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Thermal Decomposition of Tertiary Alkyl Peroxides. Substituent Effects in Peroxide Bond Homolysis and β Scission of Alkoxy Radicals

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Rate coefficients for the thermal decomposition of a series of substituted tertiary alkyl peroxides in chlorobenzene at 150° were obtained. The sum of the polar substituent constant ranged over approximately one unit for the peroxides to give $\log k + 4 = (-0.131 \pm 0.030)\Sigma\sigma^* + 0.578$. From this correlation, the reaction constants ρ_I and f were calculated to be -0.291 and -0.175, respectively. The corresponding reaction constants for meta-substituted benzoyl peroxides, obtained from a multiple-linear-regression analysis of published data in dioxane at 80°, are $\rho_I = -0.327$ and $f = -0.174$. For comparison to alkyl peroxides, the latter values were corrected to 150°, where $\rho_I = -0.273$ and $f = -0.145$. Considering the change in solvent and approximations in relating alkyl peroxide and benzoyl peroxide reaction constants, there appears to be little difference in substituent effects between these two types of peroxides. Alkyl peroxides of the type $(CH_3)_3COOC(CH_3)_2R$ with $R = CH_2OH$ (**7**) or COOH (**8**) showed unusually fast rates of decomposition and enhanced yields of *tert*-butyl alcohol. The alcohol **7** also showed a small deuterium isotope effect ($k_H/k_D = 1.35$). Mechanistic schemes are considered to explain the kinetic data, as well as the products from **7** and **8**. Substituent effects in β scission of unsymmetrically substituted *tert*-alkoxy radicals, produced from alkyl peroxides, are reported. These data are considered in terms of a Polanyi relationship.

Certain peroxides undergo reaction by ionic pathways;[2] however, free-radical decomposition looms as an alternative process. In order to use kinetic data to distinguish between ionic and radical processes, it is sometimes necessary to estimate rates of radical decomposition of peroxides from substituent effect correlations. This situation arose in a study of the neighboring *tert*-butylperoxy group.[3] Although a substituent effect correlation is reported for the radical decomposition of benzoyl peroxides,[4,5] no such correlations are reported for alkyl peroxides. The reported kinetic data for alkyl peroxides are devoted to variations in alkyl and aryl alkyl hydrocarbon substituents, where there are small changes in the substituent constant.[5,6] Furthermore, primary and secondary alkyl peroxides are included in these data, which are subject to induced decomposition and can then lead to erroneous rate data.[5,6b] For these reasons, we have obtained kinetic data for the thermal decomposition of *tertiary* alkyl peroxides, where the sum of the polar substituent constant for the groups vary over approximately 1.0 σ^* unit.

In the course of this study, it was noted that peroxides of the type $(CH_3)_3COOC(CH_3)_2R$ with $R = CH_2OH$ or COOH undergo unusually rapid decomposition and give enhanced yields of *tert*-butyl alcohol. Possible explanations for these observations are considered. In addition, product studies from the thermal decomposition of alkyl peroxides allowed us to calculate relative rates of β scission from unsymmetrically substituted *tert*-alkoxy radicals.

Results

Kinetic data were obtained by following the rate of disappearance of the peroxides by glc and the results are given in Table I. Tertiary alkyl peroxides are not highly susceptible to induced decomposition in most solvents,[5-7] but in order to suppress this potential reaction 2,6-di-*tert*-butyl-*p*-cresol or styrene were used as radical traps. The rate coefficient (4.6×10^{-4} sec^{-1}) for thermolysis of *tert*-butyl peroxide in benzene at 150°, calculated from reported activation param-

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[1] National Science Foundation Undergraduate Research Participant: (a) summer 1965; (b) summer 1968.

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[7] (a) S. H. Goh and S. H. Ong, *J. Chem. Soc. B*, 870 (1970); (b) S. H. Goh, *J. Org. Chem.*, **37**, 3098 (1972); (c) E. S. Huyser and C. J. Bredeweg, *J. Amer. Chem. Soc.*, **86**, 2401 (1964).

TABLE I

RATE COEFFICIENTS FOR THE THERMAL DECOMPOSITION OF TERTIARY ALKYL PEROXIDES IN CHLOROBENZENE AT 150°

Peroxide (P)[a]	$10^2[P]_0$, *M*	10^4k,[d] sec^{-1}	$\Sigma\sigma^*$
$(CH_3)_3COOC(CH_3)_3$ (**1**)[a]	7.93	4.45 ± 0.08	−0.600
$(CH_3)_3COOC(CH_3)_2CO_2CH_3$ (**2**)[a]	6.24	4.68 ± 0.08	+0.234
$(CH_3)_3COOC(CH_3)_2CH_2Cl$ (**3**)[a]	4.99	4.15 ± 0.05	−0.115
$ClCH_2(CH_3)_2COOC(CH_3)_2CH_2Cl$ (**4**)[a]	6.27	3.11 ± 0.08	+0.390
$(CH_3)_3COOC(CH_3)_2CH_2Br$ (**5**)[a]	4.98	3.63 ± 0.04	−0.133
$(CH_3)_3COOC(CH_3)_2CH_2OCOCH_3$ (**6**)[a]	4.88	4.12 ± 0.08	−0.174
$(CH_3)_3COOC(CH_3)_2CH_2OH$ (**7**)[b]	7.62	16.1 ± 0.5	−0.296
$(CH_3)_3COOC(CH_3)_2CH_2OD$ (**7D**)[b]	5.11	12.3 ± 0.4[e]	−0.296
$(CH_3)_3COOC(CH_3)_2CO_2H$ (**8**)[c]	7.00	24.0	+0.550

[a] With 0.005 *M* 2,6-di-*tert*-butyl-*p*-cresol. [b] With 0.102 *M* styrene. [c] Without a radical trap and the rate coefficient is calculated from activation parameters: W. H. Richardson and R. S. Smith, *J. Amer. Chem. Soc.*, **91,** 3610 (1969). [d] By least-squares fit with probable error. [e] **7D** is 90% deuterated. No correction is made for partial deuteration; however the corrected value is 11.9 ± 0.4 × 10^{-4} sec^{-1}.

eters ($\Delta H^{\ddagger} = 35$ kcal/mol and $\Delta S^{\ddagger} = 8$ eu),[8] is in good agreement with our value (4.45 × 10^{-4} sec^{-1} at 150°) in chlorobenzene. These rate coefficients are greater than those calculated for *tert*-butyl peroxide at 150° in *tert*-butylbenzene (2.8 × 10^{-4} sec^{-1}, $E_a = 38.0$ kcal/mol, $\log A = 16.04$)[9] and cumene (2.9 × 10^{-4} sec^{-1}, $E_a = 37.5$ kcal/mol, $\log A = 15.80$).[9] The increased rate of decomposition of *tert*-butyl peroxide in chlorobenzene relative to *tert*-butylbenzene (1.4-fold at 110°) was noted previously.[7a] The origin of this increase in rate is uncertain in chlorobenzene and benzene, but induced decomposition was considered unlikely in the latter solvent.[7c]

Table I also includes the sum of the polar substituent constants for each peroxide. Where polar substituent constants are not reported[10] for R in ROOR, they are calculated.[11] With the omission of peroxides **7** and **8**, the data from Table I give $\rho^* = -0.131 \pm 0.030$ with probable error (eq 1). The mechanism of decomposition of the omitted peroxides **7** and **8** is considered later.

$$\log k + 4 = (-0.131 \pm 0.030)\Sigma\sigma^* + 0.578 \qquad (1)$$

Yields of acetone and *tert*-butyl alcohol from thermolysis of the peroxides are given in Table II. Products from **3** were not determined, but yields of products can be reasonably estimated from the data for **1** and **4**. The latter two peroxides serve to predict acetone and *tert*-butyl alcohol yields from *tert*-butoxy and chloro-*tert*-butoxy radicals, respectively. Thus, the predicted yields of acetone and *tert*-butyl alcohol for **3** are 1.87 and 0.005 mmol/mmol **3**, respectively. We estimate the error in yields given in Table II to be approximately ±5%.

