It should further be noted that the respectable correlations obtained with $E_s{}^c$ and $E_s{}^0$ for sets 7-9 which supposedly include hyperconjugation effects that have been removed from $E_s{}^c$ and $E_s{}^0$ further suggest that hyperconjugation corrections are of very dubious validity. In our opinion, the υ values are eminently suited for the correlation of steric effects upon rate and equilibria data and physical data as well. No "corrected" constants are necessary.

References and Notes

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Concerted Mechanism and Phase Effects in Decompositions of Alkyl Peroxy Esters[1]

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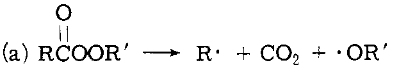
Abstract: Two primary alkyl peroxyacetates (*n*-butyl and isobutyl) and two secondary peroxyacetates (*sec*-butyl and cyclohexyl) were prepared and their liquid and gas-phase decomposition rates and products compared with those of *tert*-butyl peroxyacetate. Thermal, liquid-phase, decompositions of the primary and secondary peroxy esters, either pure, in chlorobenzene solution, or in α-methylstyrene solution, yielded mainly acetic acid and the aldehyde or ketone corresponding to the alcohol moiety of the ester (E_{act} = 24–28 kcal/mol, log A = 10–12). Both products and kinetics are in accord with a concerted six-centered mechanism analogous to the pyrolytic decomposition of esters. By contrast, thermal decomposition of *n*-butyl peroxyacetate in the vapor phase gives products and kinetic parameters (E_{act} = 36.0 kcal/mol, log A = 16.0) indicative of a simple O–O homolysis. In this respect, the vapor-phase decomposition of *n*-butyl peroxyacetate corresponds to the homolytic decomposition of *tert*-butyl peroxyacetate both in the liquid and vapor phase (E_{act} = 35.8 kcal/mol, log A = 16.1). The striking difference between liquid- and gas-phase thermal decomposition of *n*-butyl peroxyacetate parallels previous observations of peroxide decompositions involving a concerted hydrogen transfer and may be general for this class of reactions. We tentatively conclude that the cyclic concerted reaction proceeds *via* a transition state with significant ionic character which is solvent stabilized, thereby lowering the energy of activation of the liquid phase decomposition. In the gas phase, without this solvent stabilization of the cyclic concerted transition state, the normal homolytic cleavage of the O–O bond takes precedence.

It seems useful to describe three categories for the nonheterolytic decompositions of organic peroxides. The first, simple O–O homolysis (type 1), needs no amplification. The second, concerted multiple bond homolysis (type 2a), is most popularly exemplified by pyrolyses of *tert*-alkyl peroxy esters[4] and can be extended to the scission of *tert*-butyl tetroxide,[5,6] (type 2b). Our main focus here will be on what we shall label type 3 decompositions, the cyclic concerted, six-center cleavage and its relevance to the decomposition of nontertiary alkyl peroxy esters. Typical of this category is the "Russell Mechanism"[7] (type 3a) for the breakdown of nontertiary tetroxides,[8] the formation of H_2 from certain alkylidene peroxides[9] (type 3b), the decomposition of *sec*-alkyl peroxides[10] (type 3b), and the decomposition of nontertiary peroxy esters[11] (type 3c), the subject of this paper.

(type 1) $\quad ROOR \longrightarrow 2RO\cdot$

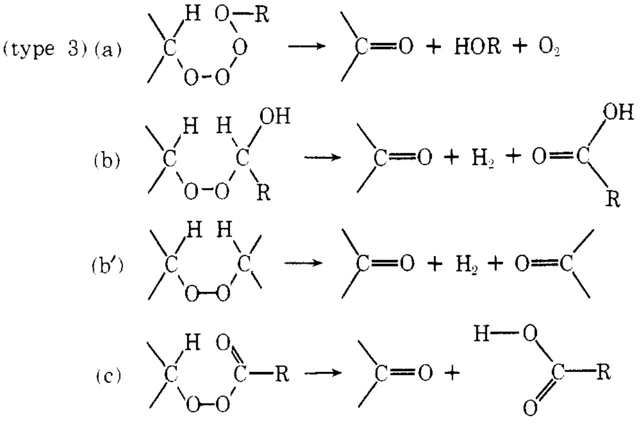
(type 2)



$$\text{(a) } R\overset{O}{\overset{\|}{C}}OOR' \longrightarrow R\cdot + CO_2 + \cdot OR'$$

$$\text{(b) } ROOOOR \longrightarrow RO\cdot + O_2 + \cdot OR$$

An intriguing aspect of this type of reaction is its apparent preference for the liquid phase. Thus peroxides which yield substantial amounts of H_2 when decomposed in solution give little or none on vapor-phase pyrolysis.[10,12] This is not to say that type 1 or type 2 reactions do not compete with type 3 in the liquid phase; they clearly do;[8a,8b,9b,10] however, reactions of type 3 appear to be favored in the liquid phase *vs.* the vapor phase.[12] An exception may be the type 3a reaction. Recent comparative studies of liquid and gas phase *n*-butane oxidations indicate very little differences in rate and products for the primary reaction with phase change. These results are compatible with the same radical-terminating process involving a type 3a reaction in each.[13]



Beyond the preliminary communication[11] and thesis[3] which proposed a type 3c decomposition for primary and secondary alkyl peroxy esters in the liquid phase, such species have received very little attention.[14,15] The full details of that earlier report are presented here, together with an account of broader aspects of the chemistry of these compounds. Vapor-phase studies have been included in order to expand the data to include the differences between liquid and gas-phase peroxy ester decompositions. The gas-phase decompositions of two peroxy esters are reported in this paper, *tert*-butyl peroxyacetate (*t*-BuO_2Ac) and *n*-butyl peroxyacetate (*n*-BuO_2Ac), which in solution give decompositions representative of types 1 and 3, respectively.

Table I. Physical Properties of Primary and Secondary Peroxyacetates,[3] ROOAc

R	Refractive index $n^{20}D^a$	Refractive index $n^{20}D^b$	Infrared[c] carbonyl λ, cm^{-1}	Nmr α-hydrogens[d] Perester δ	Nmr α-hydrogens[d] Ester δ
n-Bu	1.4108[e]	1.4097	1771	4.15	4.00
i-Bu	1.4098	1.4062	1768	3.91	3.80
s-Bu	1.4090	1.4076	1776	4.21	4.78
Cyclohexyl	1.4529	1.4526	1770	4.15	4.70

[a] From acetyl chloride–pyridine method. [b] From ketene method. [c] Infrared absorption of neat liquids. [d] Center of multiplet for the alkyl protons α to oxygen; values in parts per million downfield from TMS, neat liquids, Varian A-60 spectrometer. [e] Acetyl chloride without pyridine.

Experimental Section

Synthesis of Peroxy Esters.[3] In Table I are recorded the physical properties of the new peroxyacetates.

***n*-Butyl Peroxyacetate.**[3,14] Freshly distilled acetyl chloride (2.60 g, 0.0331 mol) was added dropwise to *n*-butyl hydroperoxide[16] (3.00 g, 0.333 mol) cooled in an ice bath. The mixture was stirred for 10–15 min, poured onto ice, and extracted with 3 × 10 ml of peroxide-free ether. The combined extracts were washed successively with water, 20% KOH, and saturated NaCl solution until neutral. After drying with $MgSO_4$ at −10° overnight, the ether was removed by vacuum distillation (25 mm) through a short Vigreux column. Bulb-to-bulb vacuum distillation of the residual oil [30° (0.03 mm)] gave *n*-BuO_2Ac in 74% yield.

Anal. Calcd. for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.70; H, 9.09.

Attempts to prepare this peroxy ester using pyridine and acetyl chloride by the method employed for the preparation of *tert*-butyl peroxyacetate[17] failed.

***sec*-Butyl Peroxyacetate.** This secondary peroxy ester was prepared according to the method of Bartlett and Miatt[17] by adding acetyl chloride to a cooled pentane solution of pyridine and *sec*-butyl hydroperoxide;[18] on a 0.02-mol scale, a 44% yield of *sec*-butyl peroxyacetate was obtained, distilling at 27° (0.03 mm).

Anal. Calcd for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.89; H, 9.13.

Isobutyl Peroxyacetate and Cyclohexyl Peroxyacetate. These were prepared from isobutyl hydroperoxide[17] and cyclohexyl hydroperoxide[19] with acetyl chloride and pyridine by the same procedure used for synthesis of *sec*-butyl peroxyacetate.

Isobutyl peroxyacetate had: bp 25° (0.04 mm); 65% yield.

Anal. Calcd for $C_6H_{12}O_3$: C, 54.53; H, 9.15. Found: C, 54.49; H, 9.29.

Cyclohexyl peroxyacetate had: bp 39° (0.06 mm); 67% yield.

Anal. Calcd for $C_8H_{14}O_3$: C, 60.73; H, 8.92. Found: C, 60.88; H, 8.88.

Synthesis Using Ketene. Alternatively the primary and secondary peroxyacetates were prepared by the addition of ketene to the hydroperoxide.[20] The synthesis of *sec*-butyl peroxyacetate by this method is typical. Ketene (1.91 g, 0.0454 mol), made by the method of Hurd and Williams,[21] was bubbled into *sec*-butyl hydroperoxide (2.15 g, 0.0238 mol) dissolved in 15 ml of pentane containing 1 drop of concentrated H_2SO_4 and cooled to −78°. After 3 hr at −78°, the solution was allowed to warm slowly to 0° and poured onto ice. The aqueous portion was extracted with pentane, and the pentane extracts were washed successively with water, 10% $NaHCO_3$, and saturated NaCl solution, dried (Na_2SO_4), and distilled to give 2.51 g (80% yield). The yields of the other peroxyacetates were comparable; properties are given in Table I.

***tert*-Butyl Peroxyacetate.**[17] This tertiary peroxyacetate was prepared as previously described.[17,22]

Purity of Peroxy Esters. Since iodometric analysis for peroxy esters is unreliable,[17] the purity of the products was ensured in so far as possible by using pure starting materials and by work-up procedures designed to remove expected by-products. Analyses for carbon and hydrogen were satisfactory; ir and nmr spectra showed no extraneous peaks.

Procedure for Decompositions in the Liquid Phase.[3] **Product Studies.** Thermal decompositions which produced little or no gaseous products were done in Pyrex test tubes with Teflon-lined screw caps or fused silica test tubes with 14/20 ₸ caps held on with springs. These decompositions were done either neat or in solution by heating in a constant-temperature bath for a period equal to 8 or more half-lives. Products were analyzed by glc using a 5 ft × 0.25 in. column of 20% Carbowax 4000 on firebrick.

Photolytic decompositions of the peroxy esters were done by irradiating using a Mineralight Model V-43, 2537-Å mercury vapor lamp. The sample was contained in a fused silica bulb in a constant-temperature bath which was sealed to a condenser which was attached *via* a cold trap (−78°) to a gas-collecting buret. The noncondensable gases were analyzed by mass spectrometer, while the condensable gases were analyzed by infrared spectroscopy. The nonvolatile products were analyzed by glc 5 ft × 0.25 in. Carbowax 4000 on firebrick). Products in the glc analyses were identified by isolation and comparison of ir with authentic compounds. Quantitative estimation of products from those samples which were decomposed neat was based on the direct proportionality of integrated peak areas to weight, a relationship established by comparison with known mixtures to be satisfactory. Quantification of products from decomposition of peroxy esters in solution required correction factors determined experimentally from synthetic mixtures of known composition.[3] In a few instances, quantitative estimation of products was made by ir analysis based on calibration with known mixtures.[3]

Rate Studies. Samples under nitrogen in fused silica test tubes with 14/20 ₸ fused silica caps held in place by springs and lubricated with silicone grease were immersed in a constant-temperature bath. The tubes were withdrawn at intervals, cooled to −78°, and analyzed by quantitative ir by monitoring the peroxycarbonyl absorption.[17]

Procedure for Decomposition in the Vapor Phase. Peroxy ester samples were charged by standard vacuum techniques into a 500-ml fused silica reaction cell connected to a pressure transducer. Variations in total pressure were achieved by addition of CO_2, C_2F_6, or CH_3CF_3. Rates of decomposition were determined from recorder traces of pressure *vs.* time which invariably yielded first-order plots. After complete decomposition, the products were condensed into a sampling bulb and revaporized for glc analysis.

For *n*-butyl peroxyacetate, it was necessary to charge and reevacuate the reaction cell three times before obtaining a sample consisting of mainly undecomposed peroxy ester. The validity of this apparently successful technique was judged by the simplicity of the product mixture compared with the mixture from those experiments in which less than three repetitions of these changing cycles were employed and by a pressure increase on decomposition corresponding to that expected from the products found. For this peroxy ester, rate constants determined by pressure measurements were checked by intermittent sampling of carbon dioxide and propane yields against an internal CH_3CF_3 standard and found identical.

Products were analyzed by glc of vapor samples, using 6 ft × 0.25 in. columns of Porapak Q and 20% isodecyl phthalate on Chromosorb P, temperature programmed. Samples of known compounds were used to match retention times and measure peak areas *vs.* concentration factors. Accurate estimation of the total mass balances was difficult even in the presence of an internal standard owing to the imprecision in measuring the *absolute* very small initial pressures of peroxy ester. These were never greater than 2 mm, a circumstance dictated by the low volatility of the compounds at temperatures where decomposition occurred readily.

Results and Discussion

Product Studies, Liquid Phase. Table II lists products from primary or secondary peroxy esters decomposed by uv irradiation at 25°; Table III lists the products from thermal decomposition of these neat peroxy esters; and Table IV lists the products from the pyrolysis of the peroxyacetates in α-methylstyrene solution at 64°. Product balances in most cases account for at least 75–85% of the starting material, with the remainder comprised of unidentified compounds

Table II. Products from Photodecomposition[3] of Pure (Neat) Peroxy Esters, ROOAc, at 25°

	R			
Products[a]	*n*-Bu	*i*-Bu	*s*-Bu	Cyclohexyl
ROMe	0.02	0.16[b]	0.01	0.17
C_3H_7CHO	0.04	0.18[b]		
Ketone			0.32[c]	0.40[d]
ROH	0.27	0.35	0.26	0.34
AcOR	0.06	0.06	0.07	0.01
C_3H_7COOR	0.15	0.09		
AcOH	0.26	0.13	0.25	0.33
CO_2	0.53	0.59	0.77	0.62
MeH	0.42	0.38	0.50	0.42
EtH	0.02	0.015	0.07	0.005
C_2H_4	0.001	0.005	0.01	Trace
PrH	0.004	0.015	0.05	
BuH	Trace		0.01	
CO	0.04	0.07	0.02	0.02
Other	0.02[e]	0.005[f]	0.03[g]	
Mass balances				
Total R	0.71	0.94	0.68	0.92
Total AcO	0.85	0.78	1.12	0.96
Total Me	0.80	0.76	0.89	0.94

[a] Moles of product per mole of decomposed peroxyacetate. [b] By infrared analysis. [c] 2-Butanone. [d] Cyclohexanone. [e] *n*-Butyl formate, 0.016. [f] Isobutane, 0.005, and propylene, 0.007. [g] Methyl acetate, 0.026.

Table III. Liquid Products from Thermal Decomposition of Pure (Neat) Peroxy Esters, ROOAc, at 64°

	R			
Products[a]	*n*-Bu	*i*-Bu[b]	*s*-Bu	Cyclohexyl
ROMe	Trace	Trace	0.01	0.003
C_3H_7CHO	0.16	0.55		
Ketone			0.92[c]	0.78[d]
ROH	0.04	0.10	0.02	0.01
ROAc	0.04	0.06	0.02	0.02
C_3H_7COOR	0.11	0.07		
AcOH	0.25	0.83	0.81	0.74
Mass balance				
Total R	0.46[e]	0.86	0.97	0.81
Total AcO	0.29	0.89	0.83	0.76

[a] Moles of product per mole of decomposed peroxyacetate. [b] Gas analysis gave: CO_2, 0.09; MeH, 0.11; CO, 0.08; PrH, 0.02. In other examples, gas evolution was negligible. [c] 2-Butanone. [d] Cyclohexanone. [e] The poor mass balance in this case is due in part to the complexity of the product mixture. There were 11 other minor unidentified peaks in the glc chromatogram. It seems likely that a major cause of the poor material balance, however, was formation of polymeric material from initially formed butyraldehyde.

Table IV. Liquid Products from Thermal Decomposition of Peroxy Esters, ROOAc, 1–2 *M* in α-Methylstyrene at 64°

	R			
Products[a]	*n*-Bu	*i*-Bu	*s*-Bu[b]	Cyclohexyl[c]
ROMe	Trace		0.02	
C_3H_7CHO	0.67	0.80		
Ketone			0.99[d]	0.98[e]
ROH	0.07	0.01	0.05	
ROAc	0.041	0.03	Trace	
AcOH	0.69	0.75	0.84	0.90
Mass balances				
Total R	0.78	0.84	1.06	0.98
Total AcO	0.73	0.78	0.84	0.90

[a] Moles of product per mole of decomposed peroxyacetate. [b] At 88°. [c] In chlorobenzene. [d] 2-Butanone. [e] Cyclohexanone.

