$\simeq 0.9$, the simpler ratios are $k_{ad}/k_{ab} \simeq 0.7$ and $k_{ad}'/k_{ab}' \simeq 9$; thus the hydroperoxy radical gives more addition with nonconjugated carbon–carbon double bonds (relative to hydrogen abstraction) than alkylperoxy radicals.

Epoxide Formation. In the oxidation of neat tetramethylethylene the kinetic expression for the mole ratio of olefin consumed to epoxide formed is given by the expression[6]

$$\frac{-d[TM]}{d[E]} = \frac{1 + f_a + [O_2]k_o/k_r}{f_a} \qquad (16)$$

If we assume that tetramethylethylene in the cooxidations is attacked only by hydroperoxy radicals, a similar expression is obtained:

$$\frac{-d[TM]}{d[E]} = \frac{f_a' + [O_2]k_o'/k_a'}{f_a'} \qquad (17)$$

Since $-d[TM]/d[E]$, f_a', and $[O_2]$ are known, the ratio k_o'/k_r' is evaluated as ~90 l./mol. The reported value of k_o/k_r is 32 l./mol, while from experiment 23 (Table III) and eq 26, a value of 50 l./mol is obtained. Since k_o' should be essentially the same as k_o, k_r/k_r' = 1.5–2.0. This difference is consistent with 5 kcal/mol weaker oxygen–oxygen bonds in dialkyl peroxides than in hydroperoxides.[12] Reaction 14 and 14′ are both exothermic and only a small portion of difference in heats is seen in the rate constants (about 0.5 kcal/mol) if all the difference is in the activation energy.

Registry No.—Hydroperoxy radical, 14691-59-9.

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(9) From our data for the oxidations of butadiene (ref 5), the butadiene peroxy radical has the formula $Y(O_2C_4H_6)_xO_2$, where the end group Y is either a fragment from the initiator, a hydrogen atom, or a fragment corresponding to the cooxidant. In the oxidation of butadiene by itself, *x* averages about 30, but in the cooxidations it is generally of the order of 1–3 owing to extensive reaction of the other hydrocarbon by hydrogen abstraction. The C_4H_6 units in the final product are present as both 1,2 addition units and trans 1,4 addition units in approximately equal amounts. Thus butadiene peroxy radical comprises both primary and secondary allylperoxy radicals and is somewhat less sterically hindered than tetralin peroxy radical, which is a secondary benzylic peroxy radical.
(10) J. A. Howard in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley-Interscience, New York, N.Y., 1973, p 24.
(11) D. G. Hendry, T. Mill, L. Piszkiewicz, J. A. Howard, and H. K. Eigenman, *J. Phys. Chem. Ref. Data*, **3,** 937 (1974).
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Multi-Bond Fragmentation of *tert*-Butyl 2-Methyl-2-*tert*-butylperoxyperpropanoate

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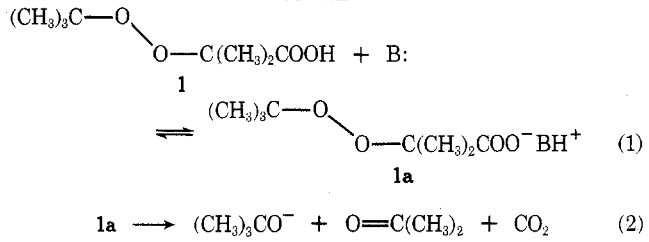
Received April 1, 1976

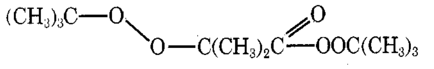
A kinetic study of the thermolysis of *tert*-butyl 2-methyl-2-*tert*-butylperoxyperpropanoate (**2**) and a model perester, *tert*-butyl 2-methoxy-2-methylperpropanoate (**5**), is presented. The decompositions follow first-order kinetics in the presence of styrene, where the activation parameters for **2** are E_a = 18.8 ± 0.4 kcal/mol, $\Delta H^{\ddagger}$ = 18.2 ± 0.4 kcal/mol, log *A* = 10.4, and $\Delta S^{\ddagger}$ = −13.0 ± 1.5 eu. Activation parameters for **5** are E_a = 20.6 ± 0.2 kcal/mol, $\Delta H^{\ddagger}$ = 20.1 ± 0.2 kcal/mol, log *A* = 12.8, and $\Delta S^{\ddagger}$ = 2.7 ± 1.0 eu. Products from the thermolysis of **2** in benzene are (in 100 mmol/mmol **2**) acetone (169), *tert*-butyl alcohol (102), and *tert*-butyl peroxide (9.5). Attempts to trap the radical $(CH_3)_3COO\dot{C}(CH_3)_2$, which could be generated by two-bond homolysis of **2**, were unsuccessful. CIDNP signals were not observed for the potential reaction of this radical with a *tert*-butoxy radical in or out of the solvent cage. However, CIDNP signals were not observed either in the thermolysis of **5**. Correlations of several peresters in $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ and $\Delta H^{\ddagger}$ vs. $\Delta H_r°$ plots were made in order to differentiate between two- and three-bond homolysis processes for **2**. Although the analysis is not unambiguous, the results tend to favor a three-bond homolysis for **2**. Excited state acetone is not produced by thermolysis of **2**, which is consistent with the maximum heat of reaction (−21.9 kcal/mol).

Previously we reported the base-catalyzed decomposition of 2-methyl-2-*tert*-butylperoxypropanoic acid (**1**). This reaction was most conveniently explained as a concerted fragmentation of the carboxylate anion (**1a**).[1]

Scheme I

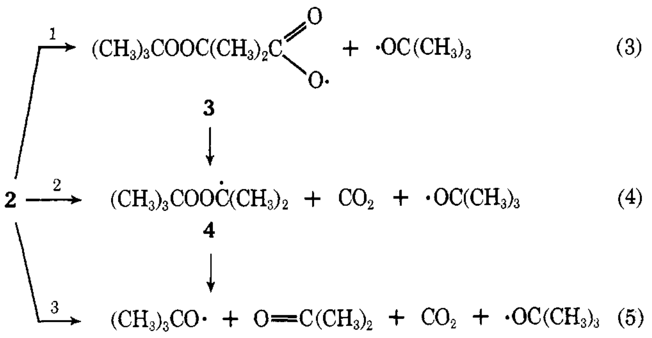


We now report an analogous free-radical decomposition in this peroxide system, namely, the thermolysis of *tert*-butyl 2-methyl-2-*tert*-butylperoxyperpropanoate (**2**). Three unimolecular homolytic reaction paths may be considered for perester **2** (Scheme II). As one proceeds from process 1 to 2 to 3, homolysis of one to two to three bonds occurs in the rate-determining step. A kinetic and product study, along with radical trapping experiments, are employed here in an attempt to differentiate between these three processes.



2

Scheme II

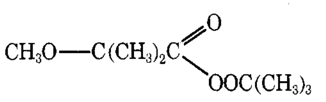


Results

Products. The products observed from the decomposition of 2 in benzene are given in Table I. Unexpectedly, no toluene was observed with an estimated detectability level of 10^{-2} mmol/mmol 2. In an attempt to provide evidence for the fragment radical 4 in Scheme II, a GLC analysis for cumyl *tert*-butyl peroxide was made for the thermolysis of 2 in benzene. Cumyl *tert*-butyl peroxide, which could result from solvent trapping of 4, was not detected. By comparison to an authentic sample of this peroxide, as little as a 1% yield should be easily detectable. Another attempt was made to trap 4 by decomposing the perester 2 in toluene. The expected product from this trapping experiment, *tert*-butyl isopropyl peroxide, was not detected within the 1% yield limit by comparison to an authentic sample. A final attempt to trap 4 by decomposing 2 in carbon tetrachloride was made, where 2-chloro-2-*tert*-butylperoxypropane is the expected product. No products were observed at the expected retention time corresponding to this peroxide.

Kinetic Studies. The effect of temperature on the rate of thermolysis of perester 2 is given in Table II. The decomposition of 2 proved to be first order in the presence of 0.218 M styrene, which was added as a precautionary measure to avoid induced decomposition. Not only were good first-order plots obtained, but in addition the first-order rate coefficient was unaffected by an 11-fold change in the initial concentration of 2. The latter check is seen by comparing the rate coefficients at 19 and 20 °C. A small correction of these data to the same temperature places the rate coefficients to within 0.7% of each other. From the data in Table II, activation parameters for the thermolysis of 2 in benzene with probable error are $E_a = 18.8 \pm 0.4$ kcal/mol, $\Delta H^{\ddagger} = 18.2 \pm 0.4$ kcal/mol, log $A = 10.4$, and $\Delta S^{\ddagger} = -13.0 \pm 1.5$ eu.

As a model for 2, where the alkyl peroxide bond is replaced with an ether linkage, the thermolysis of *tert*-butyl 2-methoxy-2-methylperpropanoate (5) in chlorobenzene was studied. The results of this kinetic study are given in Table III. Good first-order plots were obtained with 5 and changing the concentration of the free-radical trap, styrene, from 0.262 M to 1.33 M while the perester concentration was varied from 0.059 M to 0.119 M did not alter the rate coefficient within experimental error. From Table III, activation parameters for 5 are calculated to be $E_a = 20.6 \pm 0.2$ kcal/mol, $\Delta H^{\ddagger} = 20.1 \pm 0.2$ kcal/mol, log $A = 12.8$, and $\Delta S^{\ddagger} = -1.9 \pm 0.9$ eu. These values compare favorably with those reported by another laboratory ($\Delta H^{\ddagger} = 20.8 \pm 0.4$ kcal/mol, $\Delta S^{\ddagger} = 2.7 \pm 1.0$ eu)[2] where a different experimental method was employed.



$CH_3O{-}C(CH_3)_2C(=O)OOC(CH_3)_3$

5

Table I. Product Analysis of the Thermolysis of *tert*-Butyl 2-Methyl-2-*tert*-butylperoxyperpropanoate (2)[a] in Benzene at 40.0 °C[b]

	Products, 100 mmol/mmol 2		
Run	Acetone	*tert*-Butyl alcohol	*tert*-Butyl peroxide
1	169	100	9.8
2	168	104	9.3
Av	169	102	9.5

[a] 2.53×10^{-2} M. [b] After 10 half-lives. No styrene present.

Table II. Effect of Temperature on the Rate of Thermolysis of *tert*-Butyl 2-Methyl-2-*tert*-butylperoxyperpropanoate (2) in Benzene[a]

Temp, °C	[2], M	$10^4 k$,[b] s^{-1}
42.0	0.1597	24.3 ± 0.8
32.0	0.1432	7.98 ± 0.18
30.0	0.1644	6.94 ± 0.09
20.0	0.0163	2.05 ± 0.05
19.0	0.1752	1.99 ± 0.05
11.0	0.1769	0.983 ± 0.029
9.0	0.1726	0.666 ± 0.010

[a] With 0.218 M styrene. [b] Least-squares fit with probable error.

Table III. Effect of Temperature on the Thermolysis of *tert*-Butyl 2-Methoxy-2-methylperpropanoate (5) in Chlorobenzene

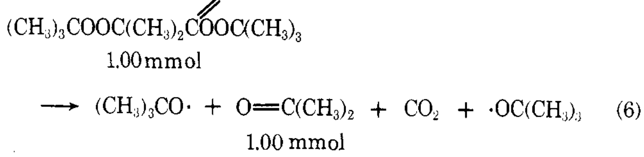
Temp, °C	[5], *M*	[Styrene], M	$10^4 k$,[a] s^{-1}
15.0	0.059	0.262	12.8 ± 0.6
15.0	0.119	1.33	12.0 ± 0.5
7.0	0.119	1.38	4.39 ± 0.11
6.0	0.119	1.47	7.72 ± 0.09
0.0	0.074	0.468	1.77 ± 0.02
−1.0	0.107	0.351	1.67 ± 0.03
−7.0	0.082	0.253	0.673 ± 0.009
−14.0	0.120	0.328	0.205 ± 0.009

[a] Least-squares fit with probable error.

Discussion

From data of Table I, a 96% (= [(169 + 102 + 2(9.5))/300] × 10^2) product balance is obtained for the thermolysis of perester 2 in benzene at 40 °C. The product balance is based on a summation of the yields of acetone, *tert*-butyl alcohol, and *tert*-butyl peroxide.

Irrespective of the rate-determining step for thermolysis of 2 (cf. Scheme II), decomposition of 2 can be written as proceeding to the stage as shown in eq 6. Thus, 1.00 mmol of acetone will result from 1.00 mmol of 2, according to eq 6. Based on the experimental data of Table I and the scheme below along with eq 6, a calculated yield of *tert*-butyl alcohol



$$\underset{1.00\,\text{mmol}}{(CH_3)_3COOC(CH_3)_2C(=O)OOC(CH_3)_3} \longrightarrow (CH_3)_3CO\cdot + \underset{1.00\,\text{mmol}}{O{=}C(CH_3)_2} + CO_2 + \cdot OC(CH_3)_3 \quad (6)$$

can be compared to the experimental value. Agreement between calculated and observed yields of *tert*-butyl alcohol is satisfactory and serves to support the overall mode of thermolysis of 2. Presumably, the benzene solvent is the hydrogen atom source (RH) for the *tert*-butoxy radicals in eq 8.[3] It should be noted that the product studies were measured in the absence of a free-radical scavenger. Although this allows for a more reliable product balance, it does increase the possibility of induced decomposition of the perester. Relevant to this

$$2(CH_3)_3CO\cdot \xrightarrow{k_f} \underbrace{2O{=}C(CH_3)_2 + 2\dot{C}H_3}_{0.69\,\text{mmol}\,(=1.69_{\text{obsd}}-1.00)} \tag{7}$$

$$2(CH_3)_3CO\cdot \xrightarrow[R-H]{k_a} 2(CH_3)_3COH \tag{8}$$

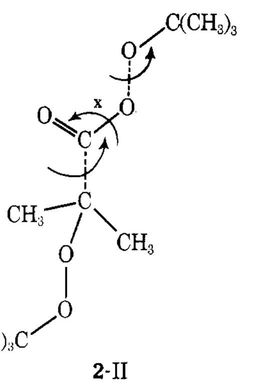
$$\text{calcd } (2.00 - 0.69 - 2(0.095)) = 1.12\,\text{mmol}$$
$$\text{obsd } 1.02\text{ mmol}$$

$$2(CH_3)_3CO\cdot \xrightarrow{k_c} (CH_3)_3COOC(CH_3)_3 \tag{9}$$
$$\text{obsd } 0.095\text{ mmol}$$

point is the fate of the methyl radicals produced in eq 7. At considerably higher temperatures than used here, methyl radicals produce toluene in benzene solution.[3] The lack of toluene from the thermolysis of 2 at 40 °C in benzene could be attributed to hydrogen atom abstraction from 2 by methyl radicals. Alternatively, reactions other than toluene formation may be more favorable for methyl radicals at this lower temperature. At this time we cannot distinguish between these two possible explanations for the lack of toluene. The above scheme is simply formulated in terms of free *tert*-butoxy radicals combining to give *tert*-butyl peroxide (eq 9). We have not investigated this aspect of the reaction, but it is likely that *tert*-butyl peroxide could be formed in a cage reaction.[4]

Considering Scheme II, it appears that one-bond homolysis (eq 3) can be eliminated with some certainty. The most restrictive differentiation of one-bond vs. multi-bond homolysis of peresters, based on the enthalpy of activation, is given by Pryor and Smith.[5] Here it is proposed that peresters with $\Delta H^{\ddagger}$ greater than 33 kcal/mol decompose by one-bond homolysis, while those with $\Delta H^{\ddagger}$ less than 27 kcal/mol decompose by multi-bond homolysis. Since $\Delta H^{\ddagger} = 18.2$ kcal/mol for thermolysis of 2, a multi-bond homolysis process is clearly indicated.

The problem of differentiating between the two- and three-bond homolyses in Scheme II (eq 4 and 5) is considerably more difficult. In their classic paper, Bartlett and Hiatt[6] noted a linear relationship between $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for a series of peresters.[7] The number of bond rotations that were frozen in the activated complex were also correlated with this plot. Such a correlation could then potentially distinguish between the two- and three-bond homolysis routes for 2. It is seen from the activated complexes for two-bond (2-II) and three-bond (2-III) homolyses that one and two bonds, respectively, are restricted in their rotation. With regard to the $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ plot, perester 2 is well correlated. With an experimental $\Delta H^{\ddagger}$ value of 18.2 kcal/mol, $\Delta S^{\ddagger}$ is calculated[7] to be −11 eu, compared to the experimental value of −13 eu. These values of $\Delta S^{\ddagger}$ are within experimental error. Since perester 2 has to our knowledge the lowest reported $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values, the Bartlett–Hiatt plot[6] does not extent to these values. However, it seems clear that this plot would predict at least three bond rotations frozen in the activated complex. Since at most only two bonds are frozen in the activated complex for 2 (cf. 2-III), the Bartlett–Hiatt plot does not allow a choice to be made between 2-II and 2-III. Similarly three bonds are expected to be frozen in the activated complex for perester 5, whereas only one bond is frozen based on a two-bond homolysis. This lack of a quantitative correlation of frozen bond rotations with activation parameters was previously noted by Pryor and Smith.[5] One possible explanation for the apparent increased number of restricted rotations for 2 and 5, as predicted by the Bartlett–Hiatt correlation, is increased solvation of the activated complex relative to the reactant. This ordering of solvent would be expected for an activated complex with significant polar character. Thus, the ordering of the activated complex is reflected in both restricted bond rotations and solvation.


2-II

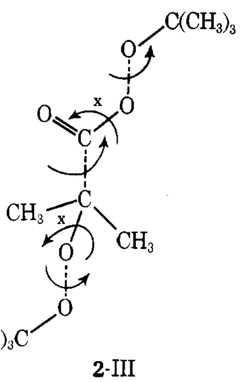
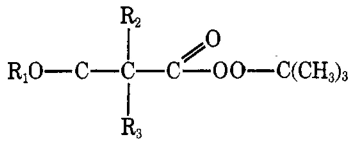

2-III

Table IV. Activation Parameters for *tert*-Butyl α-Alkoxy and α-Aryloxy Peresters 6

R_1	R_2	R_3	Solvent	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	Ref
CH_3	CH_3	CH_3	C_6H_5Cl	20.1	−1.9	This work
C_6H_5	H	H	$C_6H_5C_2H_5$	27	4	9
$C_6H_5CH_2$	H	H	$C_6H_5C_2H_5$	24	2	9
CH_3	H	H	$C_6H_5C_2H_5$	25	4	9
C_2H_5	H	H	$C_6H_5C_2H_5$	25	3.5	9
i-C_3H_7	H	H	$C_6H_5C_2H_5$	24	2	9
4-CH_3O-C_6H_4	H	H	$C_6H_5C_2H_5$	25	−1	9

Another approach to a Bartlett–Hiatt correlation is to use peresters of similar structure where solvation effects may be more uniform. As a model series for 2, α-alkoxy or α-aryloxy peresters 6 may be considered where only one bond rotation is restricted in the activated complex. Activation parameters for peresters of type 6 are given in Table IV. Activation parameters are not included where thermolyses were carried out with neat samples and where induced decomposition is likely. A least-squares correlation of the data in Table IV gives $\Delta S^{\ddagger}$ (eu) = (−20.44 ± 3.46) + (0.939 ± 0.142)$\Delta H^{\ddagger}$ (kcal/mol) with $r = 0.957$, where the last entry in Table IV deviates significantly from the plot and it is excluded. With $\Delta H^{\ddagger} = 18.2$ kcal/mol for 2, the above equation gives $\Delta S^{\ddagger} = -3.35 \pm 2.58$ eu. This calculated value of $\Delta S^{\ddagger}$, based on one frozen bond in the activated complex, may be compared to the experimental $\Delta S^{\ddagger}$ value for 2 of −13 eu. Providing that peresters of type 6 are good models for 2, this may suggest that an additional bond rotation is frozen in 2 (cf. 2-III). Considering the inherent problems in the $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ correlation, this conclusion can only be tentative.



$$R_1O{-}C{-}C(R_2)(R_3){-}C({=}O){-}OO{-}C(CH_3)_3$$

6

Another approach was used to differentiate between the two- and three-bond homolysis routes for 2. Here the heat of reaction ($\Delta H_r°$) was calculated for various perester thermolyses where one- and two-bond mechanisms were operative. It was hoped that a linear Polanyi plot[10] would be established between $\Delta H^{\ddagger}$ for the peresters and $\Delta H_r°$. If so, the $\Delta H_r°$ values for a two- and three-bond homolysis of 2 could be calculated to see which value best fits the Polanyi plot. Thus a decision could be made for two- vs. three-bond homolysis with 2. Table V presents the literature values of $\Delta H^{\ddagger}$ along with the calculated[11] $\Delta H_r°$ values and in Figure 1 these data are plotted. In addition, two points are included for 2, which correspond to a two-bond ($\Delta H_r° = 0.3$ kcal/mol) and a

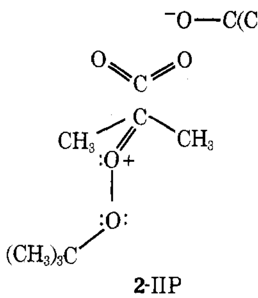
Table V. Experimental Enthalpies of Activation ($\Delta H^{\ddagger}$)[12] and Calculated Heats of Reaction (ΔH_r°)[11] for the Thermolysis of Peresters[a]