TABLE II

PRODUCT STUDIES FOR THE DECOMPOSITION OF ALKYL PEROXIDES AT 150° IN CHLOROBENZENE

Peroxide (P)	$10^2[P]_0$, *M*	Yield[a]	
		CH_3COCH_3	$t\text{-}C_4H_9OH$
1	7.29	1.99	0.011
1[b]	6.44	1.86	0.23
2	6.24	1.91	0.055
4	6.27	0.87	
5	14.0	1.30	0.010
6	9.50	1.50	0.12
7	3.09	1.35	0.51
7[b]	7.62	1.74	0.39
8	7.00	1.30	0.73

[a] Millimoles of product/millimoles of peroxide. [b] With 0.102 *M* styrene.

Discussion

Substituent Effect Correlations.—Prior to this study, the effect of substituents on the rate of homolysis of the peroxide bond rested on the thermal decomposition of aroyl peroxides.[4] Although substituents have been varied in other peroxide decompositions, the kinetic data are unsuitable for LFE correlations with homolysis of the peroxide bond. In the alkyl peroxide series, changes in the substituents amounted to small changes in σ^*. Furthermore, the variations included primary and secondary groups, which are susceptible to induced decomposition.[5,6b] There are other instances where substituent effects were determined, but simple homolysis of the peroxide bond does not occur. For example, multibond homolysis occurs with certain substituted peresters, where both the peroxide bond and the alkyl carbon–acyl carbon bond are broken in the transition state.[5,12] Also, some acyl peroxides undergo an inversion mechanism in their decomposition, which is not simply related to O–O bond homolysis.[5,13]

Benzoyl peroxide decompositions were originally correlated by the Hammett equation to give $\rho = -0.38$ at 80° in dioxane with 0.2 *M* 3,4-dichlorostyrene.[4,14] Unfortunately, this ρ value cannot be directly compared to the ρ^* value obtained for alkyl peroxides. To relate substituent effects in benzoyl peroxides to those observed in alkyl peroxides, a common reaction constant must be employed first for both series. The ρ_I constant is appropriate for this purpose, where $\rho_I = \rho^*/0.45$.[16] Thus, from eq 1 the alkyl peroxides give $\rho_I = -0.291 \pm 0.067$ [$= (-0.131 \pm 0.030)/0.45$]. A multiple-linear-regression analysis of the rate coefficients for decomposition of meta-substituted benzoyl peroxides[4] with eq 2 gives $\rho_I = -0.317 \pm 0.056$ and $\rho_R = -0.361$

$$\log k/k_0 = \rho_I\sigma_I + \rho_R\sigma_R^0 \qquad (2)$$

± 0.065 with a standard error in $\log k/k_0$ of ±0.0520 and *r* (correlation coefficient) = 0.974. If the *m,m'*-

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[8] E. S. Huyser, "Free-Radical Chain Reaction," Wiley-Interscience, New York, N. Y., 1970, p 272.

[9] J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Amer. Chem. Soc.*, **70,** 1336 (1948).

[10] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 222.

[11] Reference 10, p 224.

[12] *Cf.* (a) P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80,** 1398 (1958); (b) C. Rüchardt and H. Böck, *Chem. Ber.*, **104,** 577 (1971); (c) A. I. Dalton and T. T. Tidwell, *J. Org. Chem.*, **37,** 1504 (1972).

[13] (a) S. Oae, K. Fujimori, and S. Kozuka, *Tetrahedron*, **28,** 5327 (1972); (b) S. Oae, K. Fujimori, and Y. Uchida, *ibid.*, **28,** 532 (1972); (c) J. E. Leffler and A. A. More, More, *J. Amer. Chem. Soc.*, **94,** 2483 (1972); (d) R. A. Cooper, R. G. Lawler, and H. R. Wards, *ibid.*, **94,** 545 (1972); (e) C. Walling, H. P. Waits, J. Milovanovic, and C. G. Pappiaonnou, *ibid.*, **92,** 4927 (1970).

[14] Thenoyl peroxides gave $\rho = -0.4$ by a Hammett correlation.[5,15]

[15] (a) R. D. Shuetz and D. M. Teller, *J. Org. Chem.*, **27,** 410 (1962); (b) R. D. Shuetz, F. M. Gruen, D. R. Byrne, and R. L. Brennan, *J. Heterocycl. Chem.*, **3,** 184 (1966).

[16] *Cf.* C. D. Ritchie and W. F. Sager, *Progr. Phys. Org. Chem.*, **2,** 338 (1964).

dimethoxybenzoyl peroxide is not included, one obtains $\rho_I = -0.327 + 0.046$, $\rho_R = -0.267 \pm 0.077$ with a standard error in log k/k_0 of ± 0.0428, and $r = 0.980$. Since reaction constants are expected to be proportional to $1/T$,[17a] the ρ_I values for benzoyl peroxides at 80° are corrected to 150° (the temperature employed for alkyl peroxide kinetics). This gives $\rho_I = -0.265 \pm 0.047$ and -0.273 ± 0.038 at 150° for the benzoyl peroxides with and without the *m,m'*-dimethoxy derivative, respectively. This places the ρ_I values derived from benzoyl peroxides and alkyl peroxides (-0.291 ± 0.067) within the error limits of each other.

Another means of relating substituent effects in these two series is through the field effect parameter f in the Swain–Lupton equation (eq 3).[18] A somewhat better

$$\log k/k_0 = f\mathcal{F} + r\mathcal{R} \qquad (3)$$

correlation of the benzoyl peroxide meta-substituent effect data (excluding the *m,m'*-dimethoxy derivative) results with this equation, where $f = -0.174 \pm 0.027$, $r = -0.211 \pm 0.054$, r (correlation coefficient) $= 0.985$, and the standard error in log k/k_0 is ± 0.0377. A temperature correction from 80 to 150° gives $f = 0.145 \pm 0.022$ for the benzoyl peroxides. Swain and Lupton[18] find a good correlation between σ_I and $\mathcal{F}$, such that $\sigma_I = 0.60\mathcal{F}$. Since $\sigma_I = 0.45\sigma^*$,[16] it follows that $f = \rho^*(0.45/0.60)$ or $f = \rho^*/0.75$. From the ρ^* value given in eq 1, the alkyl peroxides give $f = -0.175 \pm 0.040$ [$= (-0.131 \pm 0.030)/0.75$] in chlorobenzene compared to $f = -0.145 \pm 0.022$ for benzoyl peroxides in dioxane at the same temperature (150°). Again the two values are within error limits of each other. Considering the change in solvent and the potential errors in relating the reaction constants, it appears that the field (or inductive) effect of the substituents does not change between alkyl and meta-substituted benzoyl peroxides.

The overall effect of substituents on alkyl peroxide decomposition is small compared with that observed for aroyl peroxides. This results from a large resonance contribution of the substituents in the aroyl peroxide series. The per cent resonance (%$\mathcal{R}$)[18] for meta-substituted benzoyl peroxides is 43%, which is significantly greater than obtained for ionization of meta-substituted benzoic acids (%$\mathcal{R}$ = 22%).[18] With para-substituted benzoyl peroxides,[4a] where through-resonance interactions are possible between the substituents and the carbonyl group, %$\mathcal{R}$ increases to 67% [$f = -0.145 \pm 0.044$, $r = -0.474 \pm 0.085$, r (correlation coefficient) $= 0.967$, standard error in log $k/k_0 = \pm 0.0798$]. This too is greater than for the ionization of para-substituted benzoic acids (%$\mathcal{R}$ = 53%).[18] Although electron release to the peroxide reaction site increases the rate and resonance contributions are significant for aroyl peroxides, it cannot be discerned whether this is due to an increase in the ground-state energy of the peroxides or a decrease in the transition-state energy. It is possible that electron release to the peroxide group increases the ground-state energy by increasing the electron repulsions between the peroxy oxygen atoms. Alternatively, the alkoxy or acyloxy radical, which is reflected in the transition state, is electron deficient and electron release may then stabilize the activated complex.

Decomposition of 7 and 8.—Both alcohol **7** and acid **8** decompose at rates faster than predicted from the Taft correlation (eq 1). The correlation predicts rate coefficients for **7** and **8** of $4.14 \pm 0.09 \times 10^{-4}$ and $3.21 \pm 0.13 \times 10^{-4}$ sec^{-1} compared to observed values of $16.1 \pm 0.5 \times 10^{-4}$ and 24.0×10^{-4} sec^{-1}, respectively. The alcohol **7** and the acid **8** then undergo decomposition by factors of 3.9 and 7.5 times faster, respectively, than predicted by eq 1. The significance of the carboxylic acid hydrogen atom in rate acceleration of **8** is seen by comparing **8** with its methyl ester **2**. The methyl ester is well correlated by eq 1, as opposed to the acid **8**. The involvement of the alcoholic hydrogen atom in rate acceleration of **7** is suggested by an isotope effect ([$k_H/k_D = 1.35$ (corrected)] when this atom is replaced by deuterium. The yield of *tert*-butyl alcohol is also significantly increased in the decomposition of **7** and **8** compared with *tert*-butyl peroxide. Production of only free *tert*-butoxy radicals from **7** and **8** cannot explain the unusually high *tert*-butyl alcohol yields.

As a starting point, two competing decomposition paths can be considered for **7** and **8**, namely, simple homolysis (eq 4 and 6) and cyclic decomposition (eq 5 and 7). Qualitatively, the latter paths (eq 5 and 7) will offer an explanation for enhanced yields of *tert*-butyl alcohol from **7** and **8** as well as the involvement of the OH hydrogen atom. Considering that **7** shows intramolecular hydrogen bonding between the hydroxyl and peroxide groups,[19] **7c**‡ and **8c**‡ appear reasonable.

A further consideration of kinetic and product data indicates that these two modes of decomposition cannot wholly explain the results. For **8**, the per cent simple homolysis is given by $k'_h/k_{obsd} \times 10^2 = (3.21 \times 10^{-4})/(24.0 \times 10^{-4}) \times 10^2 = 13.4\%$, where k'_h is predicted from the LFER for homolysis and k_{obsd} is the observed rate coefficient. If **10** yields acetone exclusively,[20] then the simple homolysis of **8** will produce 0.27 mmol acetone/mmol **8** (= 0.134 × 1.99) based on the acetone yield from *tert*-butyl peroxide. An insignificant amount of *tert*-butyl alcohol (0.0008 mmol = 0.134 × 0.006) would be produced in eq 6, based on *tert*-butyl peroxide. In the cyclic decomposition (eq 7), equivalent yields of acetone and *tert*-butyl alcohol are predicted. Since 0.73 mmol of *tert*-butyl alcohol is produced per mmol of **8**, essentially this entire amount must arise from eq 7 and 0.73 mmol of acetone will be formed also in this step. The total yield of acetone from eq 6 and 7 is expected to be 1.00 mmol/mmol **8** (= 0.27 + 0.73), while 1.30 mmol of acetone/mmol **8** is observed. Thus, 0.30 mmol of acetone/mmol **8** is unaccounted for if only eq 6 and 7 are considered. Similarly, if it is assumed that **10** does not yield acetone, 0.44 mmol of acetone/mmol of **8** is unaccounted for by eq 6 and 7. By similar arguments it can be shown that 0.91–1.14 mmol of acetone/mmol **7** is unexplained by solely eq 4 and 5 with styrene present and 0.32–0.59 mmol of acetone/mmol **7**

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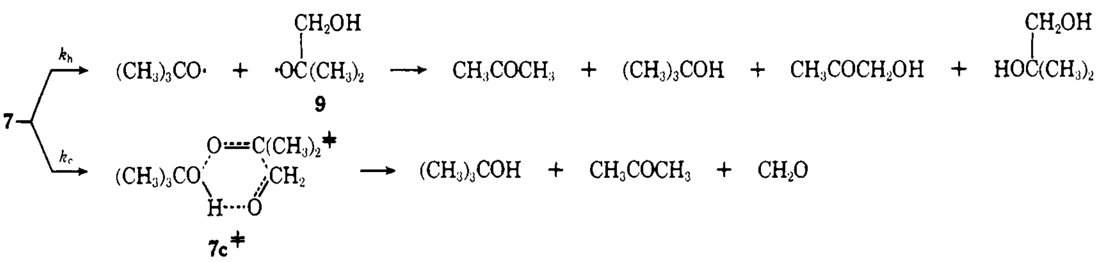
[17] P. R. Wells, "Linear Free Energy Relationships," Academic Press, New York, N. Y., 1968: (a) p 20; (b) p 3.

[18] C. G. Swain and E. C. Lupton, *J. Amer. Chem. Soc.*, **90**, 4328 (1968).

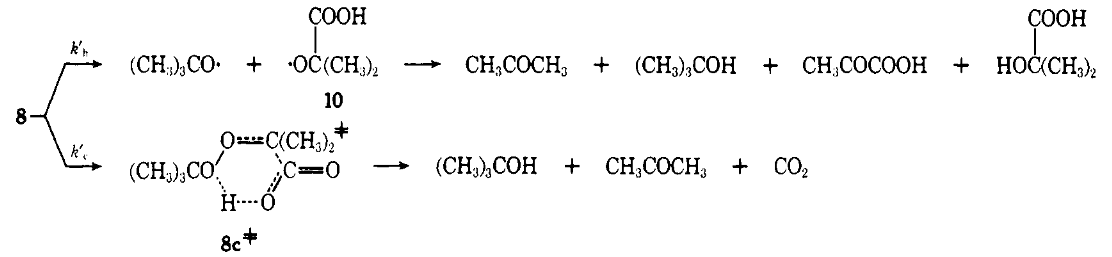
[19] W. H. Richardson and R. S. Smith, *J. Org. Chem.*, **33**, 3882 (1968).

[20] The difference in enthalpies of reaction ($\Delta\Delta H_r°$) for acetone formation less pyruvic acid production from **10** is the same (5.90 kcal/mol) as for the two similar processes from $(CH_3)_2(CO_2CH_3)CO\cdot$. The statistically corrected relative rates of acetone/methyl pyruvate formation from the latter radical is 23 (*cf.* β scission of alkoxy radicals). Thus, the relative amounts of these two products will be 11.5. Since $\Delta\Delta H_r°$ is the same for the two alkoxy radicals, the expected ratio of acetone/pyruvic acid from **10** is 11.5.



$$7 \xrightarrow{k_h} (CH_3)_3CO\cdot + \cdot OC(CH_3)_2CH_2OH\ (\mathbf{9}) \longrightarrow CH_3COCH_3 + (CH_3)_3COH + CH_3COCH_2OH + HOC(CH_3)_2CH_2OH \quad (4)$$

$$7 \xrightarrow{k_c} \mathbf{7c}^{\ddagger} \longrightarrow (CH_3)_3COH + CH_3COCH_3 + CH_2O \quad (5)$$

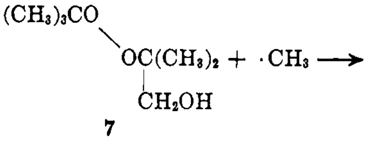


$$8 \xrightarrow{k'_h} (CH_3)_3CO\cdot + \cdot OC(CH_3)_2COOH\ (\mathbf{10}) \longrightarrow CH_3COCH_3 + (CH_3)_3COH + CH_3COCOOH + HOC(CH_3)_2COOH \quad (6)$$

$$8 \xrightarrow{k'_c} \mathbf{8c}^{\ddagger} \longrightarrow (CH_3)_3COH + CH_3COCH_3 + CO_2 \quad (7)$$

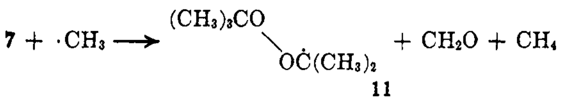
without styrene. The ranges in unaccounted acetone arise in each case by assuming that **9** gives exclusively or no acetone.[21]

A decomposition path for **7** and **8** must be considered, in addition to homolysis (eq 4 and 6) and cyclic decomposition (eq 5 and 7), to explain acetone formation without an appreciable amount of *tert*-butyl alcohol. The kinetics dictate that the rate of this reaction be faster than simple homolysis. Two possible reaction types for **7** and **8** that could accommodate these requirements are given below. The reactions are shown with methyl radicals, although radicals derived from scavengers could intervene. The *tert*-butoxy radical will yield almost exclusively acetone and methyl radical, according to the product study with *tert*-butyl peroxide. The radical **11** (eq 9 and 11) will yield acetone and a *tert*-butoxy radical, so that eq 8–11 will allow for the

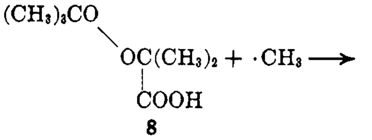


$$(CH_3)_3CO\text{-}OC(CH_3)_2CH_2OH\ (\mathbf{7}) + \cdot CH_3 \longrightarrow$$

$$(CH_3)_3CO\cdot + CH_3COCH_3 + CH_2O + CH_4 \quad (8)$$



$$7 + \cdot CH_3 \longrightarrow (CH_3)_3CO\text{-}O\dot{C}(CH_3)_2\ (\mathbf{11}) + CH_2O + CH_4 \quad (9)$$



$$(CH_3)_3CO\text{-}OC(CH_3)_2COOH\ (\mathbf{8}) + \cdot CH_3 \longrightarrow$$

$$(CH_3)_3CO\cdot + CH_3COCH_3 + CO_2 + CH_4 \quad (10)$$

$$8 + \cdot CH_3 \longrightarrow 11 + CO_2 + CH_4 \quad (11)$$

formation of acetone with essentially no *tert*-butyl alcohol production. Normally hydrogen atom abstraction from carboxylic acid or alcoholic OH atoms is unfavorable.[22] However, π-carbonyl bond formation is expected to lower the activation energy of these reactions such that they may become favorable. Some insight into this proposal can be gained by calculating the enthalpies of reaction ($\Delta H_r°$) for eq 8–11 by group additivity methods.[23] For reactions 8 and 9 with peroxide **7**, the calculated $\Delta H_r°$ values are -33.9 and $+25.1$ kcal/mol, respectively. The calculated $\Delta H_r°$ values of reactions 10 and 11 for peroxide **8** are -55.2 and $+3.8$ kcal/mol, respectively. Although $\Delta H_r°$ cannot be simply related to E_a in these reactions, the large exothermicity of reactions 8 and 10 suggests a very low activation energy. For example, hydrogen atom abstraction from methane by fluorine atoms has an E_a value of 0.2 kcal/mol[24] with a $\Delta H_r°$ value of -31.8 kcal/mol.[25] Thus, reactions 8 and 10 would appear to be quite favorable in terms of activation energies. Although the heats of reactions for eq 9 and 11 (25.1 and 3.8 kcal/mol, respectively) set only the *minimum* activation energies, these reactions are likely to have activation energies less than that found in the simple homolysis of the peroxide bond.[5,6b] Thus, either two-bond (eq 9 and 11) or three-bond homolysis could contribute to accelerated rates of decomposition of **7** and **8**.

With a combination of simple homolysis (eq 4 and 6), cyclic decomposition (eq 5 and 7), and induced decomposition (eq 8–11), the product balance for **7** and **8** is good in the absence of styrene. As outlined above, 13.4% of **8** is decomposed by simple homolysis (eq 6) and 73% by cyclic decomposition (eq 7), so that 0.14 mmol of **8** [1.00 − (0.134 + 0.73)] is consumed by induced decomposition. Thus, 0.28 mmol of acetone (2 × 0.14) is expected from the latter process. By these three processes a total of 1.27 mmol of acetone/mmol **8** (0.26 + 0.73 + 0.28) is expected compared with the observed yield of 1.30 mmol. We have assumed that alkoxy radical **10** gives a 92% yield of acetone ($11.5/11.5 + 1 \times 10^2$),[20] so that 0.26 mmol of acetone is produced by homolysis. For **7** without styrene, 25.5% of the peroxide decomposes by homolysis based on kinetic data (eq 4, $k_h/k_{obsd} \times 10^2$) and 51% of the decomposition can be attributed to cyclic decomposition (eq 5) based on the *tert*-butyl alcohol yield. Thus, 0.235 mmol of **7** [1.00 − (0.255 + 0.51)] remains for induced decomposition, so that 0.470 mmol of acetone (2 × 0.235) is expected to be produced by this process. Assuming a 31% yield of acetone from **9**, 0.33 mmol of

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[21] The $\Delta\Delta H_r°$ values **9** and $(CH_3)_2(CH_2Br)CO\cdot$ are the same (1.3 kcal/mol) for acetone to hydroxy acetone or bromo acetone formation. By the same reasoning as given in ref 20, the relative yields of acetone/substituted acetone production (0.45) are expected to be equal.