Table V. Base-Catalyzed Decomposition of *n*-Butyl Peroxyacetate,[a] in α-Methylstyrene at 64°

			Rate	
Amine	Concn, mol/l.	pK_a	10^3k_1,[b] sec^{-1}	10^3k_2,[c] M^{-1} sec^{-1}
Piperidine	0.26	2.50	~9.6	37
Triethylamine	0.24	3.25	8.2	34
Benzylamine	0.37	4.70	4.3	11.7
N,*N*-Diethylaniline	0.21	7.44	0.65	3.1
Pyridine	0.22	8.85	1.2	5.6
Pyridine[d]	0.53	8.85	2.2	4.2
Aniline	0.33	9.42	0.43	1.3

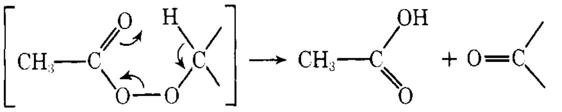
[a] 0.6–1.0 mol/l. [b] Pseudo-first-order disappearance of perester corrected for k_1 uncatalyzed (0.07×10^{-3} sec^{-1}). [c] k_1/[amine]. [d] In bromobenzene solvent.

appearing as small but distinct peaks in the glc analysis or nonvolatile polymer by-products.

Photolysis. The photolyses of two primary and two secondary peroxyacetates (Table II) were studied so that a direct comparison could be made between the products from a known radical process and those from thermal decomposition of the same peroxy ester substrates under various conditions (Table II, IV, and V). For the most part, the products from photolysis are readily interpretable in terms of an initial O–O homolysis followed by typical secondary free radical processes. The formation of CO_2 from the acetoxy radical is the best measure of minimum O–O homolysis in the primary process (eq 1): 53, 59, 77, and 62% in the four decompositions. The remainder of peroxy ester decomposition is accounted for by typical secondary processes, *i.e.*, radical-induced decompositions, disproportionations, and radical combination. We need not discuss those reactions in detail since they represent known processes; these studies *per se* do not contribute much to elucidation of the relative importance of the various possible pathways. Primarily, the results of the photolyses (Table II) serve to point up the differences between the products resulting from a known radical process (photolysis) and the thermal decomposition of the same peroxy ester substrates (Tables II, IV, and V).[23]

$$\mathrm{ROOAc} \xrightarrow{h\nu} \mathrm{RO\cdot} + [\mathrm{AcO\cdot}] \longrightarrow \mathrm{CH_3\cdot} + \mathrm{CO_2} \qquad (1)$$

Nonradical Reactions. The mixture of products from thermal decomposition of primary and secondary peroxy esters in the liquid phase, especially in the presence of the radical trap solvent, α-methylstyrene, was notable for the minimal yields of compounds such as carbon dioxide, methane, and ethane expected from O–O homolysis. The major products can be accounted for by elimination of acetic acid from the peroxyacetates by a process represented in eq 2.[24]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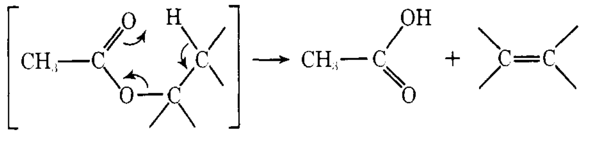
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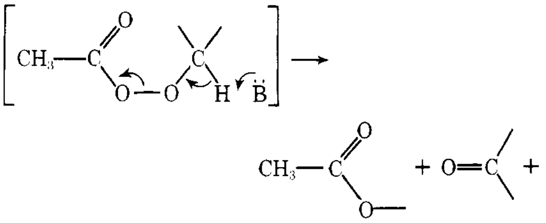
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This differs from the pyrolytic elimination of simple esters (eq 3) in that the unsaturation generated is C=O rather than C=C.[25] Base-catalyzed elimination would be predicted to give the same products (eq 4); indeed a pyridine-cata-

Table VI. Rates of Thermal Decomposition of Primary and Secondary Alkyl Peresters in α-Methylstyrene Solution

Run no.	Concn[a]	Temp, °C	Rate $10^5 k_1$, sec^{-1}	E_a, kcal/mol	Log A
		n-BuO$_2$Ac			
58	0.93	79.6	1.57	24.1	10.1
34	0.93	87.8	3.27		
33	0.93	88.2	3.48		
64	0.93	92.6	5.38		
		i-BuO$_2$Ac			
62	0.80	79.5	1.36	27.5	12.2
54	0.80	88.4	3.61		
55	0.80	88.2	3.45		
66	0.80	92.4	5.51		
67	0.80	92.8	5.58		
		c-Hex-O$_2$Ac			
57	0.93	88.6	1.63	26.1	11.0
59	0.93	88.4	1.64		
65	0.93	93.0	2.30		
60	0.93	99.3	4.75		
		s-BuO$_2$Ac			
32	0.98	88.2	1.79	24.9	10.3
53	0.98	88.6	1.81		
68	0.94	92.7	3.58		
70	0.94	92.8	3.19		
61	0.98	99.1	4.92		
63	0.98	99.5	5.34		
69	0.94	99.4	5.37		

[a] Initial molal concentration, P_0.