Registry no.	Code no.	R in $RCO_3C(CH_3)_3$	$\Delta H^{\ddagger}$, kcal/mol	ΔH_r°, kcal/mol	Homolysis type[b]
5970-01-2	1	CH_3OCH_2	24.8	19.1	2
5789-99-1	2	$C_2H_5OCH_2$	24.5	19.1	2
5790-02-3	3	$(CH_3)_2CHOCH_2$	23.6	19.1	2
7062-83-1	4	$C_6H_5CH_2OCH_2$	24.3	19.1	2
5789-77-5	5	$C_6H_5OCH_2$	27	19.1	2
6104-79-6	6	*p*-$CH_3OC_6H_4OCH_2$	25	19.1	2
29610-77-3	7	C_2H_5OCO	26.9	11.7	2
55695-98-2	8	$C_6H_5CH_2OCO$	26.6	11.7	2
59710-68-8	9	*p*-$CH_3OC_6H_4CH_2OCO$	26.2	11.5	2
107-71-1	10	CH_3	36.9	35.5	1
3990-94-1	11	$C_6H_5CH(CH_3)CH_2$	35.2	35.5	1
16474-36-5	12	$CH_3(CH_2)_7CH_2$	35.3	35.5	1
15076-84-3	13	$CH_3CH{=}CHCH_2$	25.8	6.7	2
59710-69-9	14	$C_6H_5CH{=}CHCH_2$	23.5	−4.3	2
3377-89-7	15	$C_6H_5CH_2$	28.1	8.1	2
17066-26-1	16	$CH_3C{\equiv}CCH_2$	29.8	17.1	2
614-45-9	17	C_6H_5	33.5	35.5	1
17066-27-2	18	$CH_3C{\equiv}CCH(CH_3)$	28.0	12.1	2
59710-70-2	19	$C_6H_5CH(CH{=}CH_2)$	23.0	−8.5	2
13144-32-6	20	$(C_6H_5)_2CH$	25.0	−2.8	2
927-07-1	21	$(CH_3)_3C$	30.0	15.2	2
22426-34-2	22	$CH_3(CH_2)_2C(CH_3)_2$	25.2	15.3	2
22426-33-1	23	$(CH_3CH_2)_3C$	24.7	15.3	2
24161-29-3	24	$C_6H_5C(CH_3)_2$	26.1	3.0	2
30893-89-1	25	$CH_3OC(CH_3)_2$	20.8	0.3	2
59710-71-3	26	$CH_3(CH_2)_{12}$	35.0	35.5	1
3990-91-8	27	$C_6H_{11}C(CH_3)_2CH_2$	35.2	35.5	1
2123-93-5	28	$C_6H_5CH_2CH_2$	35	35.5	1
3990-83-8	29	$C_6H_5C(CH_3)_2CH_2$	34.6	35.5	1
7482-68-0	30	$C_6H_5OCH_2CH_2$	34	35.5	1
7446-49-3	31	$C_6H_5O(CH_2)_3$	33	35.5	1
7446-56-2	32	$CH_3OCH(CH_3)CH_2$	33	35.5	1
17066-28-3	33	$C_6H_5C{\equiv}CCH_2$	28.9	17.1	2
17066-29-4	34	$C_6H_5C{\equiv}CCH(CH_3)$	26.7	2.1	2

[a] Peresters where decompositions were performed on neat samples were not included owing to the likelihood of induced decomposition.
[b] Number of bonds ruptured in the rate-determining step.

three-bond ($\Delta H_r^\circ = -21.9$ kcal/mol) process. A qualitative survey of Figure 1 reveals that two types of peresters show unusually lower $\Delta H^{\ddagger}$ values compared to the bulk of the peresters. These are peresters with unusually large steric effects[13] (code no. 22 and 23) and those with an α-alkoxy or α-aryloxy substituents (code no. 1–6 and 25). Excluding these peresters as well as *tert*-butyl peracetate (code no. 10), a least-squares fit gives a satisfactory[15] correlation ($r = 0.975$), where $\Delta H^{\ddagger} = (0.263 \pm 0.013)\Delta H_r^\circ + 24.94 \pm 0.31$. With the exception of the α-phenoxy substituted perester (code no. 5), the α-alkoxy and α-aryloxy substituted peresters crudely form a line which parallels the bulk of the peresters. A least-squares fit gives a satisfactory correlation ($r = 0.951$), where $\Delta H^{\ddagger} = (0.194 \pm 0.032)\Delta H_r^\circ + 20.74 \pm 0.55$ for these α-alkoxy and α-aryloxy peresters. With this equation and the $\Delta H^{\ddagger}$ value (18.2 kcal/mol) for **2**, a ΔH_r° value of -13.1 ± 2.6 kcal/mol is calculated, which is intermediate between the ΔH_r° values calculated for two-bond (0.3 kcal/mol) and three-bond (−21.9 kcal/mol) homolysis of **2**. A similar calculation with the correlation equation for the bulk of the peresters gives $\Delta H_r^\circ = -25.6 \pm 1.4$ kcal/mol, which is clearly in better agreement with the calculated ΔH_r° value for three-bond rather than two-bond homolysis of **2**.

The question is now whether the bulk of the peresters or the α-alkoxy and α-aryloxy peresters provide a better model for the thermolysis of **2**. To answer this question, one must account for the origin of the lower $\Delta H^{\ddagger}$ values for α-alkoxy and α-aryloxy peresters as seen in Figure 1. The most reasonable explanation for this appears to be polar effects in the activated complex. Such effects are well documented;[2,8,16] however, polar contributions are not included in the calculation of ΔH_r°. These polar contributions would make ΔH_r° more negative so as to more closely fit the correlation line of the bulk of the peresters, where polar effects are not as pronounced. Now one may ask if two-bond homolysis of **2** is characterized by large polar effects in the activated complex, as evidenced with α-alkoxy and α-aryloxy peresters, or with lesser polar effects associated with the bulk of the peresters. Examination of one of the polar canonical structures for the activated complex of **2** (i.e., **2**-IIP) suggests that polar effects should be of lesser importance here than in α-alkoxy or α-aryloxy peresters. In **2**-IIP the strongly electron-withdrawing *tert*-butoxy portion of the intact peroxide bond should destabilize the polar structure. Thus, the bulk of the peresters, where polar effects are less pronounced, would provide a better model for the thermolysis of **2**. However, the ΔH_r° value for two-bond homolysis of **2** is poorly correlated with the bulk of the per-



