cm^{-1}. Compared to 1,3-propanediol (Va), the *gem*-dimethyl substitution increases $\Delta\nu$ by 9 cm^{-1}. In contrast, the introduction of a *gem*-dimethyl group along with R_2 = *t*-butyl to give III results in a $\Delta\nu$ value of 128 cm^{-1}. This large change in $\Delta\nu$ for III as compared to the 1,3-propanediol systems must be due to a combination of the *gem*-dimethyl substitution as well as substitution on the ether oxygen atom.

Experimental Section[21]

2-*t*-Butylperoxy-2-methyl-1-propanol (I).—Isobutylene oxide[22] (180 g, 2.50 mol) was added slowly with efficient stirring to a solution of 90% *t*-butyl hydroperoxide (250 g, 2.50 mol, U. S. Peroxygen Corp.) and 0.5 ml of 30% sulfuric acid while the temperature was kept below 15°. The reaction mixture was stirred at room temperature for 2 days. The organic phase was separated and washed twice with 60 ml of water. Washings with sodium bicarbonate solution were continued until the organic phase was no longer acidic. After drying over magnesium sulfate, vacuum distillation through a 45 cm glass helices packed column gave 80 g (20% yield) of I, bp 38–40° (3 mm). The structure of I was established by its ir spectrum [O–H, 3638 (free) and 3593 (bonded); C–O, 1190 and 1143 ; O–O, tentative 865 cm^{-1}] and nmr spectrum (*gem*-dimethyl protons, 1.13 ppm, singlet, area = 6; *t*-butyl protons, 1.20, singlet, area = 9; CH_2 protons, 3.43, singlet, area = 2; OH proton, 2.35, area = 1).

Anal. Calcd for $C_8H_{18}O_3$: C, 59.23; H, 11.18. Found: C, 59.06; H, 11.29.

2-Methyl-2-neopentoxy-1-propanol (II).—Isobutylene oxide[22] (75.0 g, 1.04 mol) was added slowly with stirring to a mixture of neopentyl alcohol[23,24] (76.0 g, 0.864 mol), 0.3 ml of 50% sulfuric acid, and 16 g of carbon tetrachloride while the temperature was kept below 38°. Stirring was continued for an additional 12 hr at room temperature. The organic phase was separated, washed twice with 40 ml of water, and finally washed free of acid with sodium bicarbonate solution. After drying over magnesium sulfate, simple vacuum distillation gave 38 g (28% yield) of II, bp 38–39° (2 mm). The structure of II was confirmed by its infrared [O–H, 3638 (free), 3584 (bonded); C–O, 1145, 1075, 1045 cm^{-1}] and nmr (*t*-butyl protons, 0.85 ppm, singlet, area = 9; *gem*-dimethyl protons, 1.07, singlet, area = 6; OH proton, 2.42, area = 1; CH_2 protons, 2.93, singlet, area = 2 and 3.26, singlet, area = 2) spectra.

Anal. Calcd for $C_9H_{20}O_2$: C, 67.45; H, 12.57. Found: C, 67.52; H, 12.44.

3-*t*-Butoxy-2,2-dimethyl-1-propanol (III).[25]—A solution of 2,2-dimethyl-1,3-propanediol (100 g, 0.961 mol), *t*-butyl alcohol (81.0 g, 1.09 mol), and 200 ml of chloroform was added to 200 ml of 50% sulfuric acid with mechanial stirring while the reaction flask was cooled in an ice bath. The reaction mixture was stirred for an additional 48 hr at room temperature. The organic phase was separated and dried over magnesium sulfate, and the solvent was then removed by simple distillation. Vacuum distillation of the residue gave 30.0 g (19.5% yield) of III, bp 70–75° (8 mm). Redistillation gave a heart cut which showed only one peak by glpc analysis. The structure of III was established by its infrared [O–H, 3638 (free) and 3510 (bonded); C–O, 1070 and 1190 cm^{-1}], nmr (*gem*-dimethyl protons, 0.85 ppm, singlet, area = 6; *t*-butyl protons, 1.18 singlet, area = 9; CH_2 protons, 3.28, singlet, area = 2 and 3.15, singlet, area = 2; OH proton, 2.67, area = 1), and mass[26] (parent peak, *m/e* 160 (weak); $CH_2\overset{+}{=}OC(CH_3)$, 87; and $CH_2\overset{+}{=}OH$: 31) spectra.

Anal. Calcd for $C_9H_{20}O_2$: C, 67.45; H, 12.57. Found: C, 67.15; H, 12.51.

Infrared Spectra.—A Perkin-Elmer Model 621 grating spectrophotometer was employed. The temperature measurement and thermostating techniques were previously described.[5]

Registry No.—I, 17393-39-4; II, 17393-40-7; III, 17393-41-8.

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[21] All boiling points are uncorrected. Elemental microanalyses were performed by C. F. Geiger, Ontario, Calif. The nmr spectra were determined in 15% (w/v) carbon tetrachloride solutions on a Varian A-60 spectrometer with tetramethylsilane used as an internal standard. The mass spectra were measured with a Hitachi Perkin-Elmer RMU-6E spectrometer.

[22] H. O. House, *J. Amer. Chem. Soc.*, **77**, 5083 (1955).

[23] J. Hoffman, *Org. Syn.*, **40**, 76 (1960).

[24] We thank Mr. Gordon G. Snyder for the synthesis of this compound.

[25] We thank Mr. R. M. Castro for the preparation of this compound.

[26] See R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1967, Chapter 2.

Solvent Effects in the Decomposition of Benzoyloxy Radicals[1]

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Yields of CO_2 obtained in the decomposition of benzoyl peroxide in mixtures of hydrogen donor substrates and inert solvents have been used to determine the relative rates of hydrogen abstraction and decarboxylation of benzoyloxy radicals (k_a/k_d ratios). Kinetic schemes have been derived for both simple homolytic scission and induced decomposition and evaluated with cyclohexane and isopropyl alcohol, respectively. Measured k_a/k_d ratios show some variation with solvent, roughly paralleling the *t*-butoxy radical case. Relative rates of benzoyloxy radical attack on different substrates have been compared.

Although the course and rates of radical reactions usually show little solvent dependence, a few striking exceptions are known. The first to attract attention was the strong solvent dependence of the selectivity of chlorine atoms.[2] More recently we have shown that the competition between the hydrogen abstraction and β-scission reactions of *t*-butoxy and other alkoxy radicals is also solvent dependent, the medium having the greatest effect on the latter process.[3] Although complications arise in some systems,[4,5] our conclusions appear to remain quantitatively valid for hydrogen abstraction from aliphatic hydrocarbon substrates. Although aliphatic acyloxy radicals apparently undergo β-scission so rapidly that the process occurs largely within the solvent cage[6,7] benzoyloxy radicals from

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[1] Taken from the Ph.D. Thesis of J. C. A., Columbia University, 1966. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

[2] G. A. Russell, *J. Amer. Chem. Soc.*, **79**, 2977 (1957).

[3] C. Walling and P. J. Wagner, *ibid.*, **86**, 3368 (1964).

[4] P. J. Wagner and C. Walling, *ibid.*, **87**, 5179 (1965).

[5] J. McGuinness, Thesis, Columbia University, 1967.

[6] W. Braun, L. Rajbenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

[7] J. W. Taylor and J. C. Martin, *J. Amer. Chem. Soc.*, **88**, 3650 (1966).

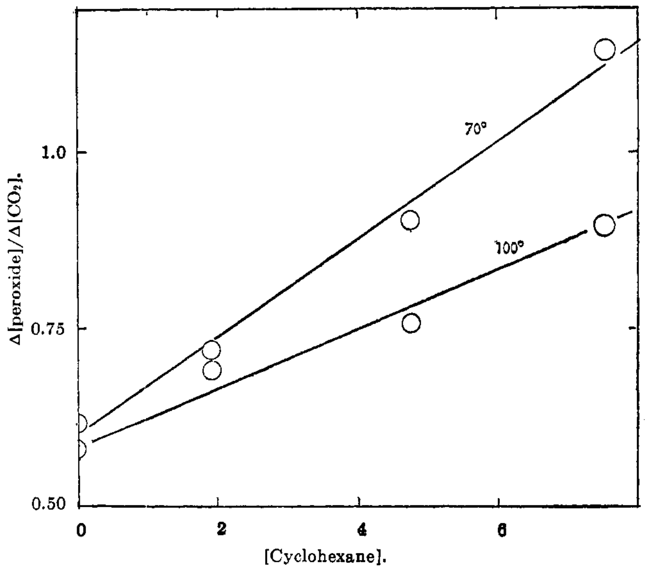

Figure 1.—CO_2 yields in decomposition of benzoyl peroxide in benzene–cyclohexane mixtures.

benzoyl peroxide are more stable and provide another system for examining such a β-scission–hydrogen abstraction competition which, in view of the enormous volume of work on the chemistry of benzoyl peroxide, has had little quantitative attention.[8] In this paper we describe an attempt to set up a quantitative model and use it to detect any solvent dependence of the competition.

Kinetic Analysis.—For our purpose we assume the simplified scheme in eq 1–4 for benzoyl peroxide decomposition in the presence of a hydrogen donor, RH, under conditions where induced chains are unimportant.

$$(C_6H_5COO)_2 \xrightarrow{k_n} 2C_6H_5COO\cdot \quad (1)$$

$$C_6H_5COO\cdot \xrightarrow{k_d} C_6H_5\cdot + CO_2 \quad (2)$$

$$C_6H_5COO\cdot + RH \xrightarrow{k_a} C_6H_5COOH + R\cdot \quad (3)$$

$$C_6H_5COO\cdot + X \xrightarrow{k_s} Y \quad (4)$$

What we are primarily concerned with is the ratio k_a/k_d, and k_s represents the combined rate of all other reactions (unspecified) consuming benzoyloxy radicals. From the above, eq 5 and 6 can be drawn whence, if a

$$-2d[(C_6H_5COO)_2]/dt = 2k_n(C_6H_5COO)_2 = (k_d + k_s + k_a[RH])[C_6H_5COO\cdot] \quad (5)$$

$$d[CO_2]/dt = k_d[C_6H_5COO\cdot] \quad (6)$$

sample of peroxide is decomposed and the yield of CO_2 determined

$$\frac{2\Delta[\text{peroxide}]}{\Delta[CO_2]} = 1 + k_s/k_d + k_a[RH]/k_d \quad (7)$$

From eq 7 k_a/k_d can be determined by plotting the reciprocal of CO_2 yield *vs.* [RH]. The validity of the treatment depends upon the assumption that the sum of reactions represented by k_s is either very small or k_s is constant as [RH] is changed, and this validity must be examined for any system studied.

In the presence of substrates such as ethers and alcohols in which benzoyl peroxide undergoes an induced decomposition a similar expression can be derived. Here, if chains are long, to a good approximation

$$-d[(C_6H_5COO)_2]/dt = k_i[R\cdot][(C_6H_5COO)_2] = (k_d + k_s + k_a[RH])[C_6H_5COO\cdot] \quad (8)$$

where RH represents the alcohol or ether and R· the α-hydroxy or α-alkoxy radical which propagates the induced chain. From eq 6 and 8 the relationship in eq 9

$$\frac{\Delta[\text{peroxide}]}{\Delta[CO_2]} = 1 + (k_s/k_d) + (k_a[RH]/k_d) \quad (9)$$

can be drawn and is identical with eq 7 except for the factor of 2 on the left-hand side of the equation.

Results

Cyclohexane was chosen as a model substrate to investigate the applicability of eq 7. Some typical plots are shown in Figure 1, and ratios of rate constants are summarized in Table I. An immediate conclusion, presaged by qualitative results in the literature, is that k_a/k_d ratios are much smaller than those observed in *t*-butoxy radical reactions. As a result large changes in cyclohexane concentration are required to produce significant changes in CO_2 yield. Qualitatively, results are consistent with prediction in that the data yield straight lines in plots such as those shown. Values of k_s/k_d are obtained from plot intercepts, and the greatest uncertainty in the treatment is whether they actually remain constant as cyclohexane–solvent ratios are changed. Here the most probable difficulty would be that the solvent, or transient intermediates derived from it, could contribute additional reactions with benzoyloxy radicals and thus depress CO_2 yields with the consequence that k_a/k_d ratios calculated from slopes would be lower than true values. Such a complication would certainly be expected in toluene systems and to a lesser extent in the presence of acetone and *t*-butyl alcohol with less reactive C–H bonds.

Table I

CO_2 Yields in Benzoyl Peroxides–Cyclohexane Systems

Solvent	Temp, °C	k_a/k_d, *M*	k_s/k_d, *M*	$E_d - E_a$, kcal/mol	Log $(PZ)_a/(PZ)_d$
CCl_4	70	0.098	0.08		
	100	0.056	0.07	4.7 ± 2	−3.97
Benzene	70	0.144	0.26		
	100	0.079	0.16	5.0 ± 1.3	−4.15
Chlorobenzene	70	0.058	0.50		
	100	0.060	0.33	−0.3 ± 2	−1.05
Toluene	70	(0.035)	(0.43)		
	100	(0.028)	(0.39)	(1.9)	(−2.64)
o-Dichlorobenzene	70	(0.076)	(0.65)		
	100	(0.079)	(0.26)	(−2.0 ± 1.3)	(+0.17)
Acetone	70	0.076	0.14		
	100	0.076	0.10	0	−1.17
t-Butyl alcohol	70	(0.149)	(0.89)		(−7.2)
	100	(0.046)	(0.73)	(9.9)	

Variable amounts of induced decomposition provide another source of error. In an effort to eliminate this difficulty, some experiments were run in the presence of varying amounts of methyl methacrylate, a particularly efficient scavenger for the dioxane peroxide system.[9] However, the viscous reaction mixtures re-

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[8] *Cf.* C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, Chapter 10; W. A. Pryor, "Free Radicals," McGraw Hill Book Co., Inc., New York, N. Y., 1966, Chapter 7.

[9] C. G. Swain, W. H. Stockmayor, and J. T. Clarke, *J. Amer. Chem. Soc.*, **72**, 5426 (1950).

sulting were difficult to analyze. Attempts to use nitrobenzene as a scavenger drastically reduced CO_2 formation and led to black reaction products. Because of these uncertainties, systems giving large k_s/k_d intercepts are suspect, and results are given in parentheses.

The applicability of eq 9 was investigated by decomposing benzoyl peroxide in the presence of isopropyl alcohol progressively diluted with several solvents. Typical plots are shown in Figure 2 and results are summarized in Table II.

TABLE II

CO_2 YIELDS IN BENZOYL PEROXIDE–ISOPROPYL ALCOHOL

Solvent	Temp, °C	k_a/k_d, M	k_s/k_d, M	$E_d - E_a$, kcal/mol	Log $(PZ)_a/(PZ)_d$
Benzene	70	0.140	−0.50		
	85	0.118	−0.50	2.5	−3.63
Acetic acid	70	0.100	0.01		
	85	0.079	−0.01	3.8	−3.45
Chlorobenzene	70	0.111	−0.03		
	85	(0.162)	(−0.20)	(1.5)	(−1.94)
CCl_4	70	(0.145)	(0.37)		
	85	(0.049)	(−0.08)	(17.6)	(−12.1)
Acetonitrile	70	(0.136)	(−0.13)		
	85	(0.072)	(−0.07)	(10.3)	(−7.5)

