Anchimerically Accelerated Bond Homolysis. VI. The Mechanism of Sulfur Participation on Perester Oxygen[1]

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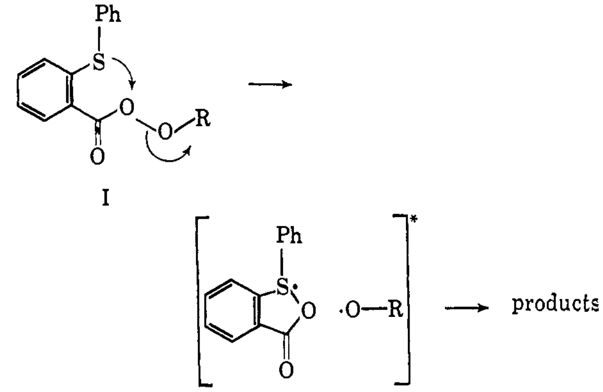
Abstract: The relative rates of decomposition of the *t*-butyl peresters of *o*-(phenylthio)benzoic acid (I), 2,6-di-(phenylthio)benzoic acid (V), 8-(phenylthio)-1-naphthoic acid (VIII), *o*-(phenylthiomethyl)benzoic acid (VII), 1-naphthoic acid, and benzoic acid in chlorobenzene at 40° are: 6.53×10^4, 4.31×10^4, 8.05×10^3, 5.6, 2.0, and 1.0, respectively. A discussion of this wide variation in relative rates, in conjunction with product studies, is understood in terms of a postulated over-all mechanism of sulfur participation. The evidence suggests a preference for a mechanism for the decomposition of peresters V and VIII involving attack on a single carboxylate oxygen and by analogy, considering the similarity of activation parameters for I and VIII, this may be extended to perester I. The decomposition of V, containing two *o*-phenylthio groups proceeds through a transition state receiving no net stabilization from bonding of oxygen to the second of these sulfur-containing substituents.

The thermal decomposition of *t*-butyl perbenzoate is tremendously accelerated by the introduction of an *o*-phenylthio or *o*-methylthio group.[4-6] This large rate enhancement is ascribed to O–S bond formation simultaneous with the homolytic O–O bond cleavage, involving a transition state in which sulfur has expanded its valence octet.[7] The question of which of the three perester oxygen atoms the sulfur attacks has been as yet unanswered. Mechanisms of sulfur participation involving attack of sulfur on any one of the three perester oxygens (mechanism A, B, or C) are compatible with the data previously available. The observed products could result from any of these decomposition pathways. Paths A and C lead to the same bridged intermediate and path B to an intermediate easily convertible to this bridged structure.

Each of the three transition states II–IV might be expected to have large contributions from dipolar structures in which a positive charge is on sulfur and a negative charge on the oxygen atom of the leaving group. This provides a basis for rationalizing the observed effects on the decomposition of perester I of polar substituents on the *o*-phenylthio group, solvent ionizing power, and added salt.[5,6] The five-membered ring formation in transition states II and IV has analogy in reactions of peresters with neighboring olefinic double bonds, and in the cyclization of several 5-hexenyl radicals.[8-10] In at least one case,[1] in which oxygen-18

Mechanism A



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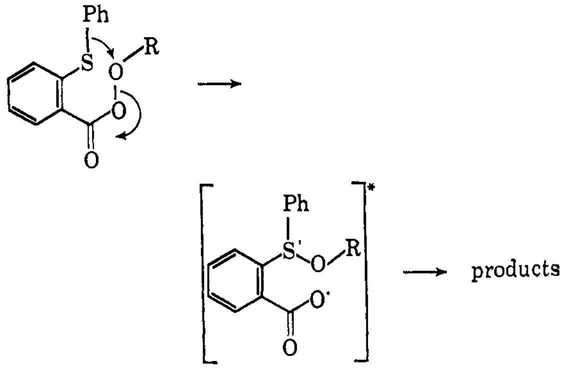
Mechanism B



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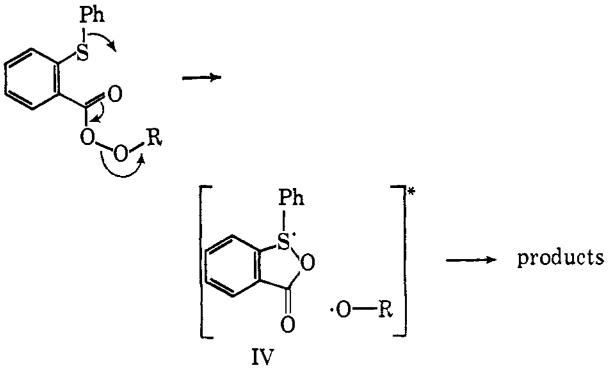
Mechanism C



IV

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[1] For part V see J. C. Martin and T. W. Koenig, *J. Am. Chem. Soc.*, **86**, 1771 (1964).

[2] Taken from the Ph.D. Thesis of T. H. F., University of Illinois, 1964.

[3] Fellow of the Alfred P. Sloan Foundation, 1962–1966.

[4] W. G. Bentrude and J. C. Martin, *J. Am. Chem. Soc.*, **84**, 1561 (1962).

[5] W. G. Bentrude, D. L. Tuleen, and J. C. Martin, *ibid.*, **85**, 1938 (1963).

[6] J. C. Martin, D. L. Tuleen, and W. G. Bentrude, *Tetrahedron Letters*, 229 (1963).

[7] Recently, R. J. Gritter and D. J. Carey, *J. Org. Chem.*, **29**, 1160 (1964), reported the reaction of some alkoxy radicals with phenyl sulfide to give sulfoxides believed to involve the intermediate, $RO\dot{S}Ph_2$, in which sulfur has expanded its octet. Also, J. W. Knapczyk, G. H. Wiegand, and W. E. McEwen, *Tetrahedron Letters*, 2971 (1965), have rationalized results of studies of the decomposition of triarylsulfonium alkoxides in terms of such intermediates.