2-IIP

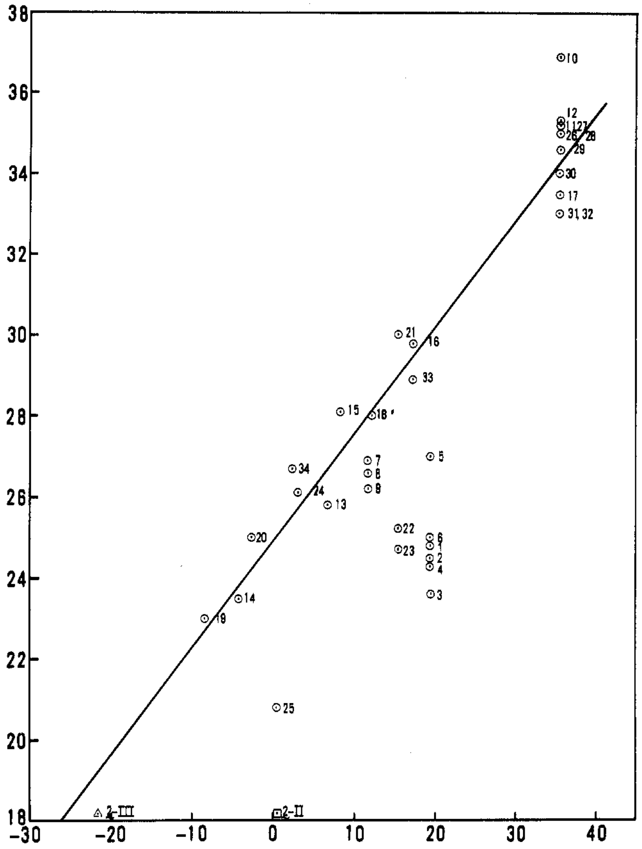


Figure 1. Experimental $\Delta H^{\ddagger}$ values vs. calculated heats of reaction ($\Delta H_r°$) for peresters in Table V. The correlation line is for the bulk of the peresters and excludes code no. 1–6, 10, 22, 23, 25, and **2**. Points shown as □ and △ correspond to ΔH_r values for two- and three-bond homolysis, respectively.

esters. Yet the $\Delta H_r°$ value for three-bond homolysis of **2** is reasonably well correlated by the bulk of the peresters. This analysis of the $\Delta H^{\neq}$ vs. $\Delta H_r°$ correlation then suggests that **2** is better represented by a three-bond homolysis process.

Experiments designed to trap the fragment radical **4** and thus to provide evidence for the two-bond homolysis process were unsuccessful. Products expected from trapping of **4** by solvent (cumyl *tert*-butyl peroxide), or hydrogen atom abstraction (isopropyl *tert*-butyl peroxide), or chlorine atom abstraction (2-*tert*-butylperoxy-2-chloropropane) were not detected from the thermolysis of **2**. Although these results are consistent with a three-bond homolysis process, the unimolecular rate of decomposition of **4** may be fast vs. the bimolecular trapping reactions. The unimolecular rate for decomposition of **4** is unknown, but a rapid decomposition seems reasonable based on the exothermicity of the reaction (−34.3 kcal/mol).

Product analysis from thermolysis of *tert*-butyl isopropoxyperacetate showed that the fragment radical $(CH_3)_2CHO\dot{C}H_2$ was trapped by the *tert*-butoxy radical to give $(CH_3)_2CHOCH_2OC(CH_3)_2$.[2] If the fragment radical **4**, resulting from two-bond homolysis of **2**, was trapped by the *tert*-butoxy radical in or out of the solvent cage, then a CIDNP signal would be expected.[17] No CIDNP signals were detected during the thermolysis of either perester **2** or **5**. Unfortunately, this leaves the CIDNP method of detecting radical **4** in doubt under our experimental conditions, since the model perester **5** did not show CIDNP signals.

In summary, an analysis of the data for thermolysis of **2** tends to favor a three-bond homolysis process. Although the arguments for a three-bond homolysis appear reasonable, the two-bond process cannot be rigorously excluded. Presently it does appear that **2** is the best candidate to date for a perester that undergoes a three-bond homolysis.[8]

In conjunction with our interests in the chemical production of excited state molecules,[18] we attempted to measure light emission during the thermolysis of **2**. No light emission was noted from **2**, which is consistent with the maximum exothermicity of the reaction (i.e., three-bond homolysis, where $\Delta H_r° = -21.9$ kcal/mol). The decomposition would have to be exothermic by at least 80 kcal/mol to produce triplet acetone.[19]

Experimental Section[20]

Materials. *tert*-Butyl hydroperoxide-90 (Lucidol) was purified by azeotropic distillation and then by vacuum distillation.[6] Pyridine (Matheson Coleman and Bell) was fractionally distilled from barium oxide, bp 111–114 °C (lit.[21] bp 115.5 °C). Thionyl chloride (MCB) was purified[22] by refluxing with triethylphosphite, and then by fractional distillation. Thiophene-free, reagent-grade benzene (MCB) was distilled from calcium hydride and a heart cut was collected, bp 79.8–80.1 °C (lit.[23] bp 80.1 °C). The solvent was stored over Drierite and under nitrogen. Chlorobenzene (MCB) was dried over calcium hydride and then over phosphorus pentoxide. The dried solvent was then fractionally distilled and a heart cut was collected, bp 131.0–131.5 °C (lit.[24] bp 132 °C). The purified solvent was stored over Drierite and under nitrogen. Stabilized styrene (MCB) was distilled and a heart cut was collected, bp 35–36 °C (10 mm) [lit.[25] 145–146 °C (760 mm)]. Cumyl *tert*-butyl peroxide[26] and isopropyl *tert*-butyl peroxide[1] were prepared by previously reported procedures.

