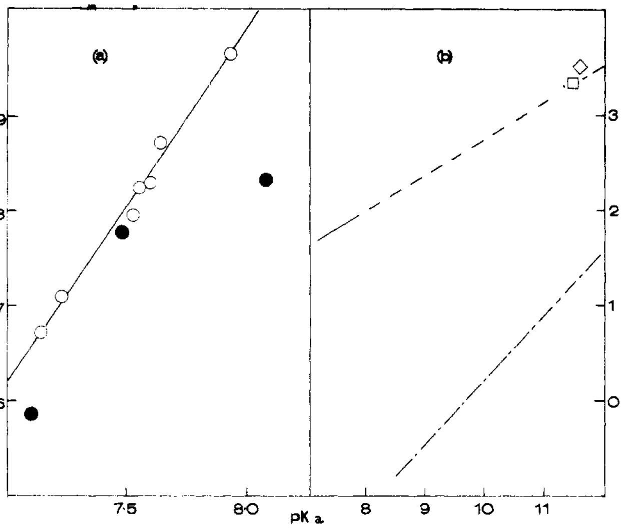

Figure 1. Brønsted-type correlations of log k_2 vs. pK_a for the reaction of oxygen nucleophiles with *p*-nitrophenyl acetate: (a) ○, meta- and para-substituted peroxobenzoic acids, ●, ortho-substituted peroxobenzoic acids; (b) – – –, data described in this work; - - -, data of ref 6 for phenoxides and alkoxides; ◇, HOO^- (ref 3); □, CH_3OO^- (ref 3).

Table I. Nucleophilic Reactivities of Peroxobenzoate Anions (PBA) toward *p*-Nitrophenyl Acetate[a]

Anion	Registry no.	pK_a[b]	k_2,[c] L mol^{-1} s^{-1}
p-OMe-PBA	64235-66-1	7.93	92.4
PBA	35683-46-6	7.64	74.7
p-Cl-PBA	64235-65-0	7.60	67.9
p-SO_3^--PBA	64235-73-0	7.56	67.1
m-Cl-PBA	64235-64-9	7.53	62.6
m-NO_2-PBA	64235-63-8	7.23	51.5
p-NO_2-PBA	64235-62-7	7.14	47.1
o-CO_2^--PBA	7770-90-3	8.08	68.3
o-Cl-PBA	64235-61-6	7.48	60.0
o-NO_2-PBA	64235-60-5	7.10	38.7

[a] Registry no.: *p*-nitrophenyl acetate, 830-03-5. [b] Measured at ionic strength 0.1 mol L^{-1} (sodium nitrate as added electrolyte), 25 °C. [c] At 25 °C, ionic strength 0.1 mol L^{-1}, pH 10 ($NaHCO_3$/Na_2CO_3 buffers).

o-carboxyperoxobenzoate, which may exhibit steric effects and pK_a values influenced by intramolecular H bonding, show experimental values below the line. Comparison of the pK_a values of the meta- and para-substituted peroxobenzoic acids with those of their parent benzoic acids gives a Hammett ρ value of 0.67.

The Brønsted correlation may be extrapolated to comprehend the activities of hydroperoxide and methyl hydroperoxide anions (Figure 1, b). Jencks and Gilchrist[7] have shown that, when data for "normal" oxygen anion nucleophiles over a wide range of basicity are considered, the Brønsted plots are nonlinear, the slope varying from 1.0 for nucleophiles which are less basic than the leaving group to a limiting value of about 0.3 for nucleophiles of high basicity. They have classified the reactions into two limiting types on the basis of this behavior. In these terms, the sensitivity to basicity of peroxo anion nucleophiles approaches limiting type I behavior, although normal nucleophiles show a much greater sensitivity in this range of basicity.

A variety of bases for quantitation of the α effect have been employed. In most recent experimental and theoretical work,[2] the comparison is made between an α nucleophile and a normal nucleophile of similar basicity (phenoxides and alkoxides in the case of oxygen anion nucleