The Base-Catalyzed Fragmentation of 2-*tert*-Butylperoxy-2-methyl-1-propanol

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A kinetic and product study of the base-catalyzed fragmentation of 2-*tert*-butylperoxy-2-methyl-1-propanol (2) is reported. The products of the reaction in 40% aqueous methanol are *tert*-butyl alcohol, acetone, and formaldehyde. An ionic mechanism is proposed in this solvent, which is consistent with the product studies and the first-order dependence on both 2 and the base. The rate of decomposition of 2 in chlorobenzene at 100° was not found to be appreciably accelerated by triethylamine. These data allow comparisons to be made with the analogous base-catalyzed fragmentation reactions of 2-*tert*-butylperoxy-2-methylpropanoic acid and 3-chloro-2,2-dimethyl-1-propanol. The fragmentation of 2 was considered as a possible source of excited-state formaldehyde. However, the lack of light emission from an acceptor (fluorescein) added to the reaction mixture indicates that excited state formaldehyde is not produced. Calculations verify this observation.
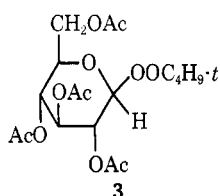
Although free-radical reactions of peroxides are well known, there is a growing body of reported ionic reactions of peroxides.[1] In this area we previously described the ionic fragmentation reaction of 2-*tert*-butylperoxy-2-methylpropanoic acid (1).[2] An anal-

$$(CH_3)_3COOC(CH_3)_2CO_2H$$

1
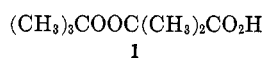
ogous fragmentation reaction was proposed more recently during the course of biological oxidations involving certain hydroxylases that require α-ketoglutarate as a cofactor.[3] We have now found that the alcohol (2) corresponding to 1 undergoes a simi-

$$(CH_3)_3COOC(CH_3)_2CH_2OH$$

2
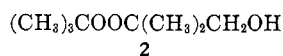
lar base-catalyzed ionic fragmentation reaction. Although there are a number of proposed fragmentation reactions of peroxides,[4] with various electrofugal and nucleofugal groups,[5] to our knowledge the fragmentation reaction of an isolated hydroxy peroxide corresponding to 2 has not been reported. Such a fragmentation reaction may have occurred during the basic methanolysis of *tert*-butylperoxy 2,3,4,6-tetraacetyl-β-D-glucoside (3);[4e] however, the fragmentation

3

may have proceeded *via* the tetrahedral alkoxide ion intermediate formed in the methanolysis of the ester.

Since 2 offers the opportunity of studying a fragmentation reaction of the simplest hydroxy peroxide, without complicating elimination reactions, we now report the products and kinetics of the base-catalyzed decomposition of this peroxide. Comparisons are made to other fragmentation and elimination reactions. The possibility of chemiluminescence from the fragmentation of 2 is also considered.

Results

Products.—In 40% aqueous methanol, the products for the basic (0.254 M sodium hydroxide) decomposition of 2 (4.13 × 10⁻² M) at 30° are *tert*-butyl alcohol (100.6 ± 1.8% yield) and acetone (64.2 ± 1.8% yield). The yields are based on eq 1 and result from an average of

$$2 \xrightarrow[\text{40\% aq MeOH}]{\text{OH}^-} (CH_3)_3COH + CH_3COCH_3 + CH_2O \quad (1)$$
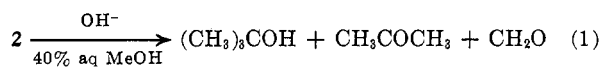
five measurements. The companion product is formaldehyde. Previously we have found that formaldehyde and acetone, under these basic conditions, undergo a condensation reaction.[6] Numerous products are reported from the base-catalyzed formaldehyde–acetone condensation reaction, where some products result from the condensation of more than one formaldehyde molecule per acetone.[7] Considering the quantitative yield of *tert*-butyl alcohol, the lower yield of acetone can be attributed to the formaldehyde–acetone condensation reactions. Furthermore, quantitative yields of both acetone and *tert*-butyl alcohol are produced in the base-catalyzed fragmentation of 1, where formaldehyde is not formed.[2]

Kinetic Data.—Typically kinetic measurements were made over 3 half-lives and acceptable first-order rate coefficients were obtained in individual measurements as indicated by the probable error. At constant base concentration (0.0821 M), the reaction is first order in 2 over a tenfold variation in the initial concentration of this reactant (Table I). First-order dependence upon base concentration is also observed, where constant second-order rate coefficients (k_2) are obtained from the ratio of the observed psuedo-first-order coefficient (k_{obsd}) to base concentration (Table II). The first-order dependence upon base concentration is further

(1) R. Curci and J. O. Edwards in "Organic Peroxides," Vol. I, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1970, p 199.

(2) (a) W. H. Richardson and R. S. Smith, *J. Amer. Chem. Soc.*, **89**, 2230 (1967); (b) *ibid.*, **91**, 3610 (1969).

(3) (a) B. Lindblad, G. Lindstedt, M. Tofft, and S. Lindstedt, *ibid.*, **91**, 4604 (1969); (b) C. K. Liu, P. M. Shaffer, R. S. Slaughter, R. P. McCroskey, and M. T. Abbott, *Biochemistry*, **11**, 2172 (1972), and references cited therein.

(4) (a) M. Schulz and H. Steinmaus, *Angew. Chem., Int. Ed. Engl.*, **2**, 623 (1963); (b) M. Schulz and H.-F. Boeden, *Tetrahedron Lett.*, 2843 (1966); (c) M. Schulz and L. Somogyi, *Angew. Chem., Int. Ed. Engl.*, **6**, 168 (1967); (d) M. Schulz, H.-F. Boeden, and E. Gründemann, *Z. Chem.*, **7**, 13 (1967); (e) M. Schulz, H.-F. Boeden, and P. Berlin, *Justus Liebigs Ann. Chem.*, **703**, 190 (1967); (f) E. Schmitz, D. Habisch, and R. Ohme, *J. Prakt. Chem.*, **37**, 252 (1968); (g) J. Hoffman, *J. Amer. Chem. Soc.*, **79**, 503 (1957); (h) D. D. Jones and D. C. Johnson, *J. Org. Chem.*, **32**, 1402 (1967); (i) D. H. R. Barton and E. Seoane, *J. Chem. Soc.*, 4150 (1956); (j) H. H. Wasserman and M. B. Floyd, *Tetrahedron Lett.*, 2009 (1963); (k) W. Reusch and R. LeMahieu, *J. Amer. Chem. Soc.*, **85**, 1669 (1963); (l) L. J. Bollyky, R. H. Whitman, R. A. Clarke, and M. M. Rauhut, *J. Org. Chem.*, **32**, 1663 (1967); (m) M. Avramoff and Y. Sprinzak, *J. Amer. Chem. Soc.*, **85**, 1655 (1963); (n) M. M. Rauhut, D. Sheehan, R. A. Clarke, B. G. Roberts and A. M. Semsel, *J. Org. Chem.*, **30**, 3587 (1965); (o) R. Hiatt in "Organic Peroxides," Vol. II, D. Swern, Ed., Wiley-Interscience, New York, N. Y., 1971, p 81.

(5) C. A. Grob and P. W. Shiess, *Angew. Chem., Int. Ed. Engl.*, **6**, 1 (1967).

(6) W. H. Richardson and V. F. Hodge, *J. Amer. Chem. Soc.*, **93**, 3996 (1971).

(7) T. White and R. N. Haward, *J. Chem. Soc.*, 25 (1943).

Table I

Effect of Variation of the Initial Concentration of
2 in the Base-Catalyzed Fragmentation of 2 in 40%
Aqueous Methanol at 30.00° [a]

$10^2 [2]$, M	$10^4 k_{obsd}$,[b] sec^{-1}	$k_2 = (k_{obsd}/[NaOH])^c \times 10^3$, l. mol^{-1} sec^{-1}
0.311	3.66 ± 0.06	4.57
0.311	3.88 ± 0.04	4.84
1.24	3.68 ± 0.04	4.60
1.24	3.67 ± 0.07	4.57
3.11	3.61 ± 0.08	4.50
3.11	3.81 ± 0.08	4.74
	Av 3.72 ± 0.06	Av 4.79 ± 0.02

[a] 0.0821 M in sodium hydroxide. Ionic strength was maintained constant at 0.433 M with sodium perchloroate. [b] Observed first-order rate coefficient with probable error. [c] Second-order rate coefficient.

Table II

Effect of Base Concentration on the Rate of
Fragmentation of 2 in 40% Aqueous
Methanol at 30.00° [a]

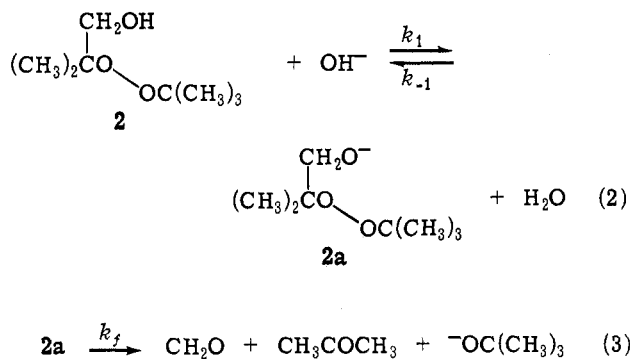| [NaOH], M	$10^4 k_{obsd}$,[b] sec^{-1}	$k_2 = (k_{obsd}/[NaOH])^c \times 10^3$, l. mol^{-1} sec^{-1}
0.0260	1.12 ± 0.01	4.29
0.0260	1.19 ± 0.01	4.57
0.0800	3.68 ± 0.04	4.60
0.0800	3.67 ± 0.07	4.57
0.268	12.7 ± 0.2	4.75
0.268	12.7 ± 0.2	4.76
		Av 4.79 ± 0.02

[a] Initial concentration of 2 is 1.24 × 10^{-2} M. Ionic strength is adjusted to a constant value of 0.433 M with sodium perchlorate. [b] Observed first-order rate coefficient with probable error. [c] Second-order rate coefficient.

confirmed by a least-squares treatment of a plot of log k_{obsd} vs. log [OH$^-$], which yields a slope and thus the order in base as 1.029 ± 0.008. The effect of temperature and the resulting activation parameters for the base-catalyzed decomposition of 2 are given in Table III.

It was hoped that the base-catalyzed decomposition of 2 could be compared directly to the basic decomposition of the peroxy-substituted acid 1, which was studied in chlorobenzene with triethylamine. The rate of the latter reaction was conveniently measured at 25°. In contrast, the reaction of 2 with triethylamine in chlorobenzene was imperceptibly slow at 30° and so measurements were made at 100° in order to obtain measurable rates. Under these conditions, nonbase-catalyzed decomposition of 2 became important. As seen from Table IV, triethylamine does not appreciably accelerate the rate of decomposition of 2 compared to the decomposition of 2 in the absence of the base. Radical traps were employed in the decomposition of 2 in the absence of base in order to avoid possible induced decomposition of the peroxide. Since a radical trap was not used with triethylamine, the rate coefficient here is a maximum value.
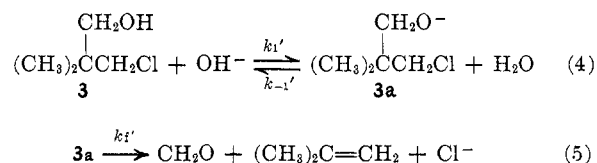
Discussion

The mechanism of the base-catalyzed fragmentation of 2 in 40% aqueous methanol appears to be analogous to that of the base-catalyzed fragmentation of the peroxy-substituted acid 1.[2] The suggested mechanism for 2 is given by eq 2 and 3, where the base is

$$
\begin{array}{c}
\text{CH}_2\text{OH} \\
| \\
(\text{CH}_3)_2\text{CO} \\
\diagdown \\
\text{OC(CH}_3)_3 \\
\mathbf{2}
\end{array}
+ \text{OH}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}
$$

$$
\begin{array}{c}
\text{CH}_2\text{O}^- \\
| \\
(\text{CH}_3)_2\text{CO} \\
\diagdown \\
\text{OC(CH}_3)_3 \\
\mathbf{2a}
\end{array}
+ \text{H}_2\text{O} \quad (2)
$$

$$
\mathbf{2a} \xrightarrow{k_f} \text{CH}_2\text{O} + \text{CH}_3\text{COCH}_3 + {}^-\text{OC(CH}_3)_3 \quad (3)
$$

represented by OH$^-$ for convenience. It was previously shown that the decomposition of 1 was concerted and presumably eq 3 is also concerted. Although radical mechanisms must be considered as a possibility when peroxides are involved, there is little doubt that the basic decomposition of 2 in 40% aqueous methanol is an ionic reaction. A primary clue to the ionic character of the reaction is seen in the quantitative yield of *tert*-butyl alcohol. A radical decomposition of 2 would undoubtedly generate *tert*-butoxy radicals, which would in part undergo fragmentation to produce acetone and methyl radicals in this polar protic solvent.[8,9] This result would be in conflict with the observed quantitative yield of *tert*-butyl alcohol. Simple homolytic decomposition of 2 at the temperatures used for the study in aqueous methanol is highly unlikely, considering that a temperature of 100° was required to produce appreciable rates for the decomposition of 2 in chlorobenzene in the absence of base (Table IV).

Fragmentation of 2a in eq 3 can be shown to be an extremely facile reaction. With reasonable approximations, the rate coefficient (k_f) for this step can be estimated. Using the steady-state approximation and the reasonable assumption that $k_{-1} \gg k_f$, which is typical in proton transfers between oxygen bases, the rate law derived from eq 2 and 3 is $-d[2]/dt = Kk_f \cdot [2][OH^-]$, where $K = k_1/k_{-1}$. The equilibrium constant K is given by $K = K_a(1/K_{auto})$, where K_a is the ionization constant of the peroxy alcohol 2 and K_{auto} is the autopyrolysis constant of 40% aqueous methanol. The value of the latter constant for this solvent was previously determined to be 10^{-14}.[10] The assumption that the ionization constant of 2 is similar to that of other primary alcohols[11] gives $K_a \cong 10^{-16}$, and thus $K = 10^{-16} \cdot 10^{14} = 10^{-2}$ M^{-1}. The rate coefficient for fragmentation of 2a is given by $k_f = k_2/K = 5 \times 10^{-3}$ M^{-1} sec$^{-1}/10^{-2}$ $M^{-1} = 0.5$ sec^{-1} at 30°, where k_2 is the observed second-order rate coefficient.

The fragmentation of 2 can be compared to the analogous fragmentation of the 1,3-chlorohydrin 3 (eq 4 and 5), which was previously studied in 40% aqueous

$$
\begin{array}{c}
\text{CH}_2\text{OH} \\
| \\
(\text{CH}_3)_2\text{CCH}_2\text{Cl} \\
\mathbf{3}
\end{array}
+ \text{OH}^- \underset{k_{-1}'}{\overset{k_1'}{\rightleftharpoons}}
\begin{array}{c}
\text{CH}_2\text{O}^- \\
| \\
(\text{CH}_3)_2\text{CCH}_2\text{Cl} \\
\mathbf{3a}
\end{array}
+ \text{H}_2\text{O} \quad (4)
$$

$$
\mathbf{3a} \xrightarrow{k_f'} \text{CH}_2\text{O} + (\text{CH}_3)_2\text{C}{=}\text{CH}_2 + \text{Cl}^- \quad (5)
$$

(8) C. Walling and P. J. Wagner, *J. Amer. Chem. Soc.*, **86**, 3368 (1964).
(9) W. H. Richardson, *ibid.*, **87**, 247 (1965).
(10) W. H. Richardson and V. F. Hodge, *J. Org. Chem.*, **35**, 4012 (1970).
(11) P. Ballinger and F. A. Long, *J. Amer. Chem. Soc.*, **82**, 795 (1960).

TABLE III

ACTIVATION PARAMETERS FOR THE BASE-CATALYZED REACTION OF 2 IN 40% AQUEOUS METHANOL[a,b]

Temp, °C	$10^4 k_{obsd}$,[c] sec^{-1}	E_a, kcal/mol	Log A	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
10.00	0.448 ± 0.007	18.5 ± 0.5	10.0	18.0 ± 0.5	−14.8 ± 2.0
20.00	1.42 ± 0.02				
30.00	3.51 ± 0.04				
40.00	11.8 ± 0.2				

[a] Initial concentration of 2 is $1.24 \times 10^{-2} M$ and [NaOH] = $0.0762 M$. Ionic strength is maintained constant at $0.433 M$ with sodium perchlorate. [b] Activation parameters are given with probable error. [c] Observed first-order rate coefficient with probable error.

TABLE IV

RATE OF DECOMPOSITION OF 2 IN CHLOROBENZENE AT 99.72°

[2], M	Additive	[Additive], M	$10^6 k_{obsd}$,[a] sec^{-1}
0.010	Triethylamine	0.200	6.1 ± 0.2
0.0713	Styrene	0.445	4.3
0.0578	2,6-Di-*tert*-butyl-*p*-cresol	5.22×10^{-3}	3.62 ± 0.08

[a] First-order rate coefficient with probable error.

methanol.[12] Here the middle fragment[5] possesses a π-carbon–carbon bond rather than a π-carbonyl bond as in the fragmentation of 2. Also, the nucleofugal fragment[5] is chloride in 3 as opposed to *tert*-butoxide in 2. The observed second-order rate coefficient $(k_{2'})$ for the base-catalyzed fragmentation of 3 is calculated to be 4×10^{-7} l. mol^{-1} sec^{-1} at 30° in 40% aqueous methanol from observed activation parameters.[12] With the approximations that were made previously, $k_{f'} = k_{2'}/K' = 4 \times 10^{-7} M^{-1} sec^{-1}/10^{-2} M^{-1} = 4 \times 10^{-5} sec^{-1}$ at 30°. Thus, the fragmentation step for 2a (eq 3) is 10^4-fold faster than the corresponding reaction for 3a (eq 5). The faster fragmentation rate of 2a as compared to 3a is no doubt related to the lower energy π-carbonyl system of the middle fragment, which results from 2a, *vs.* the π-olefinic middle fragment from 3a.[13] These energy differences between the two types of π bonds are reflected in the activated complexes in eq 3 and 5. If the same nucleofugal fragment was present in both 2 and 3, a rate enhancement considerably greater than 10^4 would be expected, since chloride is a much better leaving group than *tert*-butoxide.[16] The activation parameters for 2 and 3 reflect a composite of the fragmentation steps (eq 3 and 5) and the preequilibrium steps (eq 2 and 4). However, it is reasonable to assume that the contributions to the preequilibrium steps are similar in both reactions and that the differences in activation parameters result from differences in the fragmentation step. The effect of the two different types of middle fragments from 2 and 3 is clearly seen in the $\Delta H^{\ddagger}$ values (18.0 and 24.6 kcal/mol, respectively).

The entropy of activation is considerably more negative for the fragmentation of 2 ($\Delta S^{\ddagger} = -14.8$ eu) as compared to 3 ($\Delta S^{\ddagger} = -6.9$ eu). This may be explained by a greater dispersion of charge (*i.e.*, more bond breaking and making) at the transition for fragmentation of 2a relative to 3a, which is consistent with the lower $\Delta H^{\ddagger}$ value for 2. Solvent ordering may be greater in proceeding to the activated complex with

increased charge dispersion, which would be consistent with the more negative $\Delta S^{\ddagger}$ for 2.. There is an additional contrasting feature between the fragmentation of 2a *vs.* 3a, namely, a more polar middle fragment is produced from 2a (acetone) as compared to 3a (isobutylene). This may result in more solvent ordering in proceeding to the transition state for the fragmentation of 2a *vs.* 3a and thus contribute to a more negative $\Delta S^{\ddagger}$ for 2.

A comparison of the overall rates of base-catalyzed fragmentation (preequilibrium plus the fragmentation steps) of the peroxy-substituted acid 1 and the peroxy-substituted alcohol 2 can be made in chlorobenzene with triethylamine as the base. From the observed activation parameters for this reaction with 1,[2b] a first-order rate coefficient of $10^{-1} sec^{-1}$ {[(C$_2$H$_5$)$_3$N] = $8.00 \times 10^{-2} M$} is calculated at 100°. This may be compared to a maximum rate coefficient of 6.1×10^{-6} sec^{-1} {[(C$_2$H$_5$)$_3$N] = $0.200 M$} for 2 at 100°. This is a maximum value for 2, since nonbase-catalyzed decomposition is important under these conditions (*cf.* Table IV). Although the amine concentration differs in these two reactions, the order in amine for the fragmentation of 1 is only 0.23.[2b] This introduces a factor of only 1.2 in correcting the rate coefficient for 1 from $8.00 \times 10^{-2} M$ to $0.200 M$ in amine. Thus, the peroxy-substituted acid 1 undergoes fragmentation (overall rate) at least 10^4 times faster than the peroxy-substituted alcohol 2. If the relative values of the equilibrium constants for 1 and 2 with triethylamine could be compared, it would be possible to determine the rates of the fragmentation steps. Unfortunately, the equilibria between acids and amines in nonpolar solvents is complex[17] and this estimate does not appear possible.

Previously, we reported a rate coefficient of 1.55×10^{-6} sec^{-1} for the triethylamine (0.200 M) catalyzed elimination reaction of *tert*-butyl isopropyl peroxide in chlorobenzene at 100°.[2b] This elimination reaction is then analogous to the triethylamine-catalyzed fragmentation of 2 in chlorobenzene {$k_{max} = 6.1 \times 10^{-6} sec^{-1}$ at 100°, [(C$_2$H$_5$)$_3$N] = $0.200 M$}. For both of these reactions there is an appreciable amount of nonbase-catalyzed decomposition. Considering this, it does not appear that the fragmentation of 2 is appreciably more facile than the analogous elimination reaction.

In reactions where carbonyl compounds are produced, it is possible to generate these molecules in an excited state, providing that the sum of the activation energy and the heat of reaction is sufficiently large.[18] For example, with peroxides of sufficiently high energy,

(12) W. H. Richardson, C. M. Golino, R. W. Wachs, and M. B. Yelvington, *J. Org. Chem.*, **36**, 943 (1971).

(13) The π-bond energies in a carbonyl group and in an olefinic group are approximately 75[14] and 58[15] kcal/mol, respectively.

(14) R. Walsh and S. W. Benson, *J. Amer. Chem. Soc.*, **88**, 3480 (1966).

(15) Calculation from the data given in T. L. Cottrell, "The Strength of Chemical Bonds," Butterworths, London, 1954.

(16) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968, p 294.

(17) (a) S. Bruckenstein and D. F. Unterker, *J. Amer. Chem. Soc.*, **91**, 5741 (1969); (b) S. Bruckenstein and A. Saito, *ibid.*, **87**, 698 (1965).

(18) See (a) F. McCapra, *Quart. Rev., Chem. Soc.*, **20**, 485 (1966); (b) M. M. Rauhut, *Accounts Chem. Res.*, **2**, 80 (1969).

such as 1,2-dioxetanes, this criterion is met.[19] Since carbonyl compounds are produced from the fragmentation of **2**, which is a molecule of reasonably high energy, the question of generating an excited state carbonyl species in this reaction was probed. This was done by determining if light emission resulted from an acceptor, which was added to the reaction mixture. This technique, with fluorescein as the acceptor, has been successful in detecting excited-state carbonyl molecules produced from the decomposition of 3,3-dimethyl-1,2-dioxetane.[6] No light emission was detected with or without fluorescein as an acceptor in the base-catalyzed decomposition of **2** in 40% aqueous methanol, which suggests that excited-state carbonyl molecules are not produced in this reaction. Calculations confirm the reasonableness of this observation, although the calculations are approximate, since they are for a gas-phase system. The maximum available enthalpy (ΔH_a) for producing an excited-state carbonyl species is given by $\Delta H_a = \Delta H^{\ddagger} - \Delta H_r$.[18,19] The value of $\Delta H^{\ddagger}$, obtained experimentally, is 18.0 kcal/mol for fragmentation of **2**. The heat of reaction (ΔH_r) is given by $\Delta H_r = \Delta H^{\circ}_{fP} - \Delta H^{\circ}_{fR}$, where ΔH°_{fP} and ΔH°_{fR} are the heats of formation of the products (*tert*-butyl alcohol, acetone, and formaldehyde) and the reactant **2**, respectively. The latter values are calculated to be -154.1 and -119.0 kcal/mol, respectively, so that $\Delta H_r = -35.1$ kcal/mol. The available enthalpy (ΔH_a) is then 53.1 kcal/mol. Of the two carbonyl molecules produced from **2**, formaldehyde has the lowest singlet (81 kcal/mol)[20] and triplet (72 kcal/mol)[21] energies.[22] Thus, the calculations suggest that insufficient energy is available from the fragmentation of **2** to produce formaldehyde in the excited state, which is consistent with the results.

Experimental Section[25]

Materials.—The preparation and physical properties of 2-*tert*-butylperoxy-2-methyl-1-propanol (**2**) was reported previously by us.[26] The purity of **2** was estimated to be 98% by glc analysis. Anhydrous sodium perchlorate (G. F. Smith Co.) was prepared from the hydrated salt by heating at 110° for 48 hr under vacuum.