[22] M. Simonyi and F. Tüdös, *Advan. Phys. Org. Chem.*, **9**, 127 (1971).

[23] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

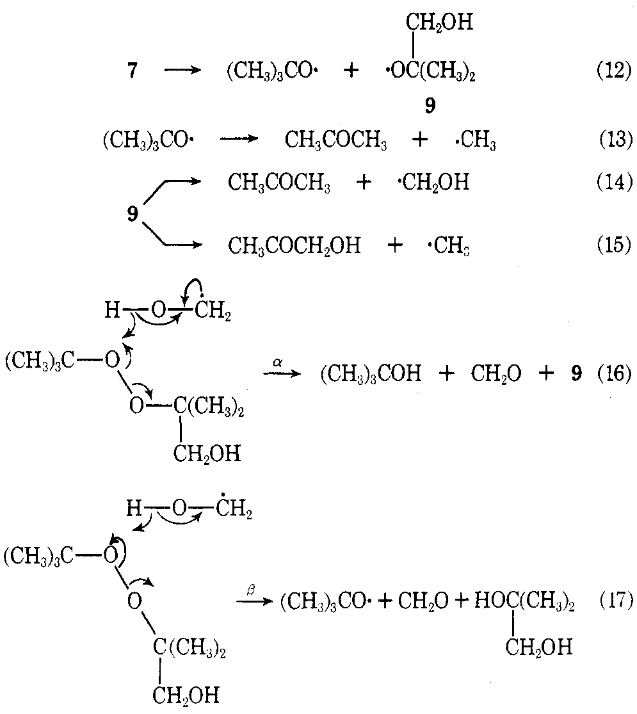
[24] W. A. Pryor, "Free Radicals," McGraw-Hill, New York, N. Y., 1966, p 155.

[25] Calculated by group additivities.[23]

acetone/mmol **7** is expected from homolysis and the total acetone yield from the three processes is 1.31 mmol/mmol **7** (0.33 + 0.51 + 0.470) compared with the observed yield of 1.35 mmol. By similar reasoning, the product balance is poor with **7** in the presence of styrene. Here, the total expected acetone yield is 1.38 (0.31 + 0.36 + 0.710) compared with the observed yield of 1.74 mmol.

Although a combination of homolysis, cyclic decomposition, and induced decomposition can explain the data reasonably well for **7** and **8** (with the exception of **7** in the presence of styrene), alternative mechanisms (Schemes I and II) can be considered. Reactions 16 and 17 have been proposed to explain induced decomposition of *tert*-butyl peroxide in alcoholic solvents.[7c]

SCHEME I



$$\mathbf{7} \longrightarrow (CH_3)_3CO\cdot + \underset{\mathbf{9}}{\cdot OC(CH_3)_2CH_2OH} \quad (12)$$

$$(CH_3)_3CO\cdot \longrightarrow CH_3COCH_3 + \cdot CH_3 \quad (13)$$

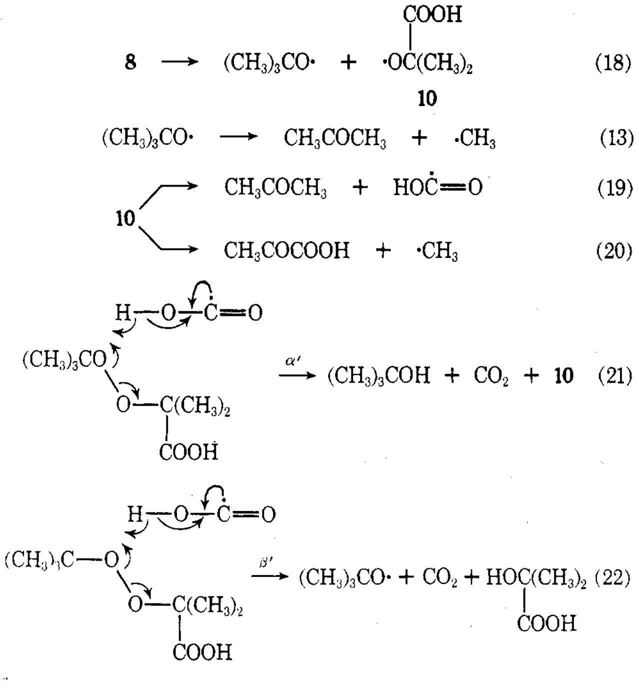
$$\mathbf{9} \longrightarrow CH_3COCH_3 + \cdot CH_2OH \quad (14)$$

$$\mathbf{9} \longrightarrow CH_3COCH_2OH + \cdot CH_3 \quad (15)$$

$$\xrightarrow{\alpha} (CH_3)_3COH + CH_2O + \mathbf{9} \quad (16)$$

$$\xrightarrow{\beta} (CH_3)_3CO\cdot + CH_2O + HOC(CH_3)_2CH_2OH \quad (17)$$

SCHEME II



$$\mathbf{8} \longrightarrow (CH_3)_3CO\cdot + \underset{\mathbf{10}}{\cdot OC(CH_3)_2COOH} \quad (18)$$

$$(CH_3)_3CO\cdot \longrightarrow CH_3COCH_3 + \cdot CH_3 \quad (13)$$

$$\mathbf{10} \longrightarrow CH_3COCH_3 + HO\dot{C}{=}O \quad (19)$$

$$\mathbf{10} \longrightarrow CH_3COCOOH + \cdot CH_3 \quad (20)$$

$$\xrightarrow{\alpha'} (CH_3)_3COH + CO_2 + \mathbf{10} \quad (21)$$

$$\xrightarrow{\beta'} (CH_3)_3CO\cdot + CO_2 + HOC(CH_3)_2COOH \quad (22)$$

Reactions 21 and 22 are then analogous to these induced decompositions. In terms of calculated heats of reaction ($\Delta H_r°$), induced decompositions 16 and 17 for **7** are suggestive of processes with low activation energies (see Scheme I). The calculated $\Delta H_r°$ values for both reactions 16 and 17 are −34.5 kcal/mol. Similarly, low activation energies are expected for induced decompositions of **8** *via* eq 21 and 22, where the $\Delta H_r°$ values are −56.8 kcal/mol for both reactions.

