

3.453 (3 H, s, COOCH₃), 3.62 (3 H, s, OCH₃), 3.64 (3 H, s, OCH₃), 5.8-6.5 (4 H, 2 AB q, benzyl CH₂'s, $J = 17.3$ Hz), 6.8-7.4 (10 H, 2 aromatic m), 8.04 (1 H, q, thiazolium H, $J = 0.7$ Hz), 8.06 (1 H, q, thiazolium H, $J = 0.7$ Hz); ¹H NMR (250 MHz, CD₃OD) 0.7-1.8 (16 H, m), 1.68 (3 H, s, CH₃), 1.70 (3 H, s, CH₃), 2.18 (3 H, s, CH₃CO), 2.20 (3 H, s, CH₃CO), 2.22 (4 H, m), 2.29-2.30 (6 H, 2 d, aromatic CH₃'s, $J = 0.7$ Hz), 2.7-2.8 (6 H, m), 3.43 (3 H, s, COOCH₃), 3.44 (3 H, s, COOCH₃), 3.54 (3 H, s, OCH₃), 3.57 (3 H, s, OCH₃), 5.5-6.5 (4 H, 2 AB q, benzyl CH₂'s, $J = 16.7$ Hz), 6.8-7.4 (10 H, 2 aromatic m), 7.80 (1 H, q, thiazolium H, $J = 0.7$ Hz), 7.82 (1 H, q, thiazolium H, $J = 0.7$ Hz); IR (CH₂Cl₂) 2940, 1728, 1683, 1578, 1432, 1128, 1055 cm⁻¹; field-desorption mass spectrum calcd for C₂₆H₃₆NO₄S₃ (M⁺ - BF₄⁻) m/e 510 (found m/e 510). Anal. Calcd for C₂₆H₃₆NO₄S₃BF₄: C, 50.25; H, 6.47; N, 2.34; S, 16.10; F, 13.01. Found: C, 50.21; H, 6.33; N, 2.44; S, 16.21; F, 13.01.

Conversion of Adduct 13 into Deuterio-10 plus Methyl Lipoate (14). To adduct 13 (2.0 mg, 3.4 μmol) in CD₃OD (0.4 mL) was added an aqueous solution of NH₂NH₃⁺BF₄⁻ (0.7 μL, 5.0 μmol). This mixture was unchanged during the course of 30 min as monitored by ¹H NMR. A second aqueous solution (1.5 μL) containing NH₂NH₂ (8.6 μmol) and NH₂NH₃⁺BF₄⁻ (8.6 μmol) was added to the ¹H NMR sample. Reintroduction of the sample to the spectrometer and ¹H NMR observation indicated rapid conversion (elapsed time ca. 10 min) of 13 into methyl lipoate (14), deuterio-10, and CH₃CONDND₂. The ¹H NMR of the mixture clearly showed absorptions attributable to these products as compared to spectra of authentic samples in CD₃OD. The ¹H NMR absorptions for deuterio-10 are consistent with its mono-deuteration by solvent: ¹H NMR (250 MHz, CD₃OD) 1.40 (3 H,

s, CH₃), 2.32 (3 H, d, aromatic CH₃, $J = 1$ Hz), 3.33 (3 H, s, OCH₃), 5.66 (2 H, s, benzyl CH₂), 7.0-7.4 (5 H, 2 m, aromatic) 7.87 (1 H, br s, thiazolium H) (cf. ¹H NMR (CD₃OD) of 10 above). ¹H NMR (CD₃OD) for methyl lipoate (14), authentic sample and mixture with deuterio-10 plus CH₃CONDND₂: 1.34 (2 H, complex m), 1.54 (4 H, complex m), 1.77 (1 H, 6-line m), 2.24 (2 H, t), 2.35 (1 H, 6-line m), 3.02 (2 H, complex m), 3.46 (1 H, 8-line m), 3.55 (3 H, s). ¹H NMR (CD₃OD) of CH₃CONDND₂, authentic sample and mixture with deuterio-10 plus 14: 1.79 (s).

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Registry No. 6, 70625-03-5; 7, 70625-04-6; 8, 70625-05-7; 8 protonated, 4356-66-5; 9b, 70625-09-1; 10, 70625-11-5; 11, 70625-84-5; 12, 76756-41-7; 13 (isomer 1), 76756-43-9; 13 (isomer 2), 76756-45-1; 14, 46236-19-5; 15, 925-33-7; 16, 76756-46-2; PhSSPh, 882-33-7; PhCH₂SSCH₂Ph, 150-60-7; EtSSEt, 110-81-6; CH₃COSPh, 934-87-2; PhSH, 108-98-5; PhCH₂SH, 100-53-8; CH₃COSEt, 625-60-5; *N*-(phenylthio)phthalimide, 14204-27-4; 4-methylthiazole, 693-95-8; acetaldehyde 2,4-dinitrophenylhydrazone, 1019-57-4; 3-benzyl-4-methylthiazolium tetrafluoroborate, 76756-47-3; 2-(α -hydroxyethyl)-4-methyl-thiazole, 7586-99-4; 2-(α -methoxyethyl)-4-methylthiazole, 76756-48-4; *N,N'*-thiobisphthalimide, 7764-29-6; 3-benzyl-2-(α -hydroxyethyl)-4-methylthiazolium bromide, 13079-87-3.

Kinetics and Mechanism of the Thermolysis of a Five-Membered-Ring Peroxide, 3,3,5,5-Tetramethyl-1,2-dioxolane

William H. Richardson,* Ronald McGinness, and H. Edward O'Neal*

Chemistry Department, San Diego State University, San Diego, California 92182

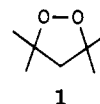
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The kinetics of the thermolysis of 3,3,5,5-tetramethyl-1,2-dioxolane (1) was studied in benzene solution with a free-radical chain inhibitor (2,6-di-*tert*-butyl-*p*-cresol) in the gas phase. The peroxide 1 was susceptible to induced decomposition both in solution without the inhibitor and in the gas phase without conditioned reactor walls. However, under optimum conditions, first-order kinetics were observed in both the gas phase and in solution. Activation parameters for the thermolysis of 1 in benzene solution with the inhibitor at 500 K are $E_a = 44.6 \pm 0.9$ kcal/mol, $\log A = 15.85 \pm 0.42$, $\Delta H^\ddagger = 43.6 \pm 0.9$ kcal/mol, and $\Delta S^\ddagger = 11.0 \pm 1.9$ eu. In the gas phase, the parameters at 500 K are $E_a = 45.5 \pm 0.3$ kcal/mol, $\log A = 15.72 \pm 0.13$, $\Delta H^\ddagger = 44.5 \pm 0.3$ kcal/mol, and $\Delta S^\ddagger = 10.4 \pm 0.6$ eu. These parameters closely approach calculated activation parameters for 1 which are based on a stepwise biradical decomposition mechanism: $E_a = 48.6$ kcal/mol, $\log A = 16.55$, $\Delta H^\ddagger = 47.6$ kcal/mol, and $\Delta S^\ddagger = 14.2$ eu at 500 K. Considering the susceptibility of 1 to induced decomposition, which will lower the activation parameters, the close approach of the experimental to the calculated parameters indicates that 1 undergoes decomposition by a stepwise biradical route. Thus, there is no mechanistic discontinuity between the stepwise biradical mechanism observed with simply substituted 1,2-dioxetanes (four-membered-ring peroxides) and the five-membered-ring peroxide 1.

Thermolysis of the four-membered-ring peroxides, 1,2-dioxetanes, is well accommodated in most instances by a stepwise decomposition process.^{1,2} Activation parameters for the thermolysis of many substituted dioxetanes fall

within a limited range, and these experimental parameters are usually in good agreement with calculated values, based on a stepwise process.²

We expected that 1,2-dioxolanes, the next higher homologue from 1,2-dioxetanes, would also undergo thermolysis in a stepwise manner. Yet, the calculated activation parameters for 3,3,5,5-tetramethyl-1,2-dioxolane (1),



1

based on a stepwise process, differed considerably from

(1) J.-Y. Koo and G. B. Schuster, *J. Am. Chem. Soc.*, **99**, 5403 (1977).
 (2) (a) W. H. Richardson, J. H. Anderegg, M. E. Price, and R. Crawford, *J. Org. Chem.*, **43**, 4045 (1978); (b) W. H. Richardson, J. H. Anderegg, M. E. Price, W. A. Tappen, and H. E. O'Neal, *ibid.*, **43**, 2236 (1978); (c) W. H. Richardson, F. C. Montgomery, P. Slusser, and M. B. Yelvington, *J. Am. Chem. Soc.*, **97**, 2819 (1975); (d) W. H. Richardson, F. C. Montgomery, M. B. Yelvington, and H. E. O'Neal, *ibid.*, **96**, 7525 (1974); (e) W. H. Richardson, M. B. Yelvington, and H. E. O'Neal, *ibid.*, **94**, 1619 (1972).

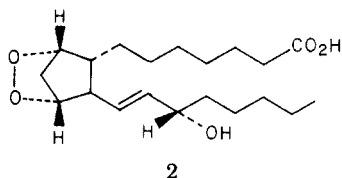
Table I. Kinetic Data for the Thermolysis of 3,3,5,5-Tetramethyl-1,2-dioxolane (1) in Benzene with 2,6-Di-*tert*-butyl-*p*-cresol (DBC)^a

temp, °C	10 ⁷ <i>k</i> , °C s ⁻¹	temp, °C	10 ⁷ <i>k</i> , °C s ⁻¹
162.35	3.08 ± 0.08	192.90	92.0 ± 4.8
162.35	2.95 ± 0.37 ^b	203.87	292 ± 32
173.10	12.1 ± 0.5	204.00	256 ± 15
182.30	25.8 ± 1.7		

^a [1] = 5.00 × 10⁻² M, [DBC] = 7.7 × 10⁻³ M, and [C₆H₅CH₃] = 1.71 × 10⁻² M as the internal GLC standard.
^b [1] = 9.69 × 10⁻⁴ M, [DBC] = 7.7 × 10⁻⁴ M, and [C₆H₅CH₃] = 1.71 × 10⁻³ M as the internal GLC standard.
^c Least-squares fit of individual measurements with standard error.

the reported experimental values.³ In an effort to resolve this apparent mechanistic discontinuity between dioxetanes and dioxolanes, we have studied the kinetics of thermolysis of 1 in benzene with a free-radical trap and in the gas phase. The results are reported here along with the calculated activation parameters for 1, based on a stepwise process.

In addition to resolution of the mechanistic relationship between dioxetanes and dioxolanes, it is of interest to have the mechanism of 1,2-dioxolane thermolysis established due to the relationship of this peroxide to the biologically important prostaglandins.⁴ In the biological oxidation of arachidonic acid, the endoperoxide is a proposed intermediate enroute to the prostaglandins.⁵ It is seen from 2, that the peroxidic function is fused in a composite 1,2-dioxolane and 1,2-dioxane system.



Results

Considering the possibility that induced decomposition might be responsible for the lower values of the experimental activation parameters as compared to calculated values, we used a radical trap [2,6-di-*tert*-butyl-*p*-cresol (DBC)] in our solution kinetic studies. Indeed, the rate was reduced in the presence of 7.7 × 10⁻³ M DBC in benzene solution with 1 (5.00 × 10⁻² M) by a factor of 2.7-fold (= 8.15 × 10⁻⁷ s⁻¹/3.08 × 10⁻⁷ s⁻¹)⁶ at 160 °C. First-order plots were usually observed with 1 in the presence of DBC, and with a 52-fold change in the initial concentration of 1, the first-order rate coefficient was reasonably constant (cf. Table I). Rate data for 1 in benzene solution with DBC are given in Table I as a function of temperature. From the data in Table I, the following activation parameters are calculated by a least-squares method, where the standard error is given: $E_a = 44.6 \pm 0.9$ kcal/mol, $\log A$ (s⁻¹) = 15.85 ± 0.42, ΔH^\ddagger

(3) (a) W. Adam and N. Durán, *J. Am. Chem. Soc.*, **99**, 2729 (1977); (b) W. Adam and N. Durán, *J. Org. Chem.*, **38**, 1434 (1973).

(4) Cf. (a) D. A. Dorp in "Chemistry, Biochemistry, and Pharmacological Activity of Prostanoids", S. M. Roberts and F. Scheinmann, Eds., Pergamon Press, New York, 1979, pp 233-242; (b) P. Crabbe, *Chem. Br.*, **11**, 132 (1975).

(5) (a) B. Samuelsson, *J. Am. Chem. Soc.*, **87**, 3011 (1965); (b) M. Hamberg and B. Samuelsson, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 899 (1973); (c) M. Hamberg, J. Svensson, T. Wakabayashi, and B. Samuelsson, *ibid.*, **71**, 345 (1974); (d) D. H. Nugteren and E. Hazelhof, *Biochim. Biophys. Acta*, **326**, 448 (1973).

(6) The rate coefficient of 8.15 × 10⁻⁷ s⁻¹ at 160 °C is calculated from the activation parameters reported in ref 3. In cumene solvent with [1] = 5.00 × 10⁻² M and no inhibitor, we obtain an initial rate (37% reaction) of 1.09 × 10⁻⁶ s⁻¹ at 160 °C.

Table II. Kinetic Data^a for the Thermal Decomposition of 3,3,5,5-Tetramethyl-1,2-dioxolane (1) in the Gas Phase

temp, °C	10 ⁷ <i>k</i> , s ⁻¹	% conversion	reactor
230.0	880 ± 54 ^c	~34	unpacked
	3210	~34	packed
	820 ^b	~5	packed
215.0	209 ± 32 ^c	~19	unpacked
	350 ± 30	~13	packed
	193 ^b	~4	packed
200.1	84 ± 12	~22	unpacked
	49 ± 7 ^{b,c}	~13	unpacked
	135 ± 10	~13	packed
185.0	27.8 ^b	16	unpacked
	47.4 ± 5	23	unpacked
	52.4 ± 5	20	packed

^a Except where noted, the rate constants are the weighted average of several runs, with the standard deviations of the slopes of the first-order plots for all runs being used to determine the weighting factors for each rate constant. The errors represent the weighted average of the standard deviations for the rate constants. ^b Single rate constant measurements. ^c Rate constants utilized in the Arrhenius equation to obtain estimates of the gas-phase, homogeneous, unimolecular dissociation process.

= 43.6 ± 0.9 kcal/mol (500 K), $\Delta S^\ddagger = 11.0 \pm 1.9$ eu (500 K).

In order to eliminate the possibility of unusual solvent effects and to reduce the likelihood of induced decomposition, we studied the thermolysis of 1 in the gas phase. It was found that the gas-phase reaction over nonconditioned surfaces is strongly surface sensitive, and repeated decompositions were required before reasonably reproducible, minimum rate behaviors were realized. Decomposition rates over nonconditioned surfaces were up to two orders of magnitude faster than those over conditioned surfaces. It was also necessary to exclude oxygen from the reactors since exposure to oxygen apparently reactivated the catalytic wall sites.

Product catalysis was also very apparent. In wall-conditioned reactors, reasonably good first-order plots of the data were realized in the initial reaction stages; however, deviations occurred at higher conversions at rates which accelerated with time: the lower the reaction temperatures, the earlier the onset of these departures. Thus, first-order kinetics extended to about 34% reaction at 230 °C, to 20% reaction at 215 °C, to 13% reaction at 200 °C, and probably to lower conversions than our observational values (~15%) at 185 °C.

The reaction was studied in two reactors, an unpacked Pyrex cell ($V = 184$ cm³) with $S/V \approx 1.2$ cm⁻¹ and a packed Pyrex cell filled with 8-mm Pyrex tubing with $S/V \approx 10.9$ cm⁻¹. Although deviations from first-order kinetics occurred at lower conversions in the packed reactor than in the unpacked reactor at the same temperature, rate constants from the packed reactor at very early stages of reaction at the higher temperatures were in reasonably good agreement with those measured in the unpacked reactor. This suggests that the initial stage of the dioxolane decomposition is not surface sensitive and that wall catalysis is not initiated by reactant-wall interactions. Rather, catalysis arises from wall interactions of a product (or products) of the reaction.

Kinetic results of the gas-phase decomposition are shown in Table II. An Arrhenius plot of the rate constants from the unpacked reactor (Figure 1) exhibits considerable curvature at the lowest temperatures, and an examination of the data suggests that this is caused by the autocatalysis discussed above. Thus at 200 °C, the rate constant evaluated at 13% conversion is a factor of 1.7 lower than

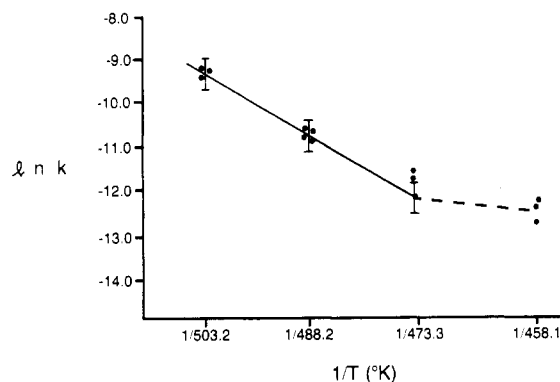


Figure 1. Arrhenius plot for the gas-phase thermolysis of 1.

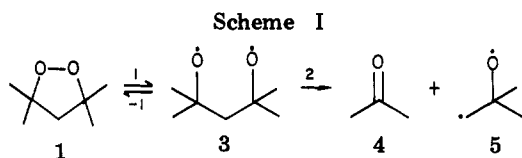


Table III. Group Additivity Calculations for 1

no. of groups	group	group values		
		$\Delta H_f^{\circ}_{300}$, kcal/mol	$S_f^{\circ}(\text{int})$, eu	$C_p^{\circ}_{400}$, eu
4	[C-(C)(H) ₃]	4(-10.2)	4(30.4)	4(7.84)
1	[C-(C) ₂ (H) ₂]	-4.93	9.42	6.95
2	[C-(C) ₃ (O)]	2(-6.6)	2(-33.6)	2(6.19)
2	[O-(O)(C)]	2(-4.5)	2(9.4)	2(3.7)
ring cor		5.90	23.30	-5.40
cor for (1) two axial methyls		2(0.54)		
(2) 1,3-diaxial methyl-methyl		1.2		
total		-59.71	105.92	52.69

the rate constants from runs carried to 22% conversions. The same trend is apparent in the 185 °C data as well. In fact, it is likely that none of the rate constants observed at 185 °C are free from autocatalysis.

If one assumes that the lowest rate constant observed at 200 °C is most representative of the true homogeneous gas-phase reaction, then a good Arrhenius plot results from the data of the upper three temperatures. The resulting Arrhenius parameters are $\log A$ (s^{-1}) = 15.72 ± 0.13 and E_a = 45.5 ± 0.3 kcal/mol. Because of the complexity of the system, the true errors in the above parameters are certainly larger. Also, since all reaction complications lead to a lowering of the experimental Arrhenius parameters, one would expect that the true values for the homogeneous, unimolecular decomposition of dioxolane 1 are either equal to or larger than the experimental values.

Activation parameters for 1 were calculated on the basis of Scheme I, where step 2 is rate determining. Values of ΔH_f° , $S_f^{\circ}(\text{int})$, and $C_p^{\circ}_{400}$ are calculated by standard group additivity methods,⁷ and they are given in Tables III and IV. The 1,3-diaxial methyl-methyl interaction is not reported to our knowledge. This interaction in 1 was approximated by assuming that it was proportional to the axial methyl interaction in cyclopentane *vs.* cyclohexane. With a 1,3-diaxial methyl-methyl repulsion of 3.7 kcal/mol in cyclohexane,⁸ the corresponding repulsion in cyclopentane is then 1.2 kcal/mol (=3.7 × 0.54/1.7), where 0.54⁹

(7) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Wiley, New York, 1976.

(8) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Interscience, New York, 1965, p 52.

Table IV. Group Additivity Calculations for 3

no. of groups	group	group values		
		$\Delta H_f^{\circ}_{300}$, kcal/mol	$S_f^{\circ}(\text{int})$, eu	$C_p^{\circ}_{400}$, eu
4	[C-(C)(H) ₃]	4(-10.2)	4(30.2)	4(7.84)
1	[C-(C) ₂ (H) ₂]	-4.93	9.42	6.95
2	[C-(C) ₃ (O)]	2(8.6)	2(-7.5)	2(9.10)
2	C,C gauche interactions	2(0.8)		
2	O,C gauche interaction	2(0.35) ¹²		
doublet cor			-2.75 ^a	
totals		-26.23	112.47	56.51

^a This value from $-2R \ln 2$.

Table V. Experimental Activation Parameters for 1 in Solution and the Gas Phase vs. Calculated Values

phase	E_a^a	$\log A^b$	$\Delta H^{\ddagger a,d}$	$\Delta S^{\ddagger c,d}$
C ₆ H ₆ (inhibitor)	44.6 ± 0.9	15.85 ± 0.42	43.6 ± 0.9	11.0 ± 1.9
gas	45.5 ± 0.3	15.72 ± 0.13	44.5 ± 0.3	10.4 ± 0.6
calcd ^d	48.6	16.55	47.6	14.2

^a In kilocalories per mole. ^b In reciprocal seconds. ^c In entropy units. ^d Calculated at 500 K.

and 1.7¹¹ kcal/mol are the axial methyl interactions in cyclopentane and cyclohexane, respectively.

From Tables III and IV, the following values for step 1 in Scheme I are obtained at 300 K: $\Delta H^{\circ}_{1,-1}$ = 33.5 kcal/mol; $\Delta S^{\circ}_{1,-1}$ = 6.55 eu. These values are corrected to average reaction temperatures by using average heat capacities, $\Delta C_p^{\circ}_{300-500}$, where the latter value is set equal to $\Delta C_p^{\circ}_{400}$ and obtained from Tables III and IV. Values for $\Delta H^{\circ}_{1,-1}$ and $\Delta S^{\circ}_{1,-1}$ are calculated at 500 K with this heat capacity correction to be $\Delta H^{\circ}_{1,-1,500}$ = 33.5 + 200(56.51 - 52.69) × 10⁻³ = 34.3 kcal/mol and $\Delta S^{\circ}_{1,-1,500}$ = 6.55 + 200(56.51 - 52.69)/400 = 8.5 eu.

Providing that the activation energy for step 2 in Scheme I is greater than for step -1, the reaction activation energy will be given by $E_a = \Delta H^{\circ}_{1,-1} + E_2$. The value of the activation energy for step 2 (i.e., E_2) can be approximated as being equal to that for β scission of the *tert*-pentoxy radical; i.e., $E_2 = E_a(\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{O}\cdot)$ = 14.3¹³ kcal/mol. The activation energy for reclosure of 3 to 1 (E_{-1}) is taken as the ring strain in a five-membered ring or 6 kcal/mol.⁷ Comparing E_{-1} to E_2 , it is seen that step 2 is rate determining. The reaction activation energy is then estimated to be $E_a = \Delta H^{\circ}_{1,-1} + E_2 = 34.3 + 14.3 = 48.6$ kcal/mol at 500 K. The entropy of activation for thermolysis of 1 is estimated from $\Delta S^{\ddagger} = \Delta S^{\circ}_{1,-1} + \Delta S^{\ddagger}(\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{O}\cdot)$ = 8.5 + 5.7¹³ = 14.2 eu at 500 K. The calculated activation parameters for thermolysis of 1 along with the experimental values in solution and the gas phase are summarized in Table V.

Discussion

Tertiary dialkyl peroxides usually do not exhibit significant induced decomposition in dilute inert solvents or in the gas phase.^{14,15} Yet, from the rate reduction by a

(9) The axial methyl interaction in cyclopentane is calculated from the difference between the experimental heats of formation for *cis*-1,3-dimethylcyclopentane (-32.47 kcal/mol) and the *trans* isomer (-31.93 kcal/mol).¹⁰

(10) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

(11) Reference 8, p 44.

(12) The [gauche C,O] value is taken as half the cyclohexane A_{OH} value,¹¹ which is a previously used approximation.^{2d}

(13) L. Batt, T. S. A. Islam, and G. N. Rattray, *Int. J. Chem. Kinet.*, **10**, 931 (1978).

factor 2.7-fold in the presence of a radical trap in benzene solution, induced decomposition is suggested with 1. This is further indicated by comparing activation parameters in benzene with and/or without a radical trap and in the gas phase. The reported activation parameters in benzene solution without a radical trap are³ $\Delta H^\ddagger = 27.0$ kcal/mol and $\Delta S^\ddagger = -24.8$ eu, while those reported here with a radical trap in benzene solution and in the gas phase are much higher (cf. Table V). Typically, induced decomposition is associated with lower values of both ΔH^\ddagger and ΔS^\ddagger .¹⁷ Considering space-filling molecular models, it is noted that the peroxidic oxygens are exposed in 1 as compared to di-*tert*-butyl peroxide. It seems that the unusual susceptibility of 1 to induced decomposition is associated with this stereochemical feature. It is then most likely that induced decomposition arises from an S_H2 reaction on the peroxide bond,^{16bc} rather than being associated with hydrogen atom abstraction from a methyl group followed by a neighboring radical attack on the peroxide function.^{16a}

The gas-phase activation parameters are in surprisingly good agreement with the maximal inhibited solution decomposition parameters, and both solution and gas-phase results are in satisfactory agreement with the transition-state estimates for the consecutive, biradical pathway. However, the estimated parameters are higher in both activation energy and entropy compared to the experimental values in Table V. This suggests some residual induced decomposition in both the gas-phase and inhibited solution decompositions. Considering the sensitivity of 1 to induced decomposition and the close approach of the experimental values to the estimated parameters, assignment of the mechanism of decomposition to that given in Scheme I is justified. Thus, there is no discontinuity between the mechanisms of thermolysis of four- and five-membered-ring peroxides. In both instances, a stepwise biradical mechanism best accommodates the data.

Experimental Section¹⁸

2,4-Dimethyl-2,4-pentanediol. This diol was prepared from

(14) Cf. W. H. Richardson and H. E. O'Neal, "Comprehensive Chemical Kinetics", Vol. 5, C. H. Bamford and C. F. H. Tipper, Eds., Elsevier, New York, 1972, pp 483, 488.

(15) Tertiary dialkyl peroxides do show induced decomposition as neat liquids or in reactive solvents at higher concentrations.^{14,16}

(16) (a) E. S. Huyser and K. J. Jankauska, *J. Org. Chem.*, **35**, 3196 (1970); (b) S. H. Goh, R. L. Huang, S. H. Ong, and I. Sieh, *J. Chem. Soc. C*, 2282 (1971); (c) S. H. Goh, *J. Org. Chem.*, **37**, 3098 (1972).

(17) Reference 14, p 483, 488, 539.

(18) Temperatures of kinetic measurements are corrected, but boiling points are uncorrected. The NMR and IR spectra were measured in 10% w/v carbon tetrachloride solutions. The NMR spectra were measured with a Varian A-60 spectrometer and the IR spectra were measured with a Perkin-Elmer 337 spectrometer. The NMR data are reported on the δ scale in parts per million as (δ , coupling, area). Mass spectral data were obtained with a Hitachi RMU-6E spectrometer, and they are reported as m/e (relative intensity). GLC analyses were performed with a Hewlett-Packard 5830A reporting chromatograph for the solution-phase kinetic data and with a Varian 1400 FID chromatograph equipped with a Sargent Model T-12 disk integrator recorder for gas-phase data.

diacetone alcohol (4-hydroxy-4-methyl-2-pentanone) and methylmagnesium iodide by a previously reported procedure:¹⁹ 49% yield; bp 86–89 °C (8 mm) [lit.¹⁹ bp 98 °C (13 mm)]; IR 3620, 3370 (OH), 2970, 2930 cm^{-1} (aliphatic C-H); NMR CH_3 (1.25, s, 12), CH_2 (1.63, s, 2.0), OH (4.62, s, 2.0).

3,3,5,5-Tetramethyl-1,2-dioxolane (1). A method similar to a previously reported procedure was employed,²⁰ except that an acid catalyst was used along with lower strength hydrogen peroxide. To 15 mL (220 mmol) of 50% hydrogen peroxide (Matheson Coleman and Bell) at 0 °C was added 1.5 mL of concentrated sulfuric acid over 10 min with stirring. Then 6.55 g (44.6 mmol) of 2,4-dimethyl-2,4-pentanediol was added over 15 min with stirring, while the acidic hydrogen peroxide solution was cooled in an ice bath. The temperature was slowly allowed to reach room temperature, and stirring was then allowed to continue for 48 h. Water (15 mL) was added dropwise, and the organic phase was separated. The aqueous phase was extracted with three 15-mL portions of pentane. The combined organic phases were washed with saturated sodium bicarbonate solution and water. The organic phase was dried over sodium sulfate and rotoevaporated (bath temperature 35 °C) to give 2.21 g of crude 1. Distillation [bp 47–49 °C (25 mm) (lit.²⁰ bp 44–46 °C (24 mm))] gave 1.08 g (17% yield) of 1: IR no OOH or OH; NMR CH_3 (1.27, s, 12), CH_2 (2.07, s, 2.05); mass spectrum, m/e (relative intensity) 131 (2.3, $M^+ + 1$), 130 (21, M), 115 (8.2, $M - \text{CH}_3$), 43 (100, CH_3CO^+). Purified 1 gave a negative potassium iodide starch paper test.

The aqueous phase from the reaction was extracted with ten 10-mL portions of methylene chloride. The organic phase was dried over sodium sulfate and rotoevaporated at 35 °C to give 2.13 g of a liquid, which by iodometric analysis was estimated to be 52% 2,4-bis(hydroperoxy)-2,4-dimethylpentane.²⁰

Kinetic Methods. Solutions of 1, DBC, and toluene as an internal standard in benzene solution were sealed in 1-mm-o.d. capillary tubes. The tubes were immersed in a constant-temperature bath and periodically withdrawn. GLC analyses for 1 (retention time 6.6 min) and toluene (retention time 4.2 min) were carried out on a 5% methylvinylsilicone on Chromosorb W column (5 ft \times 1/8 in.) with a column temperature of 65 °C, an injector temperature of 120 °C, a detector temperature of 120 °C, and a flow rate of 19 cm^3/min of nitrogen.

The gas-phase reactors were two Pyrex cylindrical cells immersed in a thermostated Dow 550 silicone oil bath. Introduction of about 1200 torr of reactant mixture (0.033% peroxide, 0.60% propylene in nitrogen) to the reactors initiated a kinetic run. Reaction rates were monitored in terms of changes in reactant concentration with time.

GLC analysis of as many aliquots²¹ as could be conveniently withdrawn in the course of the run were made on a 5 ft \times 1/8 in. 5% SEL-30 silicone oil on Chromosorb W column.

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Registry No. 1, 22431-90-9; 3, 76630-97-2; 2,4-dimethyl-2,4-pentanediol, 24892-49-7; 2,4-bis(hydroperoxy)-2,4-dimethylpentane, 61756-35-2.

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(21) In practice, the average useful number of data points per run varied as follows with temperature: 6 at 230 °C, 9 at 215 °C, 12 at 200 °C, and 12 at 185 °C. The number of points was limited by sampling times and by reaction times for first-order kinetic behavior.