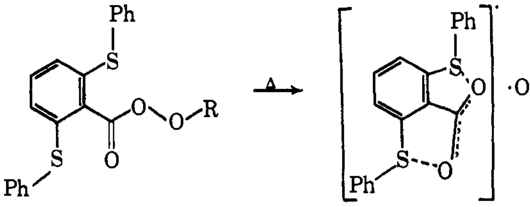
[8] R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Am. Chem. Soc.*, **85**, 3483 (1963).

[9] N. O. Brace, *ibid.*, **86**, 523 (1964).

[10] C. Walling and M. S. Pearson, *ibid.*, **86**, 2262 (1964).

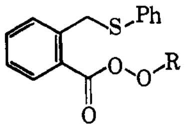
tracer studies have been carried out, evidence strongly favors a mechanism analogous to A. On the other hand, mechanism B is favored from a consideration of leaving groups alone, *i.e.*, benzoyloxy is a better leaving group than *t*-butoxy. Mechanism C can be thought of as an intramolecular free-radical SN2′ or SH2′ reaction, with allylic displacement on the carbonyl double bond.

Three peresters studied in this work are designed to provide the basis for a choice among the three above mechanisms: *t*-butyl 2,6-di(phenylthio)perbenzoate (V), *t*-butyl *o*-(phenylthiomethyl)perbenzoate (VII), and *t*-butyl 8-(phenylthio)per-1-naphthoate (VIII).

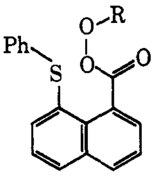


V

VI



VII



VIII

Perester V is intriguing in that it provides the possibility of participation of two sulfur atoms in its thermal decomposition through a symmetrical transition state (VI) involving a degree of delocalization of the odd electron which might be energetically significant.

Results

Perester Syntheses. The peresters were synthesized by the addition of an acid chloride to a mixture of *t*-butyl hydroperoxide and pyridine in ether at low temperature.[5,11] Purification of the peresters was effected by elution chromatography followed, for solid compounds, by recrystallization. The *t*-butyl peresters were easily identified by infrared (single carbonyl absorption near 1750 cm^{-1}) and nmr (single *t*-butyl absorption at τ 8.6) spectroscopy.

The aryl sulfides used as precursors in the syntheses were formed by the displacement of an aryl halide with thiophenolate anion by the method of Adams.[12,13] Thus, 2,6-di(phenylthio)benzoic acid was prepared by heating 2,6-dichlorobenzoic acid and cuprous thiophenolate in a quinoline and pyridine solvent at 160° for 3 hr. The 8-(phenylthio)-1-naphthoic acid was synthesized from sodium 8-bromo-1-naphthoate and sodium thiophenolate in refluxing xylene.[14]

Rate Studies. First-order rate constants for the thermal decompositions of peresters V, VII, VIII, and *t*-butyl per-1-naphthoate (IX) are listed in Table I. These kinetic measurements were made by following[5] the disappearance of the perester carbonyl near 1750 cm^{-1}, or by following the disappearance of the colored radical scavenger galvinoxyl at 575 mμ.[15] When the decomposition of perester VII was followed by infrared spectroscopy, an accurate $(OD)_\infty$ could not be obtained because of product absorption in the 1750-cm^{-1} region. A rate constant was obtained by this method but the error in this measurement may be as high as 10%. This difficulty was overcome by using the galvinoxyl method, which also eliminates radical-chain-induced decomposition and allows a measure of the per cent of scavengeable radicals.

Table I. Rate Data for Perester Decomposition in Chlorobenzene

Perester	P_0,[a] mole/l.	Temp, °C	$k \times 10^5$ sec^{-1} [c]
V	0.039	40.1	7.07 ± 0.02
VII	0.69×10^{-3}	120.1	42.0 ± 0.1
VII	0.40×10^{-3}	98.7	4.64 ± 0.01
VII	0.26	99.0	14.2 ± 0.6
VIII[b]	0.044	80.0	98.2 ± 1.5
VIII[b]	0.041	70.0	34.4 ± 0.5
VIII[b]	0.042	50.0	3.83 ± 0.04
VIII	0.74×10^{-3}	70.0	31.2 ± 1.2
IX[b]	0.044	110.1	8.69 ± 0.19

[a] Initial perester concentration; the lower concentrations ($\times 10^3$) were followed by the galvinoxyl method and all others by the infrared method. [b] 0.2 *M* styrene inhibitor added. [c] Rate constants and standard deviations determined by the method of least squares.

A summary of the relative rates of thermal decomposition, and activation parameters of some substituted *t*-butyl perbenzoates is given in Table II. Table III lists the same data for some substituted *t*-butyl per-1-naphthoates.

Table II. Decomposition of X-Substituted *t*-Butyl Perbenzoates in Chlorobenzene

X	Rel rate, 40°[a]	ΔH^*, kcal/mole	ΔS^*, eu
o-C_6H_5S	6.53×10^4	23.0	−3.4
2,6-Di-C_6H_5S	4.31×10^4		
o-CH=CPh_2	153	26.3	−5.0
o-I	80.5	28.0	−0.8
o-$C_6H_5SCH_2$	5.6	32.2	7.2
o-$(CH_3)_3C$	2.4	34.4	12.5
H	1.0	34.1	10.0
o-CH_3SO_2	0.4[b]	38.0	19.5

[a] Calculated from values of ΔH^* and ΔS^* given in this table. [b] At 120°, relative to *t*-butyl perbenzoate at 120°.