The product balances for **7** and **8** based on Schemes I and II are less satisfactory than those based on eq 4–11. With the analysis presented above, the per cent **8** decomposed by (1) homolysis and (2) α'- and (3) β'-induced decomposition is 13.4% (from kinetic data), 73% (from *tert*-butyl alcohol yield), and 13.6% [1.00 − (0.134 + 0.73)], respectively. The millimoles of acetone/mmol **8** from (1) homolysis and (2) α'- and (3) β'-induced decomposition is then 0.26, 0.67 (0.92 × (0.73), and 0.136 mmol, respectively, for a total of 1.07 mmol, compared with 1.30 mmol of acetone observed. In the same manner for **7** without styrene, the per cent **7** decomposed along with (millimoles of acetone formed/mmol **7**) from (1) homolysis and (2) α- and (3) β-induced decomposition is calculated to be 25.5 (0.33), 51(0.16), and 23.5% (0.235), respectively, for a total of 0.73 mmol, compared with 1.35 mmol of acetone observed. With styrene, the per cent **7** decomposed along with (millimoles of acetone formed/mmol **7**) from (1) homolysis and (2) α- and (3) β-induced decomposition is calculated to be 25.5 (0.31), 36 (0.11), and 38.5% (0.385), respectively, for a total of 0.81 mmol relative to 1.74 mmol of acetone observed.

In summary, a combination of homolysis, cyclic decomposition, and induced decomposition (eq 4–11) best fits the existing data for **7** and **8**. It would be unwarranted to completely exclude the alternative Schemes I and II, based on product balances, since predicted total yields of acetone depend on knowing acetone yields from β scission of alkoxy radicals **9** and **10**. In our final analysis of the product balances for eq 4–11 and Schemes I and II, we have assumed a 31% yield of acetone from **9**[21] and a 92% yield from **10**.[20] This seems to be a reasonable estimate and the relationship between relative rates of β scission from unsymmetrical alkoxy radicals and calculated differences in enthalpies of reaction ($\Delta\Delta H_r°$) for these processes are discussed further in the next section. However, it should be noted that the product balances for Schemes I and II will be improved if it is assumed that alkoxy radicals **9** and **10** give exclusively acetone. For peroxide **8**, assuming only acetone production from **10**, Scheme II predicts a total of 1.14 mmol of acetone *vs.* 1.30 mmol observed. For **7**, assuming solely acetone formation from **9**, Scheme I predicts a total of 1.26 mmol of acetone without or with styrene compared with 1.35 and 1.74 mmol observed without and with styrene.

β Scission of Alkoxy Radicals.—Competitive β scission reactions (Scheme III) from a number of unsymmetrical *tert*-alkoxy radicals has been reported.[26] To our knowledge, previous studies include only alkyl

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[26] (a) J. D. Bacha and J. K. Kochi, *J. Org. Chem.*, **30**, 3272 (1965); (b) J. K. Kochi, *J. Amer. Chem. Soc.*, **84**, 1193 (1962); (c) F. D. Greene, M. L. Savitz, H. H. Lau, F. D. Osterholtz, and W. N. Smith, *ibid.*, **83**, 2196 (1961); (d) C. Walling and A. Padwa, *ibid.*, 2207 (1961); (e) P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959).

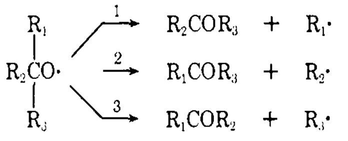
TABLE III

RELATIVE RATES OF β SCISSION OF 12 AND THERMOCHEMICAL PARAMETERS

Registry no.	12					
	R_1	R_2	R_3	k_1/k_2, 150°	$\Delta\Delta H_r°$[a,b]	ΔE_a[a,c]
42334-75-8	CO_2CH_3	CH_3	CH_3	23	5.9	3.4
42334-91-8	CH_2OCOCH_3	CH_3	CH_3	2.08	2.0	1.2
42334-92-9	CH_2Cl	CH_3	CH_3	1.54	2.3	1.3
42334-93-0	CH_2Br	CH_3	CH_3	0.90	1.3	0.75

[a] In kcal/mol. [b] $\Delta\Delta H_r° = \Delta H_{r_2}° - \Delta H_{r_1}°$. [c] $\Delta E_a = E_{a_2} - E_{a_1}$.

SCHEME III



12

hydrocarbon radicals (R_1, R_2, R_3). The yields of acetone from Table II now allow us to calculate rates of β scission, relative to $R_2 = CH_3$, for $R_1 = CO_2CH_3$, CH_2Cl, CH_2Br, and CH_2OCOCH_3. The statistically corrected rates (k_1/k_2) are given by $2(\text{acetone})_{12}/[1.00 - (\text{acetone})_{12}]$, where $(\text{acetone})_{12}$ is the millimoles of acetone/mmol **12**. Where a *tert*-butoxy radical is produced from the peroxide, as well as **12**, $(\text{acetone})_{12}$ is obtained by subtracting 1.99/2 (*cf. tert*-butyl peroxide) from the total acetone yield given in Table II.

Although Polanyi relationships[27] have met with varying success, they are potentially useful. Ideally one can calculate differences in enthalpies of reactions ($\Delta\Delta H_r°$)[23] and then determine differences in activation energies (ΔE_a) from eq 23, once sufficient data are

$$\Delta E_a = \alpha\Delta\Delta H_r° \qquad (23)$$

available to empirically determine α. From the Arrhenius equation and eq 23, one can obtain eq 24.

$$2.303RT \log (k_1/k_2) = \alpha\Delta\Delta H_r° + 2.303RT \log (A_1/A_2) \qquad (24)$$

Since our data were not determined as a function of temperature, the ratio of *A* factors is unknown. However, if the ratio A_1/A_2 is reasonably constant, eq 24 predicts a linear plot of $2.303RT \log (k_1/k_2)$ *vs.* $\Delta\Delta H_r°$. From such a plot from the data in Table III at 150°, $\alpha = 0.58 \pm 0.04$ and $A_1/A_2 = 0.40$ with *r* (correlation coefficient) = 0.989. The value of *r* indicates a satisfactory correlation.[17b] With this value of α and $\Delta\Delta H_r°$ quantities in Table III, ΔE_a for β scission can be calculated from eq 23 and recorded in Table III.

Experimental Section[28]

Materials.—Chlorobenzene (Matheson Coleman and Bell) was dried over Drierite. Styrene (Matheson Coleman and Bell) was distilled before use, bp 26° (5 mm) [lit.[29] bp 54° (30 mm)]. 2,6,Di-*tert*-butyl-*p*-cresol (Matheson Coleman and Bell) was sublimed at 70° (0.1 mm), mp 69.0–70.7° (lit.[30] mp 69.8–70.5°). *tert* Butyl peroxide (**1**) (Shell Chemical Co.) was purified by distillation, bp 52° (100 mm) [lit.[31] bp 109° (760 mm)]. Preparation of peroxides **2**,[32a] **7**,[19] and **8**[32b] were previously reported from this laboratory.

Chloro-*tert*-butyl Peroxide (**3**).—This peroxide was isolated in 44% yield, based on consumed *tert*-butyl peroxide, from the photochlorination of the latter peroxide, bp 54–55° (20 mm) [lit.[33] bp 55° (20 mm)]. The purity was estimated to be 98–99% by glc after distillation through a 1 × 90 cm glass helice column (Todd Scientific Co.). Alternatively, **3** was prepared by slowly adding 18.8 g (0.151 mol) of chloro-*tert*-butyl hydroperoxide to 140 g of concentrated sulfuric acid and 53 g of water at 0° with stirring. Then 11.2 g (0.151 mol) of *tert*-butyl alcohol was added in 256 ml of chloroform. The reaction mixture was stirred for 48 hr at room temperature and the chloroform phase was separated. The aqueous phase was extracted with three 50-ml portions of chloroform and the combined chloroform phases were washed with three 50-ml portions of water and dried over magnesium sulfate. Rotoevaporation gave 20.7 g of crude product, which was chromatographed on 60 g of acid-washed Merck alumina by elution with *n*-hexane. The residue from the *n*-hexane fractions was distilled through a 1 × 90 cm glass helice column to give 9.48 g (35% yield) of **3**, bp 54–55° (20 mm) [lit.[33] bp 55° (20 mm)]. The product was estimated to be 100% pure by glc: nmr δ 3.55 (s, 2.0, CH_2Cl), 1.28 [s, 6.0, $(CH_3)_2$], and 1.21 [s, 8.9, $(CH_3)_3$]. The ir (neat) of **3** showed the following significant absorptions: CH, 2975, 2935, 2870, 1470, 1360; CO, 1190, 1150; OO, 870; CCl, 730 cm^{-1}.

Anal. Calcd for $C_8H_{17}ClO_2$: C, 53.18; H, 9.48; Cl, 19.62. Found: C, 53.69; H, 9.76; Cl, 19.43.

Bis(chloro-*tert*-butyl) Peroxide (**4**).—The preparation and purification of **4** was the same as that given in the latter method for **3**, except that 1-chloro-2-methyl-2-propanol[34,35] was used in place of *tert*-butyl alcohol. Peroxide **4** was obtained in 16% yield, with glc-estimated purities of 96–98%: bp 54–55° (2 mm);[36] nmr 3.57 (s, 4.0, CH_2Cl), 1.29 [s, 12.0, $(CH_3)_2$]; ir (neat) CH, 2980–2880, 1470, 1370; CO, 1140; OO, 870; CCl, 740 cm^{-1}; mass spectrum *m/e* (rel intensity) (the molecular ion is M) M + 4, 218 (0.55); M + 3, 217 (0.30); M + 2, 216 (3.2); M + 1, 215 (0.46); M, 214 (5.1); M − CH_3, 199 (0.40); M − CH_2Cl, 167 (11), 165 (62); M − $(CH_3)_2CCH_2Cl(O)$, 109 (17), 107 (56), 92 (100); M − $(CH_3)_2CCH_2Cl(OO)$, 93 (73), 91 (58), and 90 (67) where the absorptions of *m/e* 90–93 are complicated by ions with *m/e* ±1.

Anal. Calcd for $C_8H_{16}Cl_2O_2$: C, 44.67; H, 7.50. Found: C, 44.20; H, 7.21.

Analysis of the reaction mixture from the photochlorination of *tert*-butyl peroxide by glc (20% SE-30 on 60/80 mesh Chromosorb W, 5 ft × 0.25 in., column temperature 125°, helium flow 50 ml/min) indicated that **4** was obtained in 17% yield along with **3** in 50% yield, both based on consumed *tert*-butyl peroxide,

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(27) (a) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **34**, 11 (1938); (b) H. E. O'Neal and S. W. Benson, "Free Radicals," Vol. II, J. K. Kochi, Ed., Wiley, New York, N. Y., 1973, Chapter 17.

(28) Melting points are corrected and boiling points are uncorrected Temperatures reported for kinetic measurements are corrected. Nuclear magnetic resonance (nmr) spectra were obtained with a Varian A-60 spectrometer. Chemical shifts are expressed in parts per million (ppm) relative to tetramethylsilane as 0 ppm (δ scale). The nmr absorptions are given as parts per million, couplng, relative area. Infrared (ir) spectra were determined with a Perkin-Elmer 621 or 337 spectrometer and mass spectra were obtained with a Hitachi RMU-6E instrument (oven 25°, ionization voltage 70 eV). Nmr and ir spectra were obtained in carbon tetrachloride solvent (10% w/v), unless specified otherwise. Gas–liquid chromatography (glc) analyses were performed on a Varian Aerograph Hy-Fi III (FID) or an an A-90P (TC) instrument. Elemental analyses were obtained from C. F. Geiger, Ontario, Calif.

(29) H. B. Dykstra, *J. Amer. Chem. Soc.*, **56**, 1625 (1934).

(30) W. C. Sears and L. J. Kitchen, *J. Amer. Chem. Soc.*, **71**, 4110 (1949).

(31) N. A. Milas and D. M. Surgenor, *J. Amer. Chem. Soc.*, **68**, 205 (1946).

(32) (a) W. H. Richardson, R. S. Smith, G. Snyder, B. Anderson, and G. L. Kranz, *J. Org. Chem.*, **37**, 3915 (1972); (b) W. H. Richardson and R. S. Smith, *J. Amer. Chem. Soc.*, **91**, 3610 (1969).

(33) J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Amer. Chem. Soc.*, **70**, 2767 (1948).

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

(35) J. Burgin, G. Hearne, and F. Rust, *Ind. Eng. Chem.*, **33**, 385 (1941).

(36) A mixture of three isomeric dichloro-tert-butyl peroxides, obtained from photochlorination of *tert*-butyl peroxide, are reported to boil at 55–70° (4–5 mm).[33]

while 76% of the latter peroxide was consumed. Unfortunately, **4** could not be completely separated from the other isomeric dichloro-*tert*-butyl peroxides by the fractional distillation.

Bromo-*tert*-butyl Peroxide (**5**).[37]—A 500-ml three-necked flask was fitted with a thermometer, a fritted glass filter stick which was connected to a chlorine lecture bottle with Tygon tubing, a Y-addition tube which was fitted with a pressure-equilibrated addition funnel and a reflux condenser to which a nitrogen inlet was connected *via* a mercury valve. The flask was charged with 129 g (0.883 mol) of *tert*-butyl peroxide and a magnetic stirring bar, while the addition funnel was charged with 35.7 g (0.223 mol) of bromine. Chlorine was slowly bubbled through the *tert*-butyl peroxide and bromine was added in 1-ml portions with stirring, while the flask was irradiated with a 250-W sun lamp. After the bromine color was discharged, another 1-ml portion was added. Temperature of the reaction mixture was maintained at 40–44° by passing a stream of compressed air over the flask. After completion of the bromine addition, the reaction mixture was washed with two 20-ml portions of saturated sodium bicarbonate solution and then with three 10-ml portions of water. After drying over magnesium sulfate, the crude product was analyzed by glc (20% SE-30 on 60/80 mesh Chromosorb W, 5 ft × 0.25 in., column temperature 125°, helium flow 50 ml/min) using biphenyl as an internal standard. The analysis indicated 50% unreacted *tert*-butyl peroxide and the following yields are based on consumed *tert*-butyl peroxide: **5** (38%), **3** (31%), and **4** (2%). Distillation of the mixture through a 1 × 90 cm glass helice column gave 16.1 g (20% yield) of **3** in 95% purity and 43.5 g (44% yield) of **5** in purity ranging between 96.1 and 98.2%, bp 53–54° (10 mm). Yields are based on 50% consumed *tert*-butyl peroxide. The nmr and ir spectra of **5** showed the following absorptions: nmr δ 3.47 (s, 2.0, CH_2Br), 1.32 [s, 6.2 $(CH_3)_2$], 1.22 [s, 9.1, $(CH_3)_3$]; ir CH, 2980, 2935, 1465, 1360; CO, 1140; OO, 870; CBr, 670 cm^{-1}. A sample of **5** was purified for analysis by preparative glc (conditions as above, except column temperature 89°).