Table VII. Products[a] from Vapor-Phase Thermal Decomposition of Peresters, ROOC(=O)CH$_3$

	t-BuO$_2$Ac, 130.7° Initial total pressure		n-BuO$_2$Ac, 128.9° Initial total pressure		
Product	3.2[b] mm	37[c,d] mm	2.1[e] mm	18[f] mm	397[g] mm
MeH			0.28	n	0.26
CO$_2$	1.00	(1.00)	[0.86]	1.32	n
EtH	1.07	1.00	0.13	0.10	n
PrH			0.28[h]	0.53[h]	0.23
BuH			0.18	0.10	0.18
n-Hexane			0.04	n	0.04
CH$_2$O			0.14	n	0.30
PrCHO			0.43		0.31
MeCOMe	1.04	0.98			
MeCOEt	1.04	0.003			
n-BuOH			0.0	n	0.01
t-BuOH	0.03	0.02			
MeOAc			0.04		0.08
n-BuOAc			Trace	n	0.01
AcOH			0.09	n	0.01
Total CH$_3$	1.07	1.00	0.81[i]		0.74
Total R	1.07	1.00	0.95		0.81

[a] Moles of product per mole of perester; "n" means "not determined". [b] Perester alone without inert gas added; yields based on pressure increase during reaction. [c] Peracetate minimum pressure is 3.2; CO$_2$ minimum pressure is 33.8. [d] The CO$_2$ yield is assumed to be 100%. [e] Peracetate without inert gas added; yields based on total CO$_2$ + HOAc + acetone = 100. [f] Peracetate, 1.2 minimum, CF$_3$CH$_3$, 16.8 minimum. [g] Peracetate, 1.7 minimum, C$_2$F$_6$, 395.2 minimum. [h] Includes 5–10% of propylene not well resolved by the glc analysis. [i] Methyls from acetoxy residues.

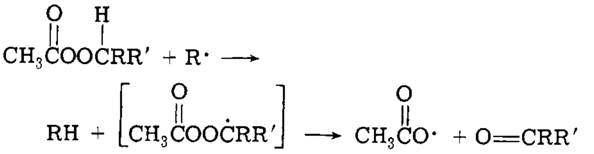
lyzed decomposition of n-butyl peroxyacetate in α-methylstyrene gave mainly butyraldehyde and acetic acid. Preliminary rate studies showed that decompositions in soft-glass vials used for product studies were somewhat faster than in the fused silica tubes. Therefore, some component of wall-catalyzed reaction may have contributed to the products listed in Tables II, III, and IV but not to the rates reported in Tables V and VI, which were performed in fused silica vessels.

Unsuccessful attempts at the preparation of n-butyl peroxyacetate using acetyl chloride-pyridine-n-butyl hydroperoxide (see Experimental Section) suggested that n-butyl peroxyacetate might be particularly sensitive to base attack. Kinetic studies showed this to be true; even aniline (0.33 M in α-methylstyrene at 64°, Table V) catalyzed a pseudo-first-order decomposition six times faster than that of the peroxy ester alone. A Brϕnsted plot of log k_2 $vs.$ pK_a for decompositions of n-butyl peroxyacetate catalyzed by a series of amines was linear with a correlation coefficient of 0.995 with the exception of pyridine, results consistent with those reported for $tert$-butyl benzyl peroxide[26] and nontertiary dialkyl peroxides.[27]

p-Toluenesulfonic acid-catalyzed decomposition of n-butyl peroxyacetate in α-methylstyrene yielded about 60% acetic acid and 40% n-butyl acetate with only traces of butyraldehyde and butanol. The analyses were complicated by the presence of polymerized solvent, and the material balance for n-butyl groups is insufficient to warrant mechanistic speculations. However, the results are definitive in ruling out any substantial acid-catalyzed component in the uncatalyzed thermal and photochemical decomposition based on the very different product composition.

Rate Studies, Liquid Phase. The rate constants for the thermal decompositions of the four primary and secondary peroxyacetates in α-methylstyrene solvent are given in Table VI. The reactions, followed by the decrease in peroxy ester carbonyl absorption in the infrared, were uniformly first order and some 8–16 times faster than the corresponding decomposition of $tert$-butyl peroxyacetate[17] extrapolated to this same temperature range.[28] Energies of activation E_a, for the thermal, liquid-phase decompositions of these primary and secondary peroxy esters were less than those of $tert$-butyl peroxyacetate by some 14–15 kcal/mol and A factors were also lower[29] by four to six powers of ten (Table VI). The decomposition rates are thus much too high for the simple type 1, O–O homolysis and are in fact similar in magnitude to values reported for the concerted type 3b scission of peroxyhemiacetals.[9b] The low A factors similarly suggest a transition state involving steric constraint and in fact are precisely those expected for the concerted type 3c mechanism (eq 2) indicated by the product studies.

The alternative explanation, a free radical-induced decomposition as shown in eq 5, although not eliminated by



$$\mathrm{CH_3\overset{O}{\overset{\|}{C}}OO\overset{H}{\overset{|}{C}}RR' + R\cdot \longrightarrow RH + \left[CH_3\overset{O}{\overset{\|}{C}}OO\dot{C}RR'\right] \longrightarrow CH_3\overset{O}{\overset{\|}{C}}O\cdot + O{=}CRR'} \quad (5)$$

the kinetic studies, can be rejected on several grounds: (a) α-methylstyrene, the solvent used in these studies, is an efficient radical trap and has been used successfully to suppress radical-induced decompositions of peroxides;[30,31] (b) there are qualitative differences in products from induced decomposition when the pure peroxyacetates were photolyzed (Table II), pyrolyzed neat (Table III) or in chlorobenzene,[3,11] as contrasted with the products obtained by pyrolyses in α-methylstyrene solvent; (c) analogy with dialkyl peroxide decompositions[32] would lead one to believe that n-butyl and sec-butyl peroxyacetates should be only slightly more subject to radical-induced decomposition than $tert$-butyl peroxyacetate, and yet there are major differences observed in their decomposition rates and products.

