Solvent and Substituent Effects in the Thermolysis of 1,2-Dioxetanes

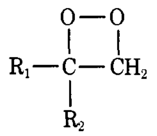
W. H. Richardson,* F. C. Montgomery, P. Slusser, and M. B. Yelvington

Contribution from the Department of Chemistry, San Diego State University, San Diego, California 92115. *Received April 4, 1974*

Abstract: Kinetic data and activation parameters for thermal decomposition of four substituted 1,2-dioxetanes in methanol are reported. The cyclic peroxides have varying phenyl and alkyl substitution at the 3 position, namely: **1a,** 3,3-dimethyl-; **1b,** 3-methyl-3-phenyl-; **1c,** 3,3-diphenyl-; and **1d,** 3,3-dibenzyl-1,2-dioxetane. Anomalous kinetic data result when **1b–d** are decomposed in distilled methanol. In contrast, reasonably good first-order kinetics result when the methanol is treated with ethylenediaminetetraacetic acid (EDTA), and the activation parameters are similar to those obtained in aprotic solvents. Low activation parameters, which result when methanol solvent is not treated with EDTA, are attributed to trace transition metal ion catalysis. Increased phenyl substitution on the dioxetane ring has little effect on the rate of thermolysis of the dioxetanes in EDTA treated methanol solvent. The effect of both solvent and phenyl substitution on the rate of thermolysis of these cyclic peroxides is most consistent with a stepwise decomposition mechanism, where the peroxide bond is ruptured initially in the rate-determining step.

Initial reports of 1,2-dioxetane thermolysis in methanolic solvents suggested pronounced solvent effects in relative aprotic systems. For example, activation parameters for decomposition of tetramethyl-1,2-dioxetane (TMD) in benzene or cyclohexane are reported to be $\Delta H^\ddagger = 25$ kcal/mol and $\Delta S^\ddagger = -1$ eu, while those in methanol are given as $\Delta H^\ddagger = 13$ kcal/mol and $\Delta S^\ddagger = -34$ eu.[1] This solvent effect was then proposed to support a concerted as opposed to a stepwise decomposition of the dioxetane.[1] A more recent measurement of the activation energy for thermolysis of TMD in methanol by a temperature-drop method indicates that this parameter is unaltered for the light-producing reaction by changing from benzene to methanol solvent.[2] We had also found that ethylenediaminetetraacetic acid (EDTA) greatly reduced the overall rate of dioxetane decomposition in methanol solvent, and that activation parameters in this solvent approached those in the aprotic solvents.

We now report a kinetic study of the thermal decomposition of the four dioxetanes (**1a–d**) in methanol solvent. According to our earlier proposal,[3] increased phenyl substitution on the dioxetane ring is expected to increase the rate if a concerted decomposition occurs. In contrast, little effect on the rate is expected if a stepwise process is operative. Thus, one can evaluate the possibility of a concerted vs. a stepwise decomposition in methanol solvent with **1a–d.** The mode of decomposition is of particular interest since the efficiency of production and the electronic state of carbonyl products may be dependent upon the decomposition mechanism.



1a, $R_1 = R_2 = CH_3$
b, $R_1 = CH_3$; $R_2 = C_6H_5$
c, $R_1 = R_2 = C_6H_5$
d, $R_1 = R_2 = C_6H_5CH_2$

Results

Kinetic data for the decomposition of the four 1,2-dioxetanes (**1a–d**) in methanol in the presence of EDTA are given in Table I. The rate of dioxetane disappearance was followed by the decay of light emission from the acceptor [9,10-diphenylanthracene (DPA)], which was contained in the aerated solutions. Good first-order plots were obtained through at least 3 half-lives. To substantiate the first-order behavior, initial concentrations of the dioxetanes were var-

Table I. Thermal Decomposition of **1a–d** in Methanol with EDTA as measured by DPA Emission

1,2-Dioxetane	Temp, °C	10^4k,[a] sec^{-1}
1a[b]	32.88	0.806 ± 0.003
	33.36	0.919 ± 0.002
	37.02	1.30 ± 0.008
	40.19	1.85 ± 0.01
	45.02	3.13 ± 0.01
	51.86	5.75 ± 0.03
	55.20	8.15 ± 0.04
	58.23	11.5 ± 0.03
	60.16	13.7 ± 0.09
	63.23	18.3 ± 0.05
	63.15	19.6 ± 0.07[c]
1b[d]	34.01	1.15 ± 0.004
	40.10	2.34 ± 0.01
	48.59	5.69 ± 0.01
	57.11	14.0 ± 0.01
	63.06	23.2 ± 0.04
	63.12	23.5 ± 0.05
	63.13	23.8 ± 0.04[e]
	63.14	23.3 ± 0.03[e]
1c[f]	30.20	1.32 ± 0.01
	34.87	2.27 ± 0.01
	40.17	3.86 ± 0.01
	40.25	4.05 ± 0.01
	49.18	10.5 ± 0.02
	49.38	11.1 ± 0.03
	52.05	14.8 ± 0.06
	56.12	22.5 ± 0.04
	59.28	33.7 ± 0.13
	63.02	46.2 ± 0.10
	63.13	47.7 ± 0.08[g]
1d[h]	34.90	0.453 ± 0.004
	40.26	0.903 ± 0.006
	45.09	1.45 ± 0.01[i]
	56.19	4.88 ± 0.05
	59.70	6.86 ± 0.03
	60.07	6.68 ± 0.04[j]
	61.06	9.18 ± 0.03[k]
	(60.07)[l]	
	62.98	9.74 ± 0.03[i]