Anal. Calcd for $C_8H_{17}BrO_2$: C, 42.68; H, 7.61; Br, 35.49. Found: C, 42.42; H, 7.67; Br, 35.61.

2-Methyl-2-*tert*-butylperoxy Acetate (**6**).—Acetyl chloride (0.77 ml, 10.9 mmol) was added dropwise over 5 min to a stirred solution containing 1.76 g (10.9 mmol) of 2-*tert*-butylperoxy-2-methyl-1-propanol (**7**)[19] and 0.88 ml (10.9 mmol) of pyridine (distilled from barium oxide) in 3.0 ml of anhydrous ether. After the addition was completed, the mixture was heated under reflux for 2 hr and then the pyridine hydrochloride was filtered and washed with ether. The ethereal filtrate was washed with three 5-ml portions of water and dried over magnesium sulfate. Concentration of the ethereal solution with a rotoevaporator (bath 30°) gave 1.95 g of crude product, which was estimated to be 87% **6** (76% yield) by glc analysis (3% SE-30 on Chromosorb W, 5 ft × 0.125 in., column 50°, flow of nitrogen 28 ml/min). Distillation through a Holtzmann column gave 1.19 g of **6** (53% yield), bp 62.3° (3 mm), without an appreciable improvement in purity. By preparative glc (3% SE-30 on Chromosorb W, 5 ft × 0.25 in., column 70°, detector and injector 110°, helium flow 40 ml/min), **6** was obtained in 98.5–100% purity as estimated by glc: nmr 1.25 [s, 15.1, $(CH_3)_3$ and $(CH_3)_2$], 2.06 (s, 2.9, CH_3CO_2), 4.08 (s, 2.0, CH_2); mass spectrum molecular ion M, 204; (M − CH_2OCOCH_3) or [M − $(CH_3)_2CO$], 131; [M − $(CH_3)_3COO$)], 115.

Anal. Calcd for $C_{10}H_{20}O_4$: C, 58.80; H, 9.87. Found: C, 58.93; H, 10.04.

2-*tert*-Butylperoxy-2-methyl-1-propanol-d_1 (**7D**).—Alcohol **7**[19] (150 mg, 0.773 mmol) in 1.0 ml of chlorobenzene was shaken three times with 0.1 ml (5.5 mmol) of deuterium oxide (99.5 mol %, Matheson Coleman and Bell) at room temperature for periods of 5, 5, and 60 min. The resulting sample was calculated to be 90% deuterated by using the ratio of absorbance of the free O–D stretching frequency in the ir to that of the sum of the O–D and O–H absorbances.

Product Studies.—Chlorobenzene solutions of the peroxides were prepared in 2-ml volumetric flasks and then sealed in melting point capillary tubes. The tubes were immersed in a thermostated Dow-550 silicone oil bath at 150° for 10–11 half-lives. Product analyses were performed by glc (FID) and yields were calculated relative to an authentic mixture of the products in chlorobenzene with the solvent as the internal standard. Areas were obtained from the chromatograms with a planimeter. The unreacted peroxide solutions were checked by glc for decomposition under the conditions of analysis. Only minor amounts of products were observed. The glc conditions for the decomposed peroxide solutions, along with product retention times (minutes), are as follows, where the flow rate of nitrogen is 28 ml/min: **1** [20% polypropylene glycol on Chromosorb W (PPG/CW), 5 ft × 0.125 in., column (C) 39°, injector (I), 100°], acetone (A) (3.5), *tert*-butyl alcohol (BA) (11), chlorobenzene (CB), (54), **1** (6.5); **2** (20% PPG/CW, 5 ft × 0.125 in., C 50°, I 100°), A (2.5), BA (4.4), CB (42); **4** and **7** (same conditions as **2**).

Kinetic Studies.—Chlorobenzene solutions of the peroxides, including radical traps, were sealed in capillary tubes and heated as described above. Tubes were removed from the bath (controlled to ±0.02°) at timed intervals and stored in a refrigerator, and analyses for the peroxides were performed by glc (FID). The peroxides were stable under the glc conditions as determined by checking the unreacted solutions. The glc conditions for analysis of the peroxides, including retention times (minutes) of the peroxide and the internal standard, are as follows, where the flow rate of nitrogen is 28 ml/min: **1** (20% PPG/CW, 5 ft × 0.125 in., C 50°, I 100°), **1** (5.8), CB (42); **2** (3% SE-30 on Varaport-30, 5 ft × 0.125 in., C 50°, I 100°), **2** (12), *p*-dichlorobenzene (DCB) (8.5); **3** and **6** (same conditions as **2**), **3** (7.6), **6** (19); **4** (3% SE-30 on Varaport-30, 5 ft × 0.125 in., C 65°, I 100°), **4** (21), DCB (6.6); **5** (same conditions as for **4**), **5** (11); **7** (10% SF-96 on Varaport-30, 5 ft × 0.125 in., C 80°, I 100°), **7** (10), DCB (15). The ratio of the areas of the peroxides to the internal standards from glc analyses and reaction times were processed by a first-order least-squares computer program. The rate coefficients were based on data collected over approximately 3 half-lives.

Acknowledgment.—We thank the U. S. Army Research Office (Durham) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also thank Professor H. Walba for valuable discussions and the use of his multiple linear regression analysis program. Pertinent comments by the referees are appreciated.

Registry No.—**1**, 110-05-4; **2**, 27492-18-8; **3**, 1068-41-3; **4**, 42334-69-0; **5**, 28531-45-5; **6**, 42334-71-4; **7**, 17393-39-4; **7D**, 42334-73-6; **8**, 16424-69-4.

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[37] The preparation of **5** is claimed in patents, but physical properties are not reported.[38]

[38] (a) F. F. Rust, W. E. Vaughan, and R. W. Wheatcroft, U. S. Patent 2,501,966 (1950); *Chem. Abstr.*, **44**, 5376*b* (1950). (b) W. E. Baughan and F. F. Rust, U. S. Patent 2,501,967; *Chem. Abstr.*, **44**, 5376*d* (1950).