2-Methyl-2-*tert*-butylperoxypropanoic Acid. This acid was prepared according to a previously reported method.[1] The acid was purified by sublimation at 1 mm pressure (bath 70 °C) and dried in a vacuum desiccator over phorphorus pentoxide, mp 62.0–64.0 °C (lit.[1] mp 62.0–63.5 °C). The NMR spectrum showed the following absorptions: $(CH_3)_3C$ 1.23, s, 9; $C(CH_3)_2$ 1.43, s, 6; and COOH 11.6, s, 1.

2-Methyl-2-*tert*-butylperoxypropanoyl Chloride. An aluminum foil wrapped flask was charged with 1 ml (1.65 g, 13.9 mmol) of purified thionyl chloride and then 1.57 g (8.92 mmol) of 2-methyl-2-*tert*-butylperoxypropanoic acid in 3 ml of methylene chloride was added dropwise with magnetic stirring. The system was protected from moisture with a calcium chloride drying tube and the solution was stirred for 22 h at room temperature.

Thionyl chloride and methylene chloride were distilled at room temperature (4 mm). Flash distillation of the residue at room temperature (2 mm) into an isopropyl alcohol/dry ice cooled receiver gave 0.99 g (58% yield) of the acid chloride. The NMR spectrum of the acid chloride showed the following absorptions: $(CH_3)_3C$ 1.25, s, 9; and $C(CH_3)_2$ 1.48, s, 6.

***tert*-Butyl 2-Methyl-2-*tert*-butylperoxyperpropanoate (2).** An aluminum foil wrapped flask was charged with 0.30 g (1.5 mmol) of 2-methyl-2-*tert*-butylperoxypropanoyl chloride and 2 ml of carbon tetrachloride. The flask was cooled to −24 °C in a carbon tetrachloride/dry ice bath. To the cold solution, 0.17 g (2.1 mmol) of purified pyridine was slowly added dropwise over 5 min with shaking. After precipitation was complete, 0.18 g (2.0 mmol) of purified *tert*-butyl hydroperoxide was slowly added dropwise over 20 min with shaking. During the additions, the reaction flask was swept with a slow stream of nitrogen.

After the additions were completed, the reaction mixture was stored in a freezer (−20 °C) for 3 h and then rapidly filtered through a sintered glass funnel and into a receiver which was cooled in a carbon tetrachloride/dry ice bath. The precipitate was washed with 0.5 ml of cold carbon tetrachloride. The filtrate was washed once with 0.5 ml of 10% (w/v) cold sulfuric acid, once with 0.5 ml of 10% (w/v) cold sodium carbonate, and once with 0.5 ml of cold water. The filtrate was then dried over Drierite for 1 h at −20 °C and finally distilled. The distilling flask was placed in an ice bath and the receiver was immersed in an isopropyl alcohol/dry ice bath. After pumping for 20 min at 4 mm pressure to remove the carbon tetrachloride, 3 ml of benzene was immediately added and the solution was frozen in an isopropyl alcohol/dry ice bath until it was used. The approximate yield, by NMR, was 33%. The NMR spectrum of **2** showed the following absorptions: *gem*-dimethyl protons 1.42, s, 6; *tert*-butylperoxy protons 1.22, s, 9; and *tert*-butyl perester protons 1.28, s, 9.

2-Methoxy-2-methylpropanoic Acid. This acid was prepared according to the procedure of Weizmann, Sulzbacher, and Bergmann,[27] bp 100.0–100.5 °C (22 mm) [lit.[27] bp 98.0–99.0 °C (20 mm)], yield 74%. The NMR spectrum showed the following absorptions: $C(CH_3)_2$ 1.42, s, 6; CH_3O 3.28, s, 3; and COOH 11.6, s, 1.

2-Methoxy-2-methylpropanoyl Chloride. A flask was charged with 2 ml (3.3 g, 28 mmol) of thionyl chloride and 2.40 g (20.3 mmol) of 2-methoxy-2-methylpropanoic acid in 3 ml of methylene chloride was added dropwise with magnetic stirring. The flask was protected from moisture with a calcium chloride drying tube and the solution was stirred for 3 h at room temperature. Thionyl chloride and methylene chloride were distilled at room temperature (4 mm). Flash distillation of the residue at 2 mm pressure (bath 40 °C) gave 1.13 g (41% yield) of the acid chloride. The NMR spectrum showed the following absorptions: $C(CH_3)_2$ 1.48, s, 6; and CH_3O 3.30, s, 3.

***tert*-Butyl 2-Methoxy-2-methylperpropanoate (5).** An aluminum foil wrapped flask was charged with 1.0 g (7.3 mmol) of 2-methoxy-2-methylpropanoyl chloride and 2 ml of Freon-11. The flask was cooled in an isopropyl alcohol/dry ice bath (−78 °C) and then 0.79 g (10 mmol) of purified pyridine was added dropwise over 5 min with shaking. After precipitation was complete, 0.86 g (9.6 mmol) of purified *tert*-butyl hydroperoxide was slowly added dropwise with shaking. During the additions, the flask was swept with a slow stream of nitrogen.