Table III. Decomposition of *t*-Butyl Peresters of 8-X-Substituted 1-Naphthoic Acids in Chlorobenzene

X	Rel rate, 110°	ΔH^*, kcal/mole	ΔS^*, eu
H (IX)	1.0		
Br	1.8		
C_6H_5S (VIII)	180[a]	23.7	−5.5

[a] At 40° this value would be 4.02×10^3.

Product Studies. The products obtained from the decomposition of perester VIII are listed in Table IV. The remaining 35% of the unidentified residue was not resolved.

The products of the decomposition of perester VII are listed in Table V. The major neutral decomposition

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(11) P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958).
(12) R. Adams and M. D. Nair, *Croat. Chem. Acta.*, **29**, 277 (1957).
(13) R. Adams and A. Ferretti, *J. Am. Chem. Soc.*, **81**, 4930 (1959).
(14) H. G. Rule and H. M. Turner, *J. Chem. Soc.*, 317 (1935).
(15) T. W. Koenig and J. C. Martin, *J. Org. Chem.*, **29**, 1520 (1964).

Table IV. Products of the Decomposition of *t*-Butyl 8-(Phenylthio)per-1-naphthoate (VIII) in Chlorobenzene at 80°

Product	Mole/mole of perester
Acetone	0.36
Isobutylene	0.29 (0.16)[a]
t-Butyl alcohol	0.32
Chlorotoluenes	0.11
Carbon dioxide	0.02[a]
Phenyl 8-carboxy-1-naphthyl sulfide (XIV)	0.60
Phenyl 8-carboxy-1-naphthyl sulfoxide (XIII)	0.05
Mole % of *t*-butyl residue identified	0.97
Mole % of carbonyl identified	0.65

[a] Isolated by vacuum-line techniques.

Table V. Products of the Decomposition of *t*-Butyl *o*-(Phenylthiomethyl)perbenzoate in Chlorobenzene at 110°

Product	Mole/mole of perester
t-Butyl alcohol	0.65
Acetone	0.28
2-Carboxybenzyl phenyl sulfide (XIX)	0.3
3-(Phenylthio)phthalide (XVI)	0.5–0.6

product, a light yellow solid, mp 95–97°, was identified as 3-(phenylthio)phthalide on the following basis. The infrared spectrum of this compound shows a strong absorption at 1775 cm^{-1} (phthalide carbonyl), and no O–H absorption. Its nmr spectrum has peaks at τ 2.0–2.8 (aromatic) and a singlet at 3.3 with the relative areas of 9.0:0.82. The compound is unstable and tends to lose thiophenol during recrystallization.

Discussion

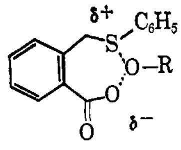
Intramolecular Attack of Sulfur on Perester Oxygen. Participation of both sulfur atoms in the decomposition of *t*-butyl 2,6-di(phenylthio)perbenzoate (V) through transition state VI might be expected to accelerate the decomposition of V relative to the analogous perester (I) bearing only a single *o*-phenylthio substituent. The geometry of the system is such as to allow simultaneous direct backside displacement on the peroxidic carboxyl oxygen and SH2′ displacement on the carbonyl oxygen. The SH2′ displacement could occur through a transition state involving the *cis* relationship of entering and leaving groups found by Stork and White[16] to be favored in at least one example of the SN2′ reaction. The resemblance in charge distribution between these radical-forming displacements and ordinary nucleophilic displacements suggests that parallel geometrical requirements might be encountered in the two types of reaction.

The effects attributable to the presence of the second *o*-phenylthio substituent in V are (a) steric, (b) electronic (transmitted through the ring), and (c) direct interaction (neighboring group participation). The first effect, assuming a nonbonded repulsion between the second sulfur and an oxygen atom of a carboxyl group approaching coplanarity with the aromatic ring in the transition state, would be a decelerating effect. The second effect (b) would be expected, from our knowledge of substituent effects in the decomposition of I, to be a very small effect. The small rate reduction (an estimated[17] factor of 0.6), expected from the electronic interaction of the second thiophenyl group with the first, is essentially canceled by the statistical factor of two encountered when comparing V with I. The interaction of the second thiophenyl substituent with the carbonyl group in a transition state similar to II or IV cannot be quantitatively predicted, but would be expected to be small.

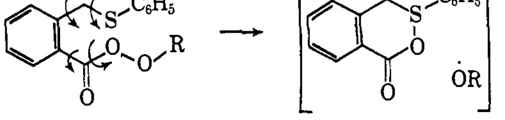
The observation of very similar rates for the decomposition of I and V (6.53×10^4 and 4.31×10^4 times faster than *t*-butyl perbenzoate, respectively, at 40° in chlorobenzene) leads us to conclude that the anchimeric acceleration provided by the second sulfur atom in V is very small or zero, certainly no larger than would be required to counteract the decelerating steric effect (a).

The small rate factor (0.66) is most easily rationalized in terms of a transition state for decomposition similar to that of I, involving bridging to one sulfur atom only. While this does not allow a choice between mechanisms A, B, and C it does suggest that the simultaneous operation of A and C (as in VI) is not likely.

The importance of dipolar structures with a positive charge on sulfur and a negative charge on the oxygen of the leaving group in the transition states II–IV was mentioned earlier. The dependence of the rate of perester decomposition on the nature of the leaving group, in particular its ability to accommodate a negative charge, has been shown for molecules containing neighboring iodine[5] and neighboring 2,2-diphenylvinyl[15] groups. The same is undoubtedly true in the case of a neighboring sulfide group. This dependence on the nature of the leaving group is the major consideration in favor of mechanism B since benzoate is a much better anionic leaving group than is *t*-butoxy. A molecule designed to provide insight into the importance of mechanism B is *t*-butyl *o*-(phenylthiomethyl)perbenzoate (VII). A mechanism involving a leaving benzoate group (resembling B) would entail, for this molecule, formation of a seven-membered ring transition state with its attendant highly unfavorable entropy of activation.



If sulfur participation as described by mechanism A (or C) were important in the decomposition of perester VII, then the six-membered ring transition state X would be formed, involving the loss of rotational freedom about the four bonds indicated in the figure. We may assume that participation would lower the ΔH^*



VII X

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(16) G. Stork and W. N. White, *J. Am. Chem. Soc.*, **75**, 4119 (1953).

(17) Estimated using the σ_m value for the methylthio group reported by H. C. Brown, Y. Okamoto, and T. Inukai, *ibid.*, **80**, 4967 (1958), 0.15, as an approximation of that for the phenylthio group.

for this decomposition to the same extent as in perester I.

Extrapolating an entropy value from the correlation of Bartlett and Hiatt[11] for the loss of rotational freedom about four bonds, we predict for the decomposition of perester VII a ΔS^* of approximately -12 eu. Using these activation parameters, an approximately 50-fold rate acceleration over *t*-butyl perbenzoate would be predicted at 100°.

The rate of decomposition of *t*-butyl *o*-(phenylthiomethyl)perbenzoate is determined to be 4.3 (by the galvinoxyl method, trapping efficiency 67%) or 13.1 (by the infrared method) times faster than *t*-butyl perbenzoate at 99°. The difference in these two rates suggests the destruction of 66% of the perester by a radical-chain-induced decomposition in the reactions carried out in the absence of radical scavenger (this will be discussed in more detail later). Activation parameters for the decomposition of perester VII are: $\Delta H^* = 32.2$ kcal/mole and $\Delta S^* = 7.2$ eu. This lack of an appreciable rate acceleration and the high values of ΔH^* and ΔS^* indicate the absence of sulfur participation in the decomposition of perester VII, and suggest a simple homolytic cleavage of the O–O bond as in *t*-butyl perbenzoate.

Lack of participation in the decomposition of VII can be rationalized in two ways.

(a) The favored reaction path for sulfur participation might involve attack on *t*-butoxy oxygen, in this case through a seven-membered cyclic transition state, with a resulting highly unfavorable ΔS^*.

(b) Sulfur participation involving attack on carboxyl oxygen through six-membered cyclic transition state X might be less favored on entropy grounds than the gross extrapolation above would indicate, with the result that the entropy loss required to reach X (involving the loss of rotational freedom about four bonds) is not counterbalanced at this temperature by the lowered enthalpy which would result from sulfur participation.

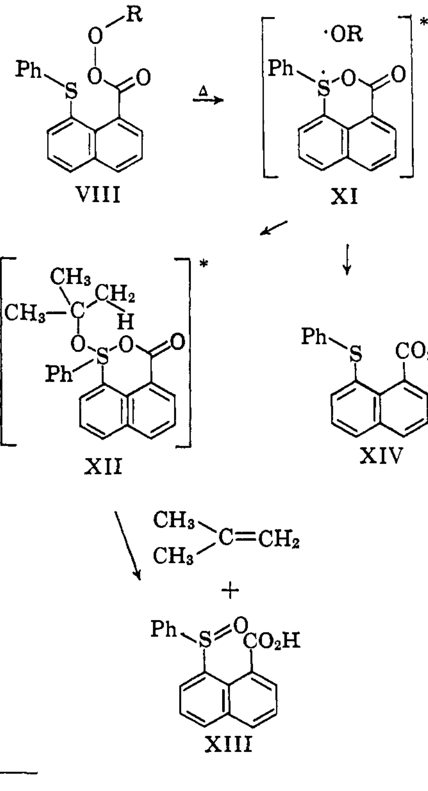
With these two possible explanations for the failure to observe anchimerically accelerated decomposition of VII, we are unable to choose between mechanisms similar to A and B for this compound. The imperfections in the analogy with perester I are great enough to render any mechanistic conclusion suspect.

In order to choose between the mechanisms of sulfur participation for perester I, a system was devised in which the leaving group would be *t*-butoxy in a displacement on acyloxy oxygen through a six-membered ring transition state whose formation might be expected to involve a more favorable ΔS^*. By providing in the ground state of *t*-butyl 8-(phenylthio)per-1-naphthoate (VIII) some of the constraint necessary to form the six-membered ring, we need to lose rotational freedom about only three bonds on going to transition state XI. The decomposition of *t*-butyl per-1-naphthoate was also studied to provide a model for comparison of relative rate data.

Cooper,[18] in a study of the initiation of vinyl polymerization with a variety of substituted diacyl peroxides, reported the relative rates of decomposition of 1-naphthoyl, 2-naphthoyl, and benzoyl peroxides to be 32.7, 1.1, and 1.0, respectively, at 70°. The increased rate of decomposition of 1-naphthoyl peroxide (32.7 times) over benzoyl peroxide, as reflected in the gross polymerization rates, was attributed to steric strain and a polarization effect. This rate effect is larger than would be predicted from the rate studies of benzoyl peroxides substituted with bulky *o*-aryl and *o*-alkyl groups,[19–21] and related peresters.[4]

We find *t*-butyl per-1-naphthoate (IX) to decompose 2.0 times faster than *t*-butyl perbenzoate in chlorobenzene at 110°. This rate effect is considerably smaller than that reported by Cooper for the diacyl peroxides, and is consistent with the usual small rate effect observed in the peresters and peroxides mentioned above.