Since intercepts giving k_s/k_d are uncertain by at least 0.05 units, most values of this ratio are indistinguishable from zero, as should be the case if we are dealing with long kinetic chains since the processes described by k_s presumably represent chain terminations. Results in CCl_4 are anomalous as they show a large change in both slope and intercept with temperature. We doubt that the values are significant, probably because of interference by another chain sequence (RH = isopropyl alcohol) (eq 10 and 11) which has been observed in similar systems by Rasuvaev.[10]

$$R\cdot + CCl_4 \longrightarrow RCl + \cdot CCl_3 \qquad (10)$$

$$CCl_3\cdot + RH \longrightarrow CHCl_3 + R\cdot \qquad (11)$$

A few other substrates were investigated briefly, all in CCl_4 or benzene with results listed in Table III.

TABLE III

REACTIONS OF BENZOYL PEROXIDE WITH OTHER SUBSTRATES (70°)

Substrate	Solvent	k_a/k_d, M	Rel reactivity	t-$C_4H_9O\cdot$[a]
Diethyl ether	CCl_4	1.96	20	2.0
Benzaldehyde	Benzene	0.50	3.5	3.43
Isopropyl alcohol		[b]	1.45[c]	
Cyclohexane (standard)		[b]	1.00	1.00
Anisole	Benzene	0.12	0.83	0.125
2,3,4-Trimethylpentane	Benzene	[d]	<0.1	0.53[e]
Cumene	Benzene	[d]	<0.1	0.47[e]

[a] At 0° unless noted. [b] *Cf.* Tables I and II. [c] Average of values in CCl_4, benzene, and chlorobenzene. [d] Indistinguishable from zero. [e] At 40°.

Most data were treated by eq 7 but two need special mention. In CCl_4 the induced chain decomposition involving diethyl ether seems to be completely suppressed, presumably by reaction of ether radicals with solvent as in eq 10. Thus the quantity $2\Delta[\text{peroxide}]/\Delta[CO_2]$ approaches unity and CO_2 yields are not changed significantly in the presence of 0.3 M styrene. Benzaldehyde shows a sharp twofold change in slope at about 1 M, suggesting inhibition of the known induced chain[11] below this concentration, but application of the appropriate equation to each portion of the data gives the same value of k_a/k_d.

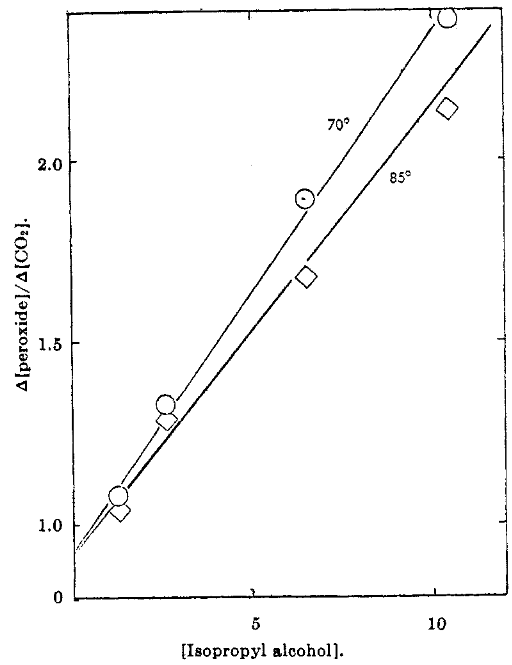

Figure 2.—CO_2 yields in decomposition of benzoyl peroxide in benzene–isopropyl alcohol mixtures.

Discussion

The general consistency of our data indicates that our simplified kinetic scheme is valid for a number of substrate–solvent systems, and gives reasonable values for k_a/k_d and k_s/k_d. In others it breaks down, and we have here indicated results in parentheses in Tables I and II.

The more consistent results, taken at face value, lead to several interesting conclusions. First, k_a/k_d ratios are considerably smaller than those observed with t-butoxy radicals and the difference in activation energies for β scission and hydrogen abstraction are considerably smaller. For comparison, with t-butoxy radicals in $C_2F_3Cl_3$ systems[3] $k_a/k_d = 12.2$ at 70° and $E_a - E_d = 9.65$ kcal. Presumably k_a's are larger for the more energetic t-butoxy radical, but whether k_d is smaller as well is not known.