[a] Least-squares fit with probable error. [b] 1.06×10^{-3} *M.* [c] 1.06×10^{-4} *M.* [d] 1.38×10^{-3} *M.* [e] 1.38×10^{-4} *M.* [f] 1.12×10^{-3} *M.* [g] 1.12×10^{-4} *M.* [h] $1.33 \times 10^{-}$ *M.* [i] $7.86 \times 10^{-}$ *M.* [j] 1.12×10^{-3} *M.* [k] 1.12×10^{-2} *M.* [l] The 61.06° run is corrected to 60.07° by the activation parameters in Table II for comparison of tenfold concentration variation.

Table II. Activation Parameters for the Thermal Decomposition of Substituted 1,2-Dioxetanes in Methanol with EDTA[a]

1,2-Dioxetane	E_a[b]	Log A	$\Delta H^{\ddagger}$[b]	$\Delta S^{\ddagger}$[c]	δE_a[b,d]	$\delta\Delta G^{\ddagger}$[b,e]
1a	20.7 ± 0.1	10.72	20.1 ± 0.1	−11.6 ± 0.5	2.3	0.2
1b	21.2 ± 0.1	11.33	20.5 ± 0.1	−9.68 ± 0.38	1.7	0.4
1c	22.2 ± 0.2	12.12	21.6 ± 0.2	−5.11 ± 0.50	0.5	0.1
1d	22.4 ± 0.3	11.55	21.8 ± 0.3	−7.72 ± 1.12	1.9	-0.2

[a] Activation parameters are given with probable error, and they are obtained by least-squares fit. [b] In kcal/mol. [c] In eu. [d] E_a(aprotic solvent) − $E_a(CH_3OH)$. [e] $\Delta G^{\ddagger}$(aprotic solvent) − $\Delta G^{\ddagger}(CH_3OH)$ at 60°.

Table III. Thermal Decomposition of 1,2-Dioxetanes **1b–d** in Methanol in the Absence of EDTA

1,2-Dioxetane	Temp, °C	10^4k, sec^{-1}	Method
1b[a]	35.05	1.37[b]	E[c]
	39.96	2.90[d]	E
	55.25	14.6	E
	63.06	34.2	E
1c[e]	19.59	0.495 ± 0.004	I[f]
	28.08	1.32 ± 0.06	I
	37.62	3.48 ± 0.10	I
	44.89	7.75 ± 0.18	I
	54.06	19.1 ± 1.8	I
	54.06	21.0[g]	I
	54.06	27.2[h]	I
1d[i]	24.73	1.96	I[f]
	35.04	4.64	I
	59.33	26.9	I

[a] $[\mathbf{1b}]_0 = 1.10 \times 10^{-3}$ *M*. [b] Initial rate. The final value in the latter part of the reaction was 1.85×10^{-4} sec^{-1}. [c] By emission with DPA in aerated solutions. [d] Initial rate. The final value was 4.61×10^{-4} sec^{-1}. [e] $[1c]_0 = 1.06 \times 10^{-3}$ *M*. [f] Iodometric method under nitrogen without an acceptor (DPA). [g] With 0.104 *M* styrene in aerated solution. [h] Initial rate in aerated solution. The final rate is 20.0×10^{-4} sec^{-1}. [i] $[\mathbf{1d}]_0 = 1.10 \times 10^{-3}$ *M*.

Table IV. Activation Parameters for the Thermal Decomposition of 1,2-Dioxetanes **1b–d** in Methanol in the Absence of EDTA[a]

1,2-Dioxetane	E_a[b]	Log A	$\Delta H^{\ddagger}$[b]	$\Delta S^{\ddagger}$[c]
1b	23.1 ± 0.7	12.57 ± 0.51	22.5 ± 0.7	−3.3 ± 2.3
1c	20.1 ± 0.2	10.72 ± 0.16	19.5 ± 0.2	−11.8 ± 0.7
1d	14.9 ± 0.1	7.21 ± 0.09	14.3 ± 0.1	−27.9 ± 0.4

[a] Activation parameters are given with probable error, and they are obtained by a least-squares fit. [b] In kcal/mol. [c] In eu.

ied tenfold, and little change in the rate coefficient was observed. Previously, rate coefficients obtained by emission were found to be in agreement with those obtained by iodometric and NMR measurements.[4] From the data in Table I, activation parameters are calculated and given in Table II. The differences between activation energies (δE_a) and free energies of activation ($\delta\Delta G^{\ddagger}$) for the dioxetanes in aprotic solvents (benzene or carbon tetrachloride) vs. methanol are included.