Stock sodium hydroxide solutions were prepared from reagent grade pellets, starting from a 50% aqueous solution, which was filtered through a sintered glass frit to remove sodium carbonate. Vacuum sublimation [70° (0.1 mm)] was used to purify 2,6-di-*tert*-butyl-*p*-cresol (Matheson Coleman and Bell). Styrene (Matheson Coleman and Bell) was distilled immediately before use as a free-radical trap. The aqueous methanol solvent was prepared by volume (40 parts methanol/60 parts water) at 25° or by weight corresponding to the volumes. Methanol (Matheson Coleman and Bell, reagent) was purified by refluxing over magnesium turnings with a catalytic amount of iodine followed by distillation.[27]

Product Studies.—The reaction of **2** with sodium hydroxide in 40% aqueous methanol was carried out in sealed ampoules for 2.5 hr at 30° (*ca.* 10 half-lives). A 1.00-ml aliquot of a stock peroxide (**2**) solution was frozen in the ampoule at $-78°$ and then 1.00 ml of a stock base solution was added. The contents of the ampoule were protected from moisture with a calcium chloride drying tube and sealed at $-78°$. Product analyses by glc were obtained with a 5 ft $\times$ 0.125 in. PAR-2 (Hewlett-Packard) column at 111° using a nitrogen flow rate of 29 ml/min. *n*-Butyl alcohol was used as an internal standard and the retention times for acetone, *tert*-butyl alcohol, and *n*-butyl alcohol were 6.6, 13, and 31 min, respectively. Areas of the chromatograms were integrated with a planimeter. Area ratios of products to the internal standard were compared to area ratios of a known mixture of compounds.

Kinetic Studies.—A solution of **2** with the internal standard (*n*-octyl alcohol) and a solution of sodium hydroxide with sodium perchlorate, to keep the ionic strength constant, in 40% aqueous methanol were allowed to thermally equilibrate separately for 30 min in a thermostated bath controlled to $\pm 0.01°$. After the thermal equilibration period, the solutions were mixed in a reaction vessel under a nitrogen atmosphere. Aliquots were withdrawn periodically and quenched with a cold 10% hydrochloric acid solution in 40% aqueous methanol. Twelve aliquots were usually removed over 3 half-lives. Analysis of the quenched samples were made by glc on a 7.5 ft $\times$ 0.125 in. 10% SF-96 on Varaport-30 column at 85° with a nitrogen flow rate of 24 ml/min. The retention times for **2** and *n*-octyl alcohol are 3.0 and 6.2 min, respectively. The ratio of the areas of **2**/*n*-octyl alcohol from the glc analyses were processed by a first-order least-squares computer program.

The decomposition of **2** in chlorobenzene was carried out in sealed capillary tubes immersed in a thermostated bath at 100°. The rate of disappearance of **2** was followed by glc using a 15 ft $\times$ 0.125 in. 10% SF-96 on Varaport-30 column at 80° with a nitrogen flow rate of 24 ml/min. The retention times for chlorobenzene and **2** were 10 and 18 min, respectively. The ratio of the areas of **2**/chlorobenzene were processed by a first-order least-squares computer program.

(19) H. E. O'Neal and W. H. Richardson, *J. Amer. Chem. Soc.*, **92**, 6553 (1970).

(20) J. C. D. Brand, *J. Chem. Soc.*, 858 (1956).

(21) G. W. Robinson and V. E. DiGiorgio, *Can. J. Chem.*, **36**, 31 (1958).

(22) The lowest singlet and triplet energies of acetone are 88.8[23] and 80 kcal/mol.[24]

(23) M. O'Sullivan and A. C. Testa, *J. Amer. Chem. Soc.*, **90**, 6245 (1968).

(24) R. F. Borkman and D. R. Kearns, *J. Chem. Phys.*, **44**, 945 (1966).

(25) Temperatures of kinetic measurements are corrected. Gas–liquid chromatography (glc) measurements were performed on a Varian Aerograph Hy-Fi (FID) instrument.

(26) W. H. Richardson and R. S. Smith, *J. Org. Chem.*, **33**, 3882 (1968).

(27) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath, Boston, Mass., 1941, p 359.