t-Butyl 8-(phenylthio)per-1-naphthoate (VIII) decomposes 4000 times as fast as *t*-butyl per-1-naphthoate at 40° in chlorobenzene. The activation parameters for the decomposition of this perester are: $\Delta H^* = 23.7$ kcal/mole and $\Delta S^* = -5.5$ eu. This large rate acceleration is consistent with sulfur participation through a singlet transition state such as XI. This is very similar to mechanism A or C, except that here a six-membered ring transition state is involved. The formation of XI involves the loss of rotational freedom about three bonds instead of four bonds as in the six-membered ring transition state X. The activation parameters for decomposition of perester VIII fall into the range of values observed by Bartlett and Hiatt[11] for reactions involving the loss of rotational freedom about three bonds. This large rate acceleration is considered strong evidence against mechanism B. Displacement on *t*-butoxy oxygen would, in this case, involve a seven-membered ring transition state, unfavored both on entropy and enthalpy grounds. The near identity of the activation parameters for decomposition of I and VIII may be taken as evidence



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[18] W. Cooper, *J. Chem. Soc.*, 3106 (1951).

[19] F. D. Greene, G. R. Van Norman, J. C. Cantrill, and R. D. Gilliom, *J. Org. Chem.*, **25**, 1790 (1960).

[20] D. F. DeTar and C. C. Chu, *J. Am. Chem. Soc.*, **82**, 4969 (1960).

[21] A. T. Blomquist and A. J. Buselli, *ibid.*, **73**, 3883 (1951).

for the preferred attack on carboxyl oxygen in I as well (mechanism A or C). Linearity of Eyring plots (ln k/T *vs.* $1/T$) over 30–40° temperature ranges for each of these peresters is good evidence against the simultaneous operation of mechanisms A and B; mechanisms expected to differ greatly in ΔS^* since the transition state for B involves the introduction of considerably more geometrical constraint than does that for A.

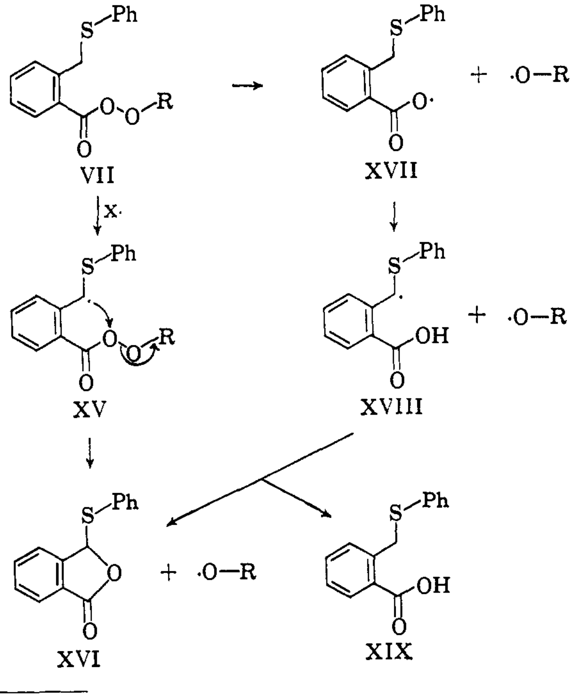
All of the products observed from the decomposition of *t*-butyl 8-(phenylthio)per-1-naphthoate are consistent with the indicated mechanism. Evidence for the radical nature of this decomposition was obtained by use of the radical scavenger galvinoxyl. The first-order rate constants were the same determined by either the galvinoxyl method (trapping efficiency of 40%) or the infrared method. Acetone and *t*-butyl alcohol are products expected from an intermediate *t*-butoxy radical. The fairly large amount of isobutylene formed here is similar to that observed[6] in the decomposition of perester I and is probably the result of a similar reaction. One of the more probable modes of formation of isobutylene is by way of the six-membered transition state XII in reaction 1. Although equal amounts of sulfoxide XIII and isobutylene were not isolated, about 35% of the products were unidentified, making quantitative correlations less reliable than one would wish.

The major decomposition product of perester I results from phenyl migration from sulfur to oxygen. The possibility of phenyl participation was considered as an explanation of the large rate effects but was rejected[4] after careful consideration of the evidence. Phenyl migration follows the rate-determining step. The absence of any phenyl ester products in the decomposition of perester VIII reflects the unfavorable nature of the seven-membered ring transition state which is required for phenyl migration from sulfur to oxygen in this compound and further strengthens the argument that sulfur participation, not phenyl participation, is responsible for the anchimeric acceleration observed in the decomposition of these peresters.

Several isotopic labeling studies are pertinent to the differentiation of mechanism A and C. The decomposition of *t*-butyl *o*-(2,2-diphenylvinyl)perbenzoate with O^{18} in the carbonyl position retained 88% of the O^{18} in the carbonyl of the products.[1] This supports bridging in this olefinic system similar to that in mechanism A, at least to the extent of 76%. In a superficially similar case, the decomposition of 3,3,3-triphenylpropanoyl peroxide with O^{18}-labeled carbonyl involves a path in which about 65% of the excess O^{18} is bonded to the phenyl ring of the product phenyl esters.[22] This result has been interpreted in terms of the presence of the peroxide in the more stable conformer with the large triphenylmethyl group and the peroxide linkage *trans*. Migration of a phenyl group follows the rate-determining, unassisted O–O bond cleavage with a rate somewhat more rapid than that of rotation about the C–C bond. This could explain a 2:1 preference for the nearest oxygen of the acyloxy radical, the carbonyl oxygen. This is consistent with the failure to observe anchimeric acceleration in the decomposition of this peroxide. Intermolecular radical displacements occur on the peroxidic oxygen of acyl peroxides. Such displacements include the induced decomposition of benzoyl peroxide in diethyl ether,[23,24] the reaction of trityl radicals with benzoyl peroxide,[25] and the reaction of the sodium ketyl of benzophenone with benzoyl peroxide.[26] All of these results provide a consistent set of precedents suggesting the operation of mechanism A, involving a displacement on the peroxidic oxygen rather than on the carboxyl oxygen (mechanism C).

Intramolecular Induced Decomposition. The decrease in the rate of decomposition of *t*-butyl *o*-(phenylthiomethyl)perbenzoate (VII) observed in the presence of added radical scavenger suggests that in the reaction in the absence of added radical scavenger about 66% of the perester was destroyed by a radical-chain-induced decomposition. A reasonable mechanism for this induced decomposition involves the radical XV. Radical XV can then undergo intramolecular-induced decomposition to give phthalide XVI and *t*-butoxy radical. The operation of this mechanism would explain the observation of a larger than usual amount of *t*-butyl alcohol. The *t*-butyl alcohol:acetone ratio found in the decomposition of perester VII (2.3) is two to three times that usually found in *t*-butyl perbenzoate decompositions[1,5,6] in chlorobenzene.

Another mechanism which may account for some of the observed products, phthalide XVI and acid XIX, is shown on the right side of the flow diagram. The rate data and activation parameters for the decomposition of perester VII in the presence of added scavenger indicate, as discussed earlier, a simple homolytic cleavage of the O–O bond to give radical XVII. Radical XVII can abstract a hydrogen atom from RH to give acid XIX, or undergo an intramolecular hydrogen transfer to give radical XVIII. Radical XVIII (or



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[22] D. B. Denney, R. L. Ellsworth, and D. Z. Denney, *J. Am. Chem. Soc.*, **86**, 1116 (1964).

[23] D. B. Denney and G. Feig, *ibid.*, **81**, 5322 (1959).

[24] J. C. Martin and E. H. Drew, *Chem. Ind.* (London), 925 (1959).

[25] W. Von E. Doering, K. Okomato, and H. Drauch, *J. Am. Chem. Soc.*, **82**, 3579 (1960).

[26] J. F. Garst, D. Walmsby, and W. Richards, *J. Org. Chem.*, **27**, 2924 (1962).

XVII) could then disproportionate to give acid XIX and phthalide XVI. This type of reaction, intramolecular hydrogen transfer followed by disproportionation, was observed by Greene[19] in the very similar decomposition of *o*-benzylbenzoyl peroxide.

Conclusion

The evidence for anchimeric acceleration of the radical decomposition of perester VIII through a six-membered cyclic transition state, together with the observed linearity of the activation plot (Eyring equation), strongly suggests that mechanism B is not important in the decomposition of perester I. The similarity in decomposition rates for I and V may be taken as evidence against the operation of both mechanisms A and C simultaneously in the same molecule of V. Several analogies point to the preference for displacement of peroxidic carboxyl oxygen, mechanism A, rather than on carbonyl oxygen, mechanism B.

Experimental Section

Materials. The purification of chlorobenzene, ether, pentane, *t*-butyl hydroperoxide, and galvinoxyl have been described elsewhere.[5]

2,6-Di(phenylthio)benzoic Acid. Using the methods of Norris and Bearse,[27] 2,6-dichlorotoluene was converted to 2,6-dichlorobenzoic acid in 51% yield, mp 142.5–143.5° (lit.[27] mp 143–144°). A mixture of 2,6-dichlorobenzoic acid (11.1 g, 0.058 mole) and cuprous thiophenolate[12] (22.2 g, 0.129 mole) was heated at 140–165° in a quinoline (90 ml) and pyridine (5 ml) solvent system for 3 hr using the general procedure of Adams and Ferretti.[13] (When the reaction was run at 200–210° for 17 hr the benzoic acid was found to be completely decarboxylated.) The reaction mixture was cooled, acidified, and extracted with ether. Removal of solvent left the desired acid which was recrystallized from ethanol-water, yield 50%, mp 170–172.5°.

Anal. Calcd for $C_{19}H_{14}S_2O_2$: C, 67.42; H, 4.17. Found: C, 67.11; H, 4.04.

***t*-Butyl 2,6-Di(phenylthio)perbenzoate.** 2,6-Di(phenylthio)benzoic acid (5.2 g, 0.015 mole) and thionyl chloride (5 ml) were heated at 70° for 1 hr. Removal of excess thionyl chloride under vacuum and recrystallization of remaining solid gave 2,6-di(phenylthio)benzoyl chloride in 85% yield, mp 79–80.5°.

An ether solution of 2,6-di(phenylthio)benzoyl chloride (4.5 g, 0.013 mole) was added over a 3-hr period to a stirred ether solution of *t*-butyl hydroperoxide (1.72 g, 0.019 mole) and pyridine (1.78 g, 0.022 mole) at −15° according to the method of Martin and Bentrude.[5] Chromatography on alumina at −15° gave the perester in 15% yield, as a colorless solid, mp 94–95° dec, characteristic single infrared absorption at 1775 cm^{-1}.

Anal. Calcd for $C_{23}H_{22}S_2O_3$: C, 67.28; H, 5.40. Found: C, 66.78; H, 5.28.

2-Carboxybenzyl Phenyl Sulfide. An ethanolic solution of sodium thiophenolate prepared from thiophenol (44.0 g, 0.4 mole) and sodium (9.3 g, 0.4 g-atom) was added to *o*-bromobenzyl bromide (100.0 g, 0.4 mole) in ether and the mixture was refluxed for 3 hr. After removal of NaBr by filtration, distillation gave *o*-bromobenzyl phenyl sulfide in 73% yield, bp 117–120° (0.1 mm).

Ethylene dibromide (6.77 g, 0.036 mole) was added to *o*-bromobenzyl phenyl sulfide (10.0 g, 0.036 mole) and magnesium (2.0 g, 0.082 g-atom) over a period of 6 hr, according to the method of Pearson.[28] After refluxing for 1 hr, the mixture was poured on solid CO_2, followed by usual Grignard work-up to give 2-carboxybenzyl phenyl sulfide in 36% yield, mp 110.5–112.0° (lit.[29] mp 109–111°).

Anal. Calcd for $C_{14}H_{12}O_2S$: C, 68.82; H, 4.85. Found: C, 68.69; H, 4.87.

***t*-Butyl *o*-(Phenylthiomethyl)perbenzoate.** *o*-Carboxybenzyl phenyl sulfide (6.3 g, 0.026 mole) and thionyl chloride (19.8 g, 0.165 mole) were heated at 60° for 1 hr. Vacuum distillation gave the acid chloride in 90% yield, bp 140–150° (0.1 mm).

t-Butyl *o*-(phenylthiomethyl)perbenzoate, a colorless oil, was synthesized from the acid chloride in the usual manner in 46% yield, sharp infrared peak at 1756 cm^{-1}.

Anal. Calcd for $C_{16}H_{20}O_3S$: C, 68.32; H, 6.37. Found: C, 68.24; H, 6.50.

***t*-Butyl Per-1-naphthoate.** 1-Naphthoic acid was converted to 1-naphthoyl chloride by the procedure of Libermann, Himbert, and Hengl,[30] bp 102–105° (0.2 mm) (lit.[30] bp 167° (10 mm)).

Treatment of 1-naphthoyl chloride (19.0 g, 0.10 mole) with *t*-butyl hydroperoxide (12.4 g, 0.14 mole) in the presence of pyridine in the usual manner gave the perester in 32% yield, mp 53–55°, strong infrared absorption at 1745 cm^{-1}.

Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.76; H, 6.60. Found: C, 73.83; H, 6.81.

***t*-Butyl 8-(Phenylthio)per-1-naphthoate.** Treatment of sodium 8-bromo-1-naphthoate with sodium thiophenolate in refluxing xylene gave 8-(phenylthio)-1-naphthoic acid in 54% yield by the procedure of Rule and Turner,[14] mp 130.5–132.5° (lit.[14] mp 131–132°). 8-(Phenylthio)-1-naphthoic acid (8.4 g, 0.030 mole) was treated with an excess of thionyl chloride (12 ml) at 50–60° for 1 hr. Evaporation of excess thionyl chloride left the acid chloride, a colorless oil, possessing a strong infrared absorption at 1780 cm^{-1}.

An ether solution of 8-(phenylthio)-1-naphthoyl chloride, (9.0 g, 0.03 mole) was added to an ether solution of *t*-butyl hydroperoxide (3.67 g, 0.041 mole) and pyridine at −15°. Chromatography on alumina at −15° gave the perester in 38% yield, which decomposes at *ca.* 92°, sharp infrared peak at 1750 cm^{-1}.

Anal. Calcd for $C_{21}H_{20}O_3S$: C, 71.56; H, 5.72. Found: C, 71.34; H, 5.82.

Kinetics. The infrared method used to determine the rates of decomposition of the peresters without added scavenger and with added styrene was the same as that described by earlier workers.[5] A Perkin-Elmer Model 21 or 521 spectrophotometer was used to determine the optical density of each sample.

The method of Koenig[15] was used to follow the rates of perester decomposition by the disappearance of the radical scavenger galvinoxyl at 575 mμ. A Cary Model 14M recording spectrophotometer was used to measure these absorptions.

The rate constants and standard deviations for each kinetic run were determined by the method of least squares[31] using an IBM 7090 computer.

Product Studies. The gaseous and volative products were analyzed by methods described by earlier workers.[5,11,15]

Products of the Decomposition of *t*-Butyl 8-(Phenylthio)per-1-naphthoate. The perester (1.732 g, 0.0049 mole) was dissolved in 25 ml of chlorobenzene, degassed, and heated at 80° for 2.0 hr.

A. Gaseous and Volatile Products. The condensible gases amounted to 166 ml at 29° (98.5 mm) or 0.87 mole. Adsorption on Ascarite showed the presence of carbon dioxide to the extent of 0.11 mmole or 2.2%. The remaining gas (0.76 mmole or 15.5%) was shown to be isobutylene by comparison with the API spectrum.[32]

The volatile products were determined by decomposing the perester (0.199 g, 0.565 mmole) in 0.5 ml of chlorobenzene in a sealed nmr tube at 80° for 2.5 hr. These products were acetone (36%) and *t*-butyl alcohol (32%); isobutylene analyses by vacuum line (16%) isolation and by nmr (29%) were different, probably because of incomplete separation of the isobutylene from the chlorobenzene solvent on the vacuum line (as was also observed by Bentrude[5]). The volatile products account for 97% of the *t*-butyl group of the perester.

B. Nondistillable Residue. The deep red chlorobenzene solution from the decomposition of 4.9 mmoles of the perester, remaining after removal of the gaseous products, was cooled overnight, filtered, and washed with chlorobenzene.

Component 1, an acid, was obtained (36 mg). Addition of pentane and cooling gave 31 mg more of the same acid. This compound, mp 198–201°, was identified as phenyl 8-carboxy-1-naphthyl sulfoxide by comparison (infrared spectra and mixture melting point) with an authentic sample prepared by the method of Rule

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[31] W. J. Youden, "Statistical Methods for Chemists," John Wiley and Sons, Inc., New York, N. Y., 1951.

[32] "Catalogue of Infrared Spectra Data," Vol. 2, No. 378, American Institute Research Project 44, National Bureau of Standards, Washington, D. C.,

and Turner.[14] This accounts for 5% of the original perester carbonyl.

The nonvolatile products remaining after removing the chlorobenzene under vacuum were found by infrared and nmr spectroscopy to consist mainly of an acid. A comparison of the area of the hydroxyl proton at τ −2.2 to the area of the aromatic protons indicated the acid was present to the extent of 70%. Several extractions of the nonvolatile products (0.603 g) in ether with 10% sodium carbonate followed by acidification gave component 2 (0.370 g), an acid, mp 128.5–131°. It was identified as 8-(phenylthio)-1-naphthoic acid by comparison with an authentic sample by infrared spectroscopy and mixture melting point. The amount of this acid isolated accounts for 60% of the perester carbonyl (70% by nmr).

Attempts to resolve the remaining deep red tarry residue (0.233 g) by column chromatography on Florisil and alumina were unsuccessful. Evidence for products containing a phenyl ester group, which could have resulted from phenyl migration, was specifically sought in the infrared spectra of various chromatographic fractions, but none was observed (lack of absorption near 1730 cm^{-1}).

Products of the Decomposition of *t*-Butyl *o*-(Phenylthiomethyl)-perbenzoate. A. Volatile Products. The perester (0.184 g, 0.585 mmole) was dissolved in chlorobenzene (0.5 ml), degassed, and heated at 110° for 19.2 hr. The volatile products were found to consist of acetone (28%) and *t*-butyl alcohol (65%), as the major products accounting for 93% of the original *t*-butyl group of the perester.

B. Nonvolatile Products. The nmr spectrum of this decomposition mixture, after removal of volatiles, consisted of the following peaks: a singlet a τ −0.6, a multiplet in the aromatic region 2–3, a singlet at 3.3, and a singlet at 5.5, with the relative areas of 1.0, 21, 1.5, and 2.0, respectively. The infrared spectrum of this mixture had a strong absorption at 1775 and a medium one near 1700 cm^{-1}.

Component 1 was identified as 2-carboxybenzyl phenyl sulfide by comparison with its known infrared and nmr spectra. Extraction of the decomposition mixture with aqueous sodium carbonate removed the peaks assigned to component 1 in the spectra of the decomposition mixture. Component 1 accounts for 33% of the original perester carbonyl.

Component 2 was left after the extraction with sodium carbonate. It was identified as 3-(phenylthio)phthalide on the basis of the following spectral evidence. The infrared spectrum has a strong absorption at 1775 cm^{-1}, and no OH absorption. The nmr spectrum has peaks at τ 2.0–2.8, a singlet at 3.3, and a small amount of absorption at 8.4–9.3 (presumably from products containing *t*-butyl residues; these peaks were not present in all spectra), with relative areas of 9.0, 0.82, and 2.6, respectively.

In order to isolate component 2, the perester (1.2 g) in 8.0 ml of chlorobenzene was heated at 110° for 46 hr. After evaporation of solvent, the residue was dissolved in ether and extracted with sodium carbonate. Removal of ether left 0.48 g of a light yellow solid (51% of perester carbonyl), mp 95–97° after recrystallization from ether–pentane. The instability of this compound was suggested by the smell of thiophenol observed in all recrystallizations. The infrared and nmr spectra were the same as those obtained above. From these data component 2 was identified as 3-(phenylthio)phthalide, and accounted for 50–65% of the perester carbonyl.

Anal. Calcd for $C_{14}H_{10}O_2S$: C, 69.39; H, 4.16. Found: C, 68.49; H, 4.46, with a small residue not burned.

Acknowledgments. We wish to acknowledge the aid afforded this investigation by fellowships held by T. H. F. from Abbott Laboratories, Monsanto Chemical Co., Union Carbide Corp., and Allied Chemical Corp. This research was supported in part by a grant from the U. S. Army Research Office, Durham, N. C.

Pyrolysis of Chlorobenzene

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Abstract: The reaction products of chlorobenzene with benzyne—from pyrolysis of phthalic anhydride—were naphthalene, chloronaphthalene, and chlorodiphenyl. Chlorobenzene alone also gave small, but definite, amounts of naphthalene and chloronaphthalene. Benzyne was evidently formed from chlorobenzene by intramolecular dehydrochlorination at elevated temperatures.

Previous investigations have found diphenyl, 4-chlorodiphenyl, 4,4′-dichlorodiphenyl, and some *p*-terphenyl as the products of pyrolysis of chlorobenzene.[1,2] On the basis of a kinetic study at 770–850° and 12 torr, in which the main products were hydrogen, hydrogen chloride, and 4,4′-dichlorodiphenyl, a chain mechanism was proposed in which chlorine atoms and chlorophenyl radicals were the chain carriers.[2]

We are presently engaged in studying the high-temperature reactions of benzyne, generated by pyrolysis of phthalic anhydride, with aromatic compounds. Benzene gives naphthalene and biphenyl;[3] chlorobenzene should give chlorodiphenyls by insertion and naphthalene and chloronaphthalenes by 1,2 and 1,4 addition and rearomatization with respective loss of chloroacetylene and acetylene.

To test this prediction, phthalic anhydride was pyrolyzed in admixture with chlorobenzene at 690°. The major products and their relative intensities in a low-voltage mass spectrum, analyzed by mass spectrometry, were: naphthalene, 3.5; chloronaphthalenes, 30.0; chlorodiphenyls, 34.6; and dichlorodiphenyls, 100.0. The postulated products from insertion and addition of benzyne were therefore indeed formed. In addition, a small amount of biphenylene, 1.2 on the same scale, resulted.

However, pyrolysis of chlorobenzene alone under identical conditions, for comparison, gave some rather surprising results. Among the products, analyzed in the same way, were: naphthalene, 0.3; chloro-

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