In the absence of EDTA, anomalous kinetic results were obtained, even though methanol was purified by distillation from magnesium turnings. Rate coefficients for the thermal decomposition of **1b–d** in methanol under these conditions are given in Table III. Although some measurements gave reasonably linear first-order plots, others showed curvature. For this reason, some of the rate coefficients in Table III were obtained graphically and others by a least-squares fit where probable error is indicated. As an example of the anomalous behavior, reasonably linear first-order plots were obtained from the decomposition of **1c** under a nitrogen atmosphere. However, in the presence of air, the initial rate increased, and then the final rate approached a value comparable to that obtained under a nitrogen atmosphere. To check the possibility of a radical chain reaction as the culprit of the anomalous kinetics, styrene was used as a radical trap with **1c**. Styrene showed little effect on the rate compared with a measurement in its absence under a nitrogen atmosphere. The kinetic data from Table III produced an unusual order of activation parameters as a function of substitution on the dioxetane ring as seen from Table IV. In aprotic solvents such as benzene[4] or carbon[3] tetrachloride, increased phenyl substitution on the dioxetane ring does not appreciably alter the activation energy for thermolysis. In methanol with EDTA, there is also little effect of phenyl substitution (Table II). The small trend that appears is in the direction of larger E_a values with increased phenyl substitution. In contrast, there is no correlation between phenyl substitution on the dioxetane ring and E_a in methanol without EDTA (Table IV). Anomalous kinetic behavior of tetramethyl-1,2-dioxetane (TMD) in methanol was described to us by Bartlett's group.[5] They found a low activation energy for TMD in methanol when the overall rate was measured by a conventional method. However, the activation energy was comparable to that in benzene when a fast cooling technique, based on light emission, was used.[2]

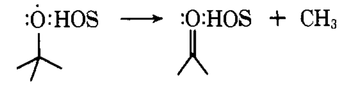
Previously, yields of ketones produced from **1a**,[3] **1b**,[3] **1c**,[4] and **1d**[4,6] were determined in carbon tetrachloride or benzene solution. The yield of acetone from **1a**, generated in situ from chloro-*tert*-butyl hydroperoxide and base in 60% aqueous methanol with EDTA, was reported earlier.[7] Yields of ketones from **1a,c,d** were checked in absolute methanol with EDTA present. Initial dioxetane concentrations were approximately 10^{-3} *M*, and the yields are: **1a**, 95% acetone; **1c**, 93% benzophenone; and **1d**, 84% dibenzyl ketone. These yields are comparable to those obtained previously in other solvents. Similarly, the yield of acetone was reported to be unaltered when TMD was decomposed in methanol compared with benzene solvent.[2]

Discussion

The effect of EDTA on the kinetics of dioxetane decomposition in methanol suggests that metal ion catalysis is responsible for the unusual results in the absence of this sequestering agent. The sensitivity to metal ion catalysis is striking, considering that the methanol solvent was purified by distillation. Catalysis was most dramatic with the dibenzyl derivative **1d**. In the absence of EDTA, the rate of decomposition was about tenfold faster at about 35°, but even more revealing was the decrease in activation parameters. The activation energy was lowered by about 7 kcal/mol and the $\Delta S^{\ddagger}$ by about 20 eu. Kinetic data in the absence of EDTA are presented only to show in a qualitative manner the spurious metal ion catalysis. Reproducibility of the kinetic data in the absence of EDTA is questionable since the kinetics are expected to be highly dependent on the method of solvent purification. The particular metal ion that is responsible for the accelerated rates is unknown. However, the suppression of catalysis by EDTA implicates a transition metal ion. The pronounced metal ion catalysis in methanol, and its effect on activation parameters, suggests that care should be used in the interpretation of these data in other polar solvents unless transition metal ions are scrupulously removed or inactivated by chelation.

Recently some mechanistic possibilities have been considered for transition metal ion-catalyzed decomposition of tetramethyl-1,2-dioxetane.[8] From a study of the catalytic effect of several transition metal ions on the decomposition of the dioxetane, it was concluded that a coordination mechanism involving the metal ion as a Lewis acid was most consistent with the data.[8] This is a particularly intriguing proposal, considering the notorious redox catalytic effect that transition metal ions show in the decomposition of peroxides.[9]

Turning now to the noncatalyzed decomposition of dioxetanes, where EDTA is present, it is noted that there are only small differences in E_a and trivial differences in $\Delta G^\ddagger$ between methanol and aprotic solvents. As a model, from which predictions may be made for the effect of a protic solvent on the rate of dioxetane decomposition, one can consider the fragmentation of the *tert*-butoxy radical (eq 1).[10] Changing from an aprotic solvent such as benzene to a protic solvent acetic acid lowers the enthalpy of activation by about 6 kcal/mol. Solvation of the developing carbonyl group by the protic solvent in the transition state, relative to solvation of the neutral *tert*-butoxy radical, is responsible for the decrease in $\Delta H^\ddagger$. The fragmentation reaction (eq 1) then serves as a model for aprotic to protic solvent changes where a neutral oxy group is transformed into a carbonyl group. The concerted decomposition of a 1,2-dioxetane would correspond to such a process (eq 2), and thus a significant decrease in the activation energy is expected with a change from an aprotic to protic solvent. In contrast, ring opening to the oxy biradical is rate determining in the stepwise decomposition of the dioxetane (eq 3).[3,4,11] Since polar carbonyl species are not involved here, but rather neutral species, little effect is expected upon changing from aprotic to protic solvent. A small lowering of the activation energy could be associated with eq 3 because of steric inhibition to ring closure (step 1) by the protic solvent. As seen from Table II, only small differences in E_a are observed upon changing from aprotic to protic solvents with the four dioxetanes. These differences are even smaller in terms of $\Delta G^\ddagger$, which may be a better measure of the effect, since compensating errors in E_a and log A are common. These results are then most consistent with a stepwise decomposition of the dioxetane (eq 3).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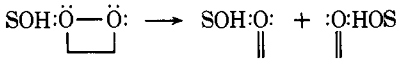
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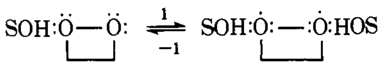
(3)

A further means of evaluating the question of concerted vs. stepwise decomposition is to consider the effect of phenyl substitution on the dioxetane ring. As stated earlier, increased phenyl substitution on the peroxide ring system is expected to decrease the activation parameters if a concerted decomposition occurs. Conversely, little change in activation parameters is expected with phenyl substitution for a stepwise decomposition (eq 3). As seen from Table II, there is little variation in E_a with varying phenyl substitution. The small change that is observed (if it is real) is in the direction of *increased* E_a with increased phenyl substitution (**1a–1c**). Once again the results are most consistent with a stepwise decomposition rather than a concerted decomposition of these dioxetanes. Although a change from an aprotic to a protic solvent might be expected to increase the probability of a concerted decomposition, there is no indication of this occurring with the dioxetanes studied here.

In summary, activation parameters for thermolysis of 1,2-dioxetanes are greatly affected by spurious trace metal ion catalysis even though the methanol solvent is purified by distillation. This catalysis can be suppressed with an appropriate chelating agent such as EDTA. Under these conditions, it appears that reliable first-order kinetics can be obtained, and that the resulting activation parameters are similar to those obtained in aprotic solvents. Considering the effect both of solvent and of phenyl substitution on the dioxetane ring, a stepwise decomposition mechanism is suggested as opposed to a concerted process.

Experimental Section

Materials. Methanol (Matheson, Coleman and Bell reagent) was purified by refluxing over magnesium turnings with a catalytic amount of iodine followed by distillation.[13] The preparation of the 1,2-dioxetanes **1a**,[3,7] **1b**,[3] **1c**,[4] and **1d**[4,6] was previously reported from this laboratory. The 1,2-dioxetanes were stored at −20° in carbon tetrachloride (Matheson Coleman and Bell Spectroquality) solution. Concentrations were determined by NMR with reference to a known quantity of methylene chloride as an internal standard.

Kinetic Methods. Methanol solutions of the 1,2-dioxetanes were prepared by transferring the carbon tetrachloride solutions with a microliter pipet to a known quantity of methanol, which was previously thermostated. For measurements with EDTA, the methanol was previously shaken for about 0.5 hr with the disodium salt of EDTA and stored over this chelating agent. In addition, about 10 mg of this salt and 10 mg of sodium sulfate were placed in the bottom of the reaction vessel. Zero time for the kinetic measurements was defined as the time of injection of the 1,2-dioxetane solution in carbon tetrachloride into the thermostated methanol. For the iodometric method, aliquots were periodically withdrawn and titrated to an end point that was determined by a biamperometric procedure.[14] For the emission method, 10 mg of DPA was added to 3 ml of the methanol solution contained in a Ŧ-stoppered 1-cm cuvette, and the kinetics were measured by a previously described procedure.[4,15]

Products. Analyses for acetone,[7] dibenzyl ketone,[4,6] and benzophenone[4] were obtained by GLC according to previously described methods.

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