 114 and a free rotor entropy of about 10.4 eu/mol.[14] Setting the rotational barrier at $V_0 \simeq 9.5$ kcal, a hindered internal rotation entropy of about 7.5 eu/mol is calculated, and thus, $\Delta S^{\ddagger}_{-1} \simeq -7.5$ eu/mol. For Scheme II, one obtains $S°^{\ddagger} = [S°_4 + \Delta S°_{4\to3} + \Delta S^{\ddagger}_{-1}]_{intrinsic} + R \ln (\eta^{\ddagger}/\sigma^{\ddagger}) = [167.6 − 10.8 − 7.5] + R \ln (2/1) = 150.6$ eu/mol. Also one obtains $S°_1 = S°_1$(intrinsic) + $R \ln (\eta/\sigma) = 150.2 + R \ln [2/(2)^3] = 147.4$ eu/mol and thus for Scheme II, $\Delta S^{\ddagger} = (S°^{\ddagger} - S°_1) = 3.2$ eu/mol or $A_{est} = (ekT/h)e^{\Delta S^{\ddagger}/R} = 7.9 × 10^{13}/s^{-1}$.

The transition state entropy of Scheme I is similarly obtained by the difference method, starting from the entropy of **5**. Removal of the two hydrogen atoms to produce the oxy biradical (**2**) involves the entropy loss of the hydrogen atom vibrations (again, essentially just the entropy associated with two HOC bends of 1150 cm⁻¹ each) and the entropy loss associated with the two hydroxy group internal rotations. For rotational barriers of about 1.0 kcal, the entropy change $\Delta S°_{5\to2} \simeq -2S°(HOC)_{1150cm^{-1}} - 2S°(HO\overset{\rightarrow}{?}\infty)_{V_0} = 1.0 = -0.1 − 2(4.6 − 0.2) = -8.9$ eu/mol. The intrinsic entropy of **2** is therefore, $S°_2 = S°_5 + \Delta S°_{5\to2} = 163.6 − 8.9 = 154.7$ eu/mol. The activation entropy for ring closure of the oxy biradical **2** to **1**, $\Delta S^{\ddagger}_{-1}$, of Scheme I is equated to minus the entropy of internal rotation about the C–C bond. For this reaction coordinate internal rotation, a reduced moment of inertia of about 125 amu Å² is estimated, which gives a free rotor entropy of 9.4 eu and a hindered rotor entropy of 6.4 eu for a potential barrier of 10.8 kcal/mol. The pertinent entropies for Scheme I are than estimated as: $S°^{\ddagger} = [S°_2 + \Delta S°^{\ddagger}_{-1}]_{intrinsic} + R \ln (\eta^{\ddagger}/\sigma^{\ddagger}) = [154.7 − 6.4] + R \ln (2/(2)^3) = 145.5$ eu/mol and $\Delta S^{\ddagger} = S°^{\ddagger} - S°_1 = (145.5 − 147.4) = -1.86$ eu/mol or $A_{est} = (ekT/h)e^{\Delta S^{\ddagger}/R} = 6.2 × 10^{12}$ s⁻¹.

The pertinent data that were used to calculate the activation parameters for the processes given in Schemes I and II are given in Table V. From these data, $\Delta H°_{1,-1}$ and the activation parameters for Schemes I and II are given in Table VI. The E_{-1} values of 8.5[2b] and 6.7[15] kcal/mol are those that have been used previously for dioxetanes and cyclobutanes.

Table V. Thermochemical Parameters for Triphenyl-1,2-dioxetane, Biradicals 2 and 3, and Related Species

Species	Registry no.	$\Delta H_f°$, kcal/mol	$S°_{intrinsic}$, eu	$S°,^a$ eu
1	65293-77-8	75.68	150.2	147.4
2	65354-53-2	92.27	154.7	151.9
3	65354-54-3	104.2	156.8	155.4
4	55504-20-6	48.8	167.6	163.4
5	464-72-2		163.6	160.8

^{a} $\sigma_1 = 2^3$, $n_1 = 2$; $\sigma_2 = 2^3$, $n_2 = 2$; $\sigma_3 = 2$ (the three phenyl group rotors have been treated here as vibrations), $n_3 = 1$; $S°_{real} = S°_{intrinsic} + R \ln (n/\sigma)$.