Decompositions in the Vapor Phase. Tables VII and VIII list products and rate measurements, respectively, for vapor-phase pyrolyses of n-butyl and $tert$-butyl peroxyacetate, both alone and in the presence of added inert gases. The product mixtures were strikingly simple, consisting almost entirely of compounds expected from radical pro-

Table VIII. Rates of Decomposition of Peresters in the Vapor Phase

Run no.	Temp, °C	Pressure^a Perester, mm	Pressure^a CO_2, mm	Rate 10^5k_1, sec^{-1}	E_a, kcal/mol	Log A
			t-BuO_2Ac			
104	117.4	2.9	10.1	11.4		
55	130.7	3.2	0	55.0	35.8	16.1
56	130.7	4.0	33	62.3		
57A	146.5	3.2	0	282		
57C	146.5	3.2	10.8	297		
59A	146.5	2.0	28	296		
59B	146.5	8.0	28	296		
			n-BuO_2Ac			
100	106.0	2.3	0	8.88		
102	117.5	2.4	0	36.8	36	16
103	117.5	2.6	7.4	38.0		
106	128.5	2.8	15.2	121		
107	128.5	1.4	10.6	120		
109	128.5	3.5	8.5	118		
113A	140.4	2.5	9.5	700		
113B	140.4	2.5	5.0	500		

[a] Initial pressures, CO_2 added.

cesses. *tert*-Butyl peroxyacetate, for example, yielded no acetic acid in contrast to the 23% found for its thermal decomposition in chlorobenzene solution.[17] The presence of some acetic acid in the products from *n*-butyl peroxyacetate vapor-phase decompositions could be due to the concerted mechanism competing with simple homolysis. However, the extreme variability of the acetic acid yields (15-fold in two runs cited in Table VII) suggests a more adventitious process, namely the partial decomposition of the peroxy ester either as pure liquid or on the Pyrex walls during the cell-charging procedure (see Experimental Section). In the initial experiments before this difficulty was appreciated, product studies showed mixtures similar in complexity to those obtained in the solution work. (The variation in material balances reported in Table VII may be due as much to this factor as to the difficulty in measuring accurately the small initial pressures of peroxyacetates.)

Rates of decomposition of these two peroxy esters (Table VIII), in the gas phase as determined by pressure measurements, exhibited first-order kinetics and were independent, within experimental error, of initial pressure or of added diluents (CO_2, C_2F_6, CH_3CF_3). *tert*-Butyl peroxyacetate decomposition rates were quite close to those found in solution, *e.g.*, at 130.7°, vapor, $k_1 = 55.0\text{-}62.3 \times 10^{-5}$ sec^{-1}; at 129° solution in chlorobenzene,[17] $k_1 = 62.9\text{-}65.2 \times 10^{-5}$ sec^{-1}. The activation energy of 35.8 kcal/mol (Table VIII) is close to the mean of the E_a's for homolysis of acetyl peroxide (30 kcal/mol) and *tert*-butyl peroxide (38 kcal/mol) as it should be[33] and is a considerably more reasonable value than the 39.8 ± 1.3 kcal/mol value found[35] for decomposition in chlorobenzene. Rates and activation parameters for *n*-butyl peroxyacetate differed little from those of *tert*-butyl peroxyacetate (Table VIII); with the supportive evidence from product studies, this leaves no doubt that the pathway for vapor-phase decompositions proceeds *via* simple type 1 homolysis.

Vapor-Phase *vs.* Liquid-Phase Decompositions. The findings[10] that *sec*-butyl peroxide yielded no hydrogen in vapor-phase decompositions at first excited a suspicion that the type 3 mechanism postulated for the solution reaction might be wrong. Two alternatives which might explain the difference between vapor and solution results, namely solvent cage reactions and abstraction of hydrogen from solvent or substrate by hydrogen atoms were proved untenable,[10] thereby leaving the six-centered type 3b mechanisms as the only viable explanation for that component of the liquid-phase thermal decomposition of *sec*-butyl peroxide which yields hydrogen.

It is quite clear that this six-centered type 3b mechanism shown by *sec*-butyl peroxide and α-hydroxybutyl butyl peroxide is repeated in the liquid-phase decomposition of primary and secondary alkyl peroxyacetates to give acetic acid and the corresponding aldehyde or ketone (type 3c mechanism). The remarkable observation which was made in the case of *sec*-butyl peroxide decomposition and now substantiated in the decomposition of *n*-butyl peroxyacetate is that this six-centered mechanism *is not important* in the gas-phase decomposition of these same compounds.

We are clearly presented with the question: Why do the liquid-phase thermal decompositions of primary and secondary butyl peroxyacetates proceed *via* a six-centered mechanism (type 3c), while the vapor-phase decomposition of *n*-butyl peroxyacetate proceeds *via* a regular homolytic cleavage process (type 1)? Is the anomaly to be found in the liquid *vs.* gas-phase concerted type 3c mechanism or in the liquid *vs.* gas-phase homolytic type 1 process?

The kinetic parameters for the vapor-phase decomposition of both *n*-butyl and *tert*-butyl peroxyacetates are so similar that it is only logical to conclude that both reactions occur by the same mechanism under these conditions. Since *tert*-butyl peroxyacetate cannot decompose by a concerted (type 3c) mechanism, and in fact its decomposition fits perfectly the characteristics of a homolytic (type 1) cleavage, we conclude that gas-phase decompositions of both of these peroxyacetates proceed predominantly *via* the homolytic route. On the other hand, the liquid-phase decompositions of these two peroxy esters show large differences in both A factors and rates as well as products. Finally, the activation parameters as well as products for either the liquid-phase or gas-phase decomposition of *tert*-butyl peroxyacetate are essentially the same. This clearly leaves the liquid-phase decomposition of *n*-butyl peroxyacetate (and presumably the other primary and secondary peroxy esters) as the anomalous case. Although there is no *a priori* reason why the cyclic concerted type 3c mechanism cannot operate in the gas phase for the primary and secondary alkyl peroxyacetates, both product and rate studies indicate that this does not happen to any appreciable extent.[36] Consequently, it must be that the inherent energy of activation of the gas-phase cyclic concerted process (type 3c) is higher than that for the homolytic mechanism (type 1). Accordingly we are forced to conclude that some effect is operating in solution (neat, chlorobenzene, α-methylstyrene) to increase the decomposition rate of the concerted process over that which it theoretically would have in the gas phase. This decrease in energy of activation for the concerted process in solution need not be large, of course, since even in solution the homolytic process competes to some extent and also benefits from a much larger A factor.

Possible Role of Chemical Activation. We have considered the possibility that the gas-phase decomposition of *n*-butyl peroxyacetate does indeed proceed *via* a concerted process (eq 2) to give acetic acid and butyraldehyde, but these initial products are formed in a highly energetic state and, in the absence of solvent to dissipate this energy, undergo further reactions thereby masking the true course of the reaction. This has been tested by conducting the reaction in the presence of an inert gas (up to 33 mm of pressure of CO_2 for the rate studies and up to 395 mm of pressure of C_2F_6 for the product studies. The results show that the gaseous decomposition products (Table VII) and rates (Table VIII) for both *n*-butyl and *tert*-butyl peroxyacetates are essentially independent of initial total pressure, a result in accord with the postulate that chemical activation of initially formed products is not important in the overall process.

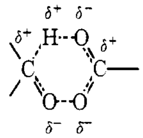
Furthermore, estimates of the exothermicity of the gas-phase decomposition of *n*-butyl peroxyacetate to give butyraldehyde and acetic acid (eq 2) indicate $\Delta H°_{400}$ is 57 ± 5 kcal/mol.[37] Even if we postulate that all this energy is concentrated in one of the two initially formed products, it would be insufficient to cause decomposition by any homolytic cleavage of a C-C, C-H, C-O, or O-H bond to give radical products.

An energetically feasible process would be the decomposition of chemically activated butyraldehyde by an intramolecular process to give ethylene and acetaldehyde (in the enol form analogous to the Norrish type II photochemical decomposition of carbonyl compounds).[23] However, this does not occur since acetaldehyde and ethylene are not observed products of the gas-phase decomposition of *n*-butyl peroxyacetate. Another energetically feasible but sterically improbable and unknown process might be the conversion of chemically activated acetic acid into methane and carbon dioxide. Although these products are observed, they are formed in grossly unequal amounts, and the yield of methane (27.6 and 26.1%) is far below that required for this reaction course to be considered seriously.

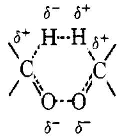
A final observation in this regard is that the pyrolytic elimination reaction of an ester to give an olefin and a carboxylic acid (eq 3) is formally analogous to the concerted peroxy ester decomposition to give an aldehyde (or ketone) and an acid (eq 2). Gas-phase ester pyrolyses have been thoroughly studied,[38] and chemical activation effects have not been reported. If they do not occur in ester pyrolysis, it seems unlikely that they will be important in the analogous peroxy ester decompositions at a much lower temperature. To our knowledge, the careful studies of ester pyrolysis have been limited to the gas phase so that no comparison of the rates of gas-phase *vs.* liquid-phase ester pyrolyses is available.

Conformation Effects. Type 1 homolysis has no particular conformational requirement for the transition state and so can readily accommodate to the preferred dihedral angle of 100-120° of the O-O bond.[39] The type 2 decomposition has a transition state which should be favored by a trans or a near-trans orientation of the peroxide substituents.[17] Models show that the type 3 reactions can be accommodated with a dihedral angle of either approximately 0° (which must be unfavorable because of the eclipsed nonbonding orbitals on oxygen) or by an angle of approximately 60° corresponding to a pseudo-chair form which should be preferred for this type of transition state.[39,40] For hydrogen peroxide, the barrier to internal rotation through the cis configuration in the vapor phase is 7.0 kcal/mol.[17] This is substantial when compared with the magnitude of the effects we are attempting to explain. However, little is known concerning the conformation of the peroxy ester groups and of the shape of the energy barrier for rotations between 0 and 180°. It seems quite possible that solvent in a general way could cause stabilization of a transition-state conformation (represented by eq 2) which would favor the concerted type 3 pathway in solution, while in the absence of solvent some unfavorable conformation might predominate. Such a hypothesis is highly speculative in the absence of good conformational data for the peroxy esters under study. However, it is amenable to experimental test; experiments with 1,2-dioxane and other cyclic nontertiary peroxides are in progress.

Ionic Contributions. We believe that the liquid-phase decompositions of the primary and secondary peroxy esters are rationalized by a six-centered concerted transition state which possesses sufficient ionic character so that it is solvent stabilized. Accordingly, this pathway becomes relatively more accessible than typical homolysis in solution, which is exemplified by the decomposition of the tertiary peroxy esters.[41] In the gas phase, without solvent stabilization of the concerted transition states, homolysis becomes the preferred reaction course.



I (type 3c)



II (type 3b)

The effects of structural variations on the relative ease of type 3 reactions, generally speaking, are in accord with that predicted based upon inductive stabilization of polar transition states I and II. Thus for type 3c, liquid-phase decomposition rates (Table VI) are in the order, $R_2CHOOAc > RCH_2OOAc$; while for type 3b the rate orders[9,10] are, $[RC(O^-)HO]_2 > [RC(OH)HO]_2 \simeq [Ph_2CHO]_2 > [R_2CHO)_2$. A further assessment of the role of ionic contribution to the cyclic concerted transition state of type 3 decompositions can be made by a study of solvent polarity on the rate of these reactions. Although product studies were conducted on the primary and secondary peroxy esters in chlorobenzene and α-methylstyrene solvents, as well as neat, rate studies were made only in α-methylstyrene because of the problem of radical-induced decomposition. However, neither di-*sec*-butyl peroxide nor dibenzyl peroxide showed much difference in the type 3b *vs.* type 1 competition when conducted in solvents as varied as fluorocarbon oil, Nujol, toluene, nitrobenzene, and acetonitrile.[10] It may be that the ionic character of the dialkyl peroxide cyclic-concerted transition state represented by II is not as pronounced as for the peroxy ester represented by I. This is curious, however, since *tert*-butyl peroxide, which shows little difference in homolysis rates between vapor-phase and nonpolar solvents,[42] undergoes homolysis some 2-2.5 times faster in acetonitrile than in cyclohexane.[43,44] This latter observation is in accord with the observed solvent effects upon the homolytic decomposition rate of *tert*-butyl peroxy ester[45] as well as with the minimal effect on the decomposition rate in changing from liquid to gaseous phase, so far as this has been determined. These observations suggest that further studies on the effect of solvent polarity upon the rates of type 3 decomposition are needed.

Conclusion

The presence of solvent in some manner increases the reaction rate of the cyclic concerted type 3c decomposition of primary and secondary peroxy esters in solution so that in the liquid phase, but not in the vapor state, this nonradical mode of decomposition takes precedence over homolytic cleavage. We postulate that this switch in mechanism between liquid and gaseous decomposition of these peroxy esters is due to solvent stabilization of the cyclic-concerted transition state which possesses considerable ionic character as represented in I.

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References and Notes

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(23) We have considered the possibility that 2537 Å irradiation of a primary or secondary peroxy ester may not only cause homolysis of the O–O bond (eq 1) but also $n \rightarrow \pi^*$ excitation of the perester carbonyl group, λ_{max} 2180 Å (ϵ *ca.* 80) [W. H. Simpson and J. G. Miller, *J. Amer. Chem. Soc.*, **90**, 4093 (1968)]. If such an excitation would be followed by a crossover from a photo-excited to a thermal-excited state, as may be the case with esters [R. Borkowski and P. Ausloos, *ibid.*, **83**, 1053 (1961)], then a concerted cyclic decomposition of type 3c might take place. Alternatively, the photo-excited perester carbonyl itself might undergo a reaction analogous to a Norrish type II process for ketones [P. J. Wagner and G. S. Hammond, *Advan. Photochem.*, **5**, 21 (1968)], which would be directly equivalent to a type 3c reaction. We feel that these possibilities cannot be contributing importantly to the production of acetic acid in the photochemical decompositions. Such a mode of decomposition is excluded for *tert*-butyl peroxy esters, which do not have a hydrogen in the crucial 1:6 position, and yet irradiation of *tert*-butyl peroxylaurate and peroxycaprate gave 30–40% yields of the corresponding lauric and capric acids [W. H. Simpson and J. G. Miller, *J. Amer. Chem. Soc.*, **90**, 4093 (1968)].

(24) The arrows indicating a direction of flow of electrons in a cyclic concerted process such as illustrated in eq 2 and 3 are probably only of diagramatic significance. However, these arrows as shown here indicate a flow of electrons as electron pairs and thereby intentionally imply an *ionic character to the transition state*.

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(28) The earlier estimated disparity[11] of 100–300-fold increase at 64° was an error arising from the differences in activation parameters between the two types of peroxy esters.

(29) The temperature range of 11–13° for these studies (Table VI) limits the usefulness of these measurements. However, regression lines for log k *vs.* $1/T$ had coefficients of correlation not less than 0.99 but still yielded 95% confidence limits of 1.5–7 kcal; within these gross limits of error, the values are substantially less than the E_a of 36 kcal/mol for the *tert*-butyl peroxyacetate decomposition.

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(35) (a) A value of 35.8 kcal/mol has been recalculated from the original data[17] using linear regression methods and 95% confidence limits. (b) More recently, C. Rüchardt and H. Brock, *Ber.*, **104**, 577 (1971), found a value of 36.9 kcal/mol for $\Delta H^{\ddagger}$ and 17.1 eu for $\Delta S^{\ddagger}$ (E_a 37.7 kcal/mol). (c) T. Koenig, J. Huntington, and R. Cruthoff, *J. Amer. Chem. Soc.*, **92**, 5413 (1970), obtained a decomposition rate in hexane at 130.1° of 5.08×10^{-4} sec^{-1} which when corrected for cage recombination gave a calculated rate of 6.4×10^{-4} sec^{-1}. This temperature is close to that for which we report the vapor-phase decompositions (Table VIII, run no. 55 and 56, 130.7°). It is seen that the rates in hexane solution and vapor phase are essentially the same.

(36) *Minor yields of hydrogen (1–27%) are reported for thermal decompositions of primary and secondary dialkyl peroxides in the vapor phase* [E. A. Arden and L. Phillips, *J. Chem. Soc.*, 5118 (1964); R. A. Livermore and L. Phillips, *J. Chem. Soc. B*, 640 (1966); R. F. Walker and L. Phillips, *J. Chem. Soc. A*, 2103 (1968); M. J. Yee Quee and J. C. J. Thynne, *J. Phys. Chem.*, **72**, 2824 (1968)]. *The yields have varied randomly*; however, they have not been closely scrutinized and are subject to the difficulties attending analysis for very small amounts of H_2.

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