After the additions were completed, the reaction mixture was stored in an isopropyl alcohol/dry ice bath for 3 h. The precipitate was rapidly filtered through a sintered glass funnel and the filtrate was cooled in an isopropyl alcohol/dry ice bath. The precipitate was washed with 3 ml of cold Freon-11. The filtrate was then rapidly washed once with 0.5 ml of 10% (w/v) cold sulfuric acid, once with 0.5 ml of 10% (w/v) cold sodium carbonate solution, and once with 0.5 ml of cold water. The organic phase was dried over Drierite in an isopropyl alcohol/dry ice bath and then the Freon-11 was distilled at room temperature (40 mm) until about 1 ml of solution remained. Now 5 ml of chlorobenzene was added and distillation was continued to remove the Freon-11 [room temperature (5 mm)]. The solution was stored in an isopropyl alcohol/dry ice bath until it was used. The percent yield (10%) was obtained by NMR analysis in comparison to a known amount of methylene chloride. The NMR spectrum showed the following absorptions: $C(CH_3)_2$ 1.40, s, 6; CH_3O 3.20, s, 3; and $(CH_3)_3C$ 1.23, s, 9.

Kinetic Methods. NMR sample tubes were prepared by using 0.8 ml of the thawed stock solution of the perester, 20 μl of methylene chloride, and 20 μl of styrene. The contents were mixed by shaking and frozen until they were to be used. Kinetic data were obtained from thermolysis of **2** by following the appearance of the acetone absorption and from **5** by following the disappearance of the methoxy absorption of **5**, both relative to the methylene chloride absorption. The initial concentration of **2** was obtained by measuring the *gem*-dimethyl protons of **2** relative to the methylene chloride absorption, where the concentration of the latter was known. Similarly, the methoxy protons were used to determine the initial concentration of **5**. Areas of the absorptions were measured with a planimeter. The NMR probe temperature was measured before and after the kinetic measurement with a thermometer which was inserted into the probe. The NMR tube was left in the NMR probe during the entire kinetic measurement (2–3 half-lives). An infinity point was measured after about 10 half-lives. Both the first-order rate coefficients and the activation parameters were obtained by means of a least-squares computer program.

Product Analyses. Initial concentrations of the perester were determined by NMR relative to a known concentration of methylene chloride. The solution was degassed in three freeze–thaw cycles on a vacuum line at 2×10^{-4} mm pressure. The sample was then heated for 3 h in an oil bath at 40 °C. An internal standard was introduced by means of a μl syringe and the sample was subjected to GLC analysis on a 20% polypropylene glycol on Chromosorb W column (5 ft × 0.125 in.), column temperature 150 °C, and flow rate 20 ml nitrogen/min. The yield of products was calculated by reference to a standard mixture which contained the internal standard (typically ethylbenzene) and the reaction products. A chart speed of 4 in./min was used and the retention times for acetone, *tert*-butyl alcohol, *tert*-butyl peroxide, and ethylbenzene were 0.7, 1.0, 1.3, and 3.0 min, respectively.

In the trapping experiments, cumyl *tert*-butyl peroxide was analyzed on a 3% SE-30 on Varaport-30 column (5 ft × 0.125 in.) with a column temperature of 70 °C, injector temperature 95 °C, and a flow rate of 22 ml/min. The $t_{1/2}$ and t_∞ reaction mixtures showed no GLC peaks with a retention time greater than that of benzene (8 min). The retention time of cumyl *tert*-butyl peroxide was 26 min. It was estimated that a 1% yield of this peroxide could be detected. Analyses for isopropyl *tert*-butyl peroxide and 2-chloro-2-*tert*-butylperoxypropane were carried out with an XF-96 column under the following conditions: column temperature 25 °C, injector 75 °C, and flow rate 25 ml/min. The retention time for 2-chloro-2-*tert*-butylperoxypropane was estimated to be greater than that for benzene and approximately the same as that of di-*tert*-butyl peroxide. No peaks were observed between benzene (14 min) and di-*tert*-butyl peroxide (33 min) or greater than 33 min. It was estimated that a 1% yield of isopropyl *tert*-butyl peroxide or 2-chloro-2-*tert*-butylperoxypropane could be detected.

Light Emission. Light emission measurements were obtained with a Hamamatsu R374 head-on photomultiplier tube as previously described.[18d] Measurements were made with nondegassed benzene solutions of **2** in the presence and absence of 9,10-diphenylanthracene at 26–28 °C.

CIDNP. An NMR tube containing 0.2 M **5** was placed in the preheated probe (18 °C, $t_{1/2}$ = 9 min) of a JEOL PS-100 spectrometer operating with an external H_2O lock. A repetitive scan from 1.0 to 2.5 ppm with a sweep time of 100 s was run through 3 half-lives of the perester decomposition. A second repetitive scan was made from 2.5 to 4.0 ppm with a fresh sample of **5**. No enhanced absorption or emission was observed. The same procedure was repeated with perester **2**, where the probe temperature was 35 °C ($t_{1/2}$ = 11 min). Again, no CIDNP signals were observed.

Acknowledgment. We thank the U.S. Army Research Office (Durham) for support of this work.

Registry No.—**2**, 59710-72-4; 2-methyl-2-*tert*-butylperoxypropanoic acid, 59710-73-5; 2-methyl-2-*tert*-butylperoxypropanoylchloride, 59710-74-6; thionyl chloride, 7719-09-7; *tert*-butyl hydroperoxide, 75-91-2; 2-methoxy-2-methylpropanoic acid, 13836-62-9; 2-methoxy-2-methylpropanoyl chloride, 56680-82-1.

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