Discussion

Activation parameters for thermolysis of triphenyl-1,2-dioxetane (1) in benzene (E_a = 23.3 kcal/mol, log A = 12.04, $\Delta S^\ddagger$ = −5.6 eu) are similar to those that we have found for dioxetanes **6a–d** in aprotic nonpolar solvents.[2bc] In the series **6a–d**, the experimental E_a values range from 22.7 to 24.3 kcal/mol with log A (and $\Delta S^\ddagger$) ranging from 12.10 (−5.3 eu) to 12.83 (−2.0 eu). A comparison of experimental activation parameters in series **6a–d** with 1 suggests a common mecha-

$$R_1 - \overset{\overset{\displaystyle O - O}{|\quad\,|}}{\underset{\displaystyle R_2}{\overset{\displaystyle |}{C}}} - CH_2$$
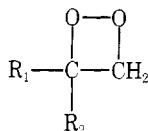
6a, $R_1 = R_2 = CH_3$
b, $R_1 = CH_3$; $R_2 = C_6H_5$
c, $R_1 = R_2 = C_6H_5$
d, $R_1 = R_2 = C_6H_5CH_2$

nism, where substituent effects have little influence. Since phenyl substitution is expected to stabilize a developing π-carbonyl bond in a concerted process, the comparison of experimental activation parameters strongly suggests a stepwise decomposition.[2] The stepwise route, which was previously suggested to explain the kinetic data and the preponderance of triplet excited state carbonyl products (T_1) relative to S_1 products, is given in Scheme III.[2b]

Further confirmation of the dioxetane thermolysis mechanism can be made by comparison of experimental and calculated activation parameters, where the latter are based on a stepwise process. Two separate processes were considered, as outlined in Schemes I and II. These two processes, which involve O–O and C–C initiated bond breaking, bracket the concerted process, where a lower activation energy is expected than for either stepwise mode.[2]

Calculated activation parameters for dioxetanes **6a–d**, based on an O–O initiated stepwise model, were in good agreement with experimental values.[2] A small increase in calculated E_a values was found with increasing steric effects.[16] For example, the calculated activation energy increased by 3.2 kcal/mol in preceding from 1,2-dioxetane to tetramethyl-1,2-dioxetane. This is qualitatively supported by the available experimental activation energies. Thus, 3,3-dimethyl-1,2-dioxetane (**6a**) and tetramethyl-1,2-dioxetane are reported to have E_a values of 23.0[2c] and 25.7–27.6[1d,17] kcal/mol, respectively. In proceeding from 3,3-diphenyl-1,2-dioxetane (**6b**) to triphenyl-1,2-dioxetane (1), an increase in E_a is expected due to steric effects. In terms of calculated E_a values for the O–O initiated process, this is noticed where the calculated values for **6b** and 1 are 22.9[2b] and 25.1 kcal/mol, respectively. In benzene solvent, the experimental E_a values are nearly identical for **6b** and 1 (22.1[2b] and 23.3 kcal/mol, respectively). Although the activation energy for 1 is somewhat

Table VI. Calculated Activation Parameters for Schemes I and II

Scheme	$\Delta H°_{1,-1}{}^a$	$E_{-1}{}^a$	$E_a{}^a$	log A	$\Delta H^{\ddagger a,b}$	$\Delta S^{\ddagger c}$
I	16.59	8,5	25.1	12.8	24.4	−1.86
II	28.5	6.7	35.2	13.9	34.5	3.2

^{a} kcal/mol. ^{b} At 60 °C. ^{c} eu.

Scheme III
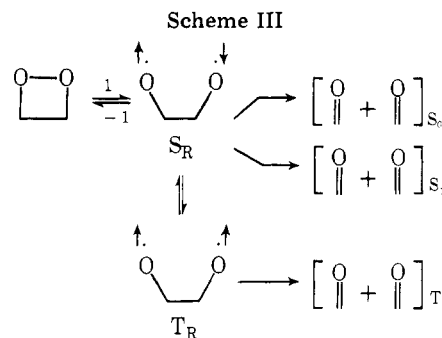
lower than predicted by the O–O initiated stepwise process, the differences are probably within the experimental error and limits of the calculated values.

Since heavy phenyl substitution could possibly change the mechanism of dioxetane thermolysis from (O–O) to (C–C) initiated stepwise rupture, calculations based on this latter mechanism (Scheme II) were made. Indeed, the calculated activation energy for Scheme II does approach the experimental E_a value and the E_a value calculated on the basis of (O–O) bond homolysis. However, the calculated E_a value for Scheme II (35.2 kcal/mol) does appear to be significantly higher than the experimental E_a value (23.3 kcal/mol). It should be noted though that there is no doubt significant error in the calculated E_a value for Scheme II.

The calculated entropy of activation for the (O–O) homolysis process (−1.86 eu), as obtained from Scheme I, is in the range of the experimental values for 1 in benzene (−5.6 eu) and methanol (−5.5 eu). This calculated value is also in the range of $\Delta S^\ddagger$ values for dioxetanes **6a–d** (−5.3 to −2.0 eu).[2bc] The calculated $\Delta S^\ddagger$ value based on Scheme II (C–C initiated homolysis) of +3.2 eu is more positive than the calculated value for (O–O) homolysis by 5 eu. This would tend to favor the (C–C) homolysis process; however, the difference is not great in terms of rate. For example, if the experimental E_a value for 1 is used and rate coefficients are calculated with the calculated $\Delta S^\ddagger$ values for the O–O and C–C homolysis processes, one obtains k_{C-C}/k_{O-O} = 13 at 60 °C.

A further comparison of experimental and calculated activation parameters for 1 can be made in terms of rate coefficients. From the calculated activation parameters given in Table VI for the O–O homolysis process (Scheme I), a rate coefficient of 2.09×10^{-4} s^{-1} is calculated at 60 °C. This may be compared with the rate coefficient calculated with experimental activation parameters for 1 at 60 °C in benzene (5.52×10^{-4} s^{-1}). In terms of relative rates, this comparison yields $k_{exptl}/k_{O-O,calcd}$ = 2.6. With the calculated activation parameters given in Table VI for the C–C homolysis process (Scheme II), a rate coefficient of 6.31×10^{-10} s^{-1} is obtained at 60 °C. In terms of relative rates, this gives $k_{exptl}/k_{C-C,calcd}$ = 3.3×10^5 (=$2.09 \times 10^{-4}/6.3 \times 10^{-10}$). Thus with our best estimates for O–O and C–C calculated activation parameters, the calculated O–O parameters yield a rate coefficient that is in excellent agreement with the observed value. In contrast, the C–C calculation parameters produce a rate coefficient that differs by over five orders of magnitude from the observed value. Considering both the agreement of the observed activation pa-

rameters with calculated parameters and the correspondence with experimental activation parameters in the series **6a–d,** it appears most reasonable that **1** is undergoing thermolysis by an O–O stepwise homolysis process.

Previously, we have used methanol to probe the mechanism of dioxetane thermolysis.[2a] Based on the decrease in enthalpy of activation in changing from an aprotic to a protic solvent in the β scission of the *tert*-butoxy radical,[18] we expected a similar solvent response for a concerted dioxetane decomposition. As seen from Table IV, the activation parameters for **1** are nearly identical in benzene and in methanol. This result is consistent with a stepwise decomposition mode for **1** in both benzene and methanol solvent, and it is not expected for a concerted process. The solvent effect results are then in agreement with the previous kinetic analysis above.

An important question that can be raised is, what magnitude of change in activation parameters is expected in proceeding from a stepwise to a concerted dioxetane thermolysis? Intimately related to this question is how substituents will influence the activation parameters of a concerted reaction. Presently, these questions are probably best answered by empirical correlations, rather than by means of calculations. Thermochemical kinetic calculations are not applicable to activation energy estimates for concerted reactions. In addition, molecular orbital calculations must be highly sophisticated in order to obtain a realistic description of the reaction surface, let alone to obtain reliable energy differences. For example, an ab initio calculation of the pyrolysis of cyclobutane[19] was required to demonstrate the biradical intermediate nature of the reaction as opposed to the earlier extended Hückel view of the reaction.[20] It can be noted that recent generalized valence bond (GVB) calculations of the thermolysis of 1,2-dioxetane are in agreement with a stepwise biradical process.[21]

An example of a concerted reaction where substituent effects have been studied is found in the pyrolysis of cyclobutenes. Substitution of methyl and of phenyl groups at the 3 position in cyclobutene increases the rate of pyrolysis by factors of 10^{22} and 2000,[23] respectively. In terms of activation energy, this corresponds to about a 5 kcal/mol decrease in E_a per phenyl substituent at the 3 and 4 positions in cyclobutene. In the concerted electrocyclic ring opening of cyclobutenones, replacement of one and two methyl groups by phenyl groups at the 4 position lowers $\Delta G^{\ddagger}$ by 3.1 and 2.3 kcal/mol, respectively.[24] In both of these reactions a π bond is developing in the transition state at the site of substitution. With these concerted electrocyclic ring openings as models, a significant lowering of E_a would be expected for phenyl substitution in dioxetanes, if the reaction were concerted.

Recently, reports of dioxetane thermolyses have appeared that are suggestive of a concerted decomposition. Activation parameters for the thermolysis of dioxetanes **7** and **8** are E_a

7   **8**
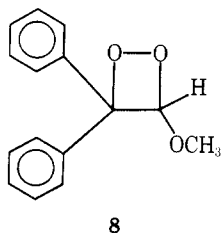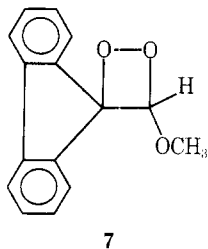
= 21.0 kcal/mol, log A = 11.6 and E_a = 26.1 kcal/mol, log A = 13.5, respectively.[25] These data, along with the unusual singlet excited state carbonyl production from **7,** may be indicative of a concerted decomposition of **7.** The unusually low activation energies observed in the thermolysis of **9** in benzene (E_a = 17.2 kcal/mol, $\Delta S^{\ddagger}$ = −5 eu) and in methylene chloride (E_a = 17.8 kcal/mol, $\Delta S^{\ddagger}$ = −1.1 eu) are also suggestive of a con-

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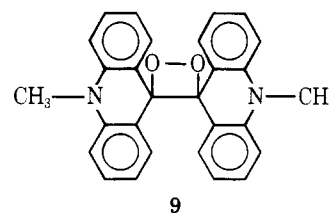
certed decomposition.[26] Thus, it appears that significant decreases in activation energy can be anticipated when dioxetanes are suitably substituted to effect a concerted decomposition. Considering the similarity in activation energies, upon substituting the dioxetane ring with up to three phenyl groups, there appears to be little evidence for a concerted process with **6a–d** and **1.** However, if there is a smooth continuum from a stepwise to a concerted process, it will be difficult to detect the concerted character in dioxetanes near the stepwise end of this reaction spectrum.

In summary, the thermolysis of alkyl-substituted dioxetanes and those with phenyl substitution up to three phenyl groups are most reasonably interpreted as undergoing an O–O stepwise initiated decomposition. This interpretation is based on the similarity of experimental activation parameters with varying phenyl substitution, the similarity in experimental activation parameters upon changing from aprotic to a polar protic solvent, and in the agreement between experimental and calculated parameters based on an O–O initiated stepwise process. The decrease in the experimental activation energy for **1,** compared to the calculated value, is too small, compared to the error in these values, to be indicative of progress to a concerted mechanism. Thus, it appears that the stepwise mechanism is common to simply substituted four-membered ring compounds with the progressive introduction of oxygen in the series cyclobutane,[27] oxetane,[28] and simply substituted dioxetanes. In addition, the stepwise decomposition of dioxetanes has the added attribute of explaining the direct production of triplet carbonyl products[1d] without violation of spin conservation.

Experimental Section[29]

Triphenylethylene. This olefin was prepared by a previously reported method in 64% yield by means of a Grignard reaction, starting with benzyl chloride and benzophenone. Recrystallization from 95% ethanol gave a white solid: mp 70.0–70.5 °C (lit.[30] mp 68–69 °C); NMR spectrum (10% deuteriochloroform solution) $(C_6H_5)_2$ 7.31 (broad singlet, 10.0); (C_6H_5) 7.08 (broad singlet, 5.0); $(=CH-C_6H_5)$ 6.98 (singlet 1.0).

1-Bromo-1,1,2-triphenyl-2-hydroperoxyethane. 1,3-Dibromo-5,5-dimethylhydantoin (MC/B) (1.4g, 4.9 mmol) was added in portions to a solution of triphenylethylene (2.5g, 9.8 mmol) and hydrogen peroxide (49 mmol) in 50 mL of tetrahydrofuran at −40 °C under a nitrogen atmosphere. The hydrogen peroxide THF solution was previously prepared from anhydrous THF and 98% hydrogen peroxide (FMC). The solution was then dried over anhydrous magnesium sulfate at 25 °C for 24 h prior to use. The temperature of the reaction mixture was maintained between −35 and −45 °C for 1.5 h and then the temperature was allowed to warm slowly to room temperature over 0.5 h. Stirring was continued for an additional 1.5 h at room temperature. The reaction mixture was then quenched in a separatory funnel containing 50 mL of ether and 25 mL of ice-cold aqueous 5% sodium bicarbonate solution. The ether fraction was further washed with sodium bicarbonate and then with cold water and finally dried over magnesium sulfate. The ether was removed under reduced pressure and the remaining yellow oil was dissolved in carbon tetrachloride. The NMR spectrum of this solution indicated a solvent dependent peroxy proton absorption at 8.7 ppm and integration of this absorption relative to the aromatic protons indicated a 60% yield of the bromohydroperoxide. The methine proton was observed at 6.08 ppm. This was further confirmed by iodometric titration.[31] Isolation of the hydroperoxide by recrystallization and by silica gel column chromatography was attempted without success.

Triphenyl-1,2-dioxetane (1). A 0.5 M sodium methoxide solution in methanol containing 2 mol % Na_2EDTA was prepared and 1.2 mL of this solution was added dropwise to a cooled (ca. 5 °C) mixture of

the bromohydroperoxide (0.5 mmol) in 5 mL of methanol (saturated with Na_2EDTA for 1 h prior to use) under a nitrogen atmosphere. The solution was stirred for an additional 0.5 h at 5–10 °C and then it was quenched with 8 mL of ice-cold water. This mixture was rapidly extracted with four 2 mL-portions of cold carbon tetrachloride. The latter extracts were further washed with cold water and dried over magnesium sulfate. An iodometric biamperometric titration[32] of this solution indicated that 1 had been formed in a 17% yield. The NMR spectrum showed the absence of the bromohydroperoxide, since no methine proton absorption was observed at 6.08 ppm. The dioxetane ring proton of 1 was buried in the aromatic envelope. A considerable effort was made to purify 1 by recrystallization and chromatography on silica gel. Recrystallization attempts failed but periodically one could obtain a partially purified sample of 1 by chromatography on silica gel. Although attempts were made to use low-temperature chromatography, it appeared that small-scale chromatography at room temperature using carbon tetrachloride as the eluent was about as satisfactory as any method.

Product Studies. A sample of 1 was purified by silica gel column chromatography and thermally decomposed in benzene–carbon tetrachloride (3:1) solvent. The thermolysis was carried out at 45 °C for greater than 20 half-lives in a sealed tube which was purged with nitrogen. The initial concentration of 1 was obtained from an iodometric biamperometric titration.[32] By NMR analysis, less than 10% of the bromohydroperoxide, based on 1, was present and benzaldehyde was not detected, although possibly 10% (based on 1) could be undetected. After thermal decomposition, the reaction mixtures were analyzed by GLC on a 5% methyl vinyl silicone column (6 ft × $\frac{1}{8}$ in) at 110 °C vs. o-dichlorobenzene as an internal standard. Retention times (min) are: benzaldehyde (3.0), o-dichlorobenzene (4.5), benzophenone (12.0), and triphenylethylene (30). Yields of products were calculated by reference to a standard mixture of these components. Peak areas were determined by digital integration and the final yields are the average of five analyses.

Kinetic Methods. Rate measurements were made by light emission methods according to a previously reported method.[2ab] The primary acceptor and light emitter in these studies was DBA in benzene solvent and DPA in methanol solvent. The kinetic data as well as the activation parameters were processed by means of a least-squares program.

Registry No.—Triphenylethylene, 58-72-0; 1-bromo-1,1,2-triphenyl-2-hydroperoxyethane, 65293-78-9; 1,3-dibromo-5,5-dimethylhydantoin, 77-48-5.

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(11) The resonance energy of the trityl radical is taken as the difference between the activation energies for the thermolysis of 2,2'-azoisobutane (43.5 kcal/mol)[12a] and benzeneazotriphenylmethane (29.3 kcal/mol).[12b] This assumes initial single bond homolysis for each compound.
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(14) The free rotor partition function is obtained from the relationship, $Q_f = 0.360/n(Ir \, T)^{1/2}$, where n is the symmetry of the rotation, Ir is the reduced moment of inertia in amu $Å^2$, and T is the temperature in K. The free rotor entropy is then, $S_f° = (R/2) + R \ln Q_f$.
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