Second, there appear to be small, but real changes in k_a/k_d ratios with solvent. Qualitatively these also parallel the t-butoxy radical case in that both k_a/k_d ratios and activation energy differences tend to be lower in aromatic solvents and we believe that the phenomenon has the same explanation[3]—solvation of the benzoyloxy radical and its transition state for β scission.

Third, comparison of k_a/k_d ratios for different substrates makes it possible to set up a rough scale of relative reactivities of substrates toward benzoyloxy radicals, and in Table III these again are compared

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[10] G. Rasuvaev, "Vistas in Free Radical Chemistry," W. A. Waters, Ed., Pergamon Press, New York, N. Y., 1959, p 227.

[11] C. Walling and E. S. Savas, *J. Amer. Chem. Soc.*, **82**, 1738 (1960).

with the *t*-butoxy radical case.[12] While the results are rather qualitative,[13] they do show that hydrogen abstraction again occurs more readily from substrates with electron-supplying groups. On the other hand, comparing the rather small difference in reactivity between isopropyl alcohol and cyclohexane with the much more rapid induced chain decomposition in the former indicates that electron-supplying groups enormously increase the rate of radical attack upon the peroxide bond (eq 8). The importance of this step in determining the rate of induced decompositions has been pointed out by Kato and Mashio,[14] and as we have shown elsewhere,[11,15] the attack of simple alkyl radicals on aroyl peroxides is chiefly on the aromatic ring.

Experimental Section

Reagents were commercial materials, purified by standard procedures. Benzoyl peroxide was recrystallized from chloroform–methanol, purity by titration $<99\%$.

Decompositions were carried out in sealed degassed tubes, using 0.0194 *M* peroxide solutions heated in thermostated baths to complete decomposition.

Analyses for CO_2 were carried out by gas chromatography using a silica gel column at 50–70°. By opening the tubes at 0°, and sampling the liquid phase it was found that essentially all the CO_2 remained in solution.

Known concentrations of CO_2 were prepared for calibration by weighing sodium carbonate into 10-ml volumetric flasks, adding 7–8 ml of acetone and then injecting acetic acid through a serum cap to bring the volumn to 10 ml. Calibrations were repeated before each set of analyses, and the method was further checked by comparing our measured CO_2 yields with literature values. Thus in cyclohexane and benzene we obtain 0.90 and 1.62 mol/1 mol of peroxide at 70° compared with 0.93 and 1.61 reported previously.[16]

Registry No.—Carbon tetrachloride, 56-23-5; benzene, 71-43-2; chlorobenzene, 108-90-7; toluene, 108-88-3; *o*-dichlorobenzene, 95-50-1; acetone, 67-64-1; *t*-butyl alcohol, 75-65-0; benzoyl peroxide, 94-36-0; cyclohexane, 110-82-7; isopropyl alcohol, 67-63-0; acetic acid, 64-19-7; diethyl ether, 60-29-7; benzaldehyde, 100-52-7; anisole, 100-66-3; 2,3,4-trimethylpentane, 565-75-3; cumene, 98-82-8.

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[12] Values at 0° are taken from C. Walling and M. J. Mintz, *J. Amer. Chem. Soc.*, **89**, 1515 (1967), and at 40° from C. Walling and B. B. Jacknow, *ibid.*, **82**, 6108 (1960).

[13] With substrates appreciably less reactive than cyclohexane the dependence of CO_2 yield on concentration is too small to determine k_a/k_d.

[14] S. Kato and F. Mashio, *Kogyo Kagaku Zasshi*, **59**, 380 (1956).

[15] C. Walling and Z. Cekovic, *J. Amer. Chem. Soc.*, **89**, 6681 (1967).

[16] P. F. Hartman, H. G. Sellers, and D. Turnbull, *ibid.*, **69**, 2416 (1947).

The Induced Decomposition of Per Esters and Mixed Peroxides in the Presence of Alcohols and Ethers[1]

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Rates and products observed in the fast decomposition of *t*-butyl peracetate and perbenzoate in alcohol and ether solvents confirm an induced chain similar to that recognized with benzoyl peroxide. High yields of *t*-butyl alcohol and only traces of CO_2 implicate the *t*-butoxy radical as the chain carrier, and it is suggested that both steric and polar effects may determine the point of attack by radicals on the peroxide bond. Induced chains are much longer with cyclic than noncyclic ethers. The latter give α-alkoxyalkyl radicals which undergo extensive β scission interfering with the induced chain. With cyclic ethers, β scission is apparently reversible since the fragments cannot separate.

Since the classic work of Cass[2] and Bartlett and Nozaki[3] over 20 years ago, the fast decomposition of benzoyl peroxide in the presence of ethers and alcohols has been recognized as an induced radical chain process, involving the propagation steps[4] in eq 1 and 2. Subsequently O^{18} tracer experiments[5] in ether systems have shown that eq 2 occurs by radical displacement on peroxide rather than carbonyl oxygen, while kinetics that are first order in peroxide in both ethers[3] and alcohols[6] imply that chains end by cross-termination between the two types of chain carrying radicals.

$$C_6H_5COO\cdot + R_2CH{-}OR(H) \longrightarrow C_6H_5COOH + R_2\dot{C}OR(H) \quad (1)$$

$$R_2\dot{C}OR(H) + C_6H_5COOOCOC_6H_5 \longrightarrow R_2C(OCOC_6H_5)OR(H) + C_6H_5COO\cdot \quad (2)$$

Other peroxides also show rapid decomposition in these solvents. With several classes including per esters,[7] per acids[8] and per sulfate,[9] retardation by radical traps indicates a chain sequence, presumably similar to eq 1 and 2. In contrast, Huyser and Bredeweg[10] have reported that di-*t*-butyl peroxide undergoes a short-chain-induced decomposition in alcohols, but not ethers, for which they suggest eq 3 as an alternative to eq 2, and Tobolsky and Matlack[11] have shown that the fast decomposition of tertiary hydroperoxides in benzyl alcohol reflects an actual increase in the rate of homolytic scission.

$$R_2\dot{C}OH + BuOOBu \longrightarrow R_2CO + BuOH + BuO\cdot \quad (3)$$

Previous results on per esters have been limited to kinetic measurements,[7] although Bartlett[12] has re-

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[1] Taken from the Ph.D. Thesis of J. C. A., Columbia University, 1966. Support of this work by a grant from the National Science Foundation is gratefully acknowledged.

[2] W. E. Cass, *J. Amer. Chem. Soc.*, **69**, 500 (1947).

[3] P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947).

[4] Since some decarboxylation of the benzoyloxy radical occurs, propagation also occurs in part through phenyl radicals.

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

[6] S. Kato and F. Mashio, *Kogyo Kagaku Zasshi*, **59**, 380 (1956).

[7] A. T. Blomquist and A. F. Ferris, *J. Amer. Chem. Soc.*, **73**, 3412 (1951).

[8] K. Tokamaro, O. Simamura, and M. Fukuyama, *Bull. Chem. Soc. Jap.*, **35**, 1673 (1962); K. Tokumaro and O. Simamura, *ibid.*, **35**, 1955 (1962).

[9] P. D. Bartlett and J. D. Cotman, Jr., *J. Amer. Chem. Soc.*, **71**, 1419 (1949); I. M. Koltoff, E. J. Meehan, and E. M. Carr, *ibid.*, **75**, 1439 (1953).

[10] E. S. Huyser and C. J. Bredeweg, *ibid.*, **86**, 2401 (1964).

[11] A. V. Tobolsky and L. R. Matlack, *J. Polym. Sci.*, **55**, 49 (1961).

[12] P. D. Bartlett, E. D. Benzing, and R. E. Pincock, *J. Amer. Chem. Soc.*, **82**, 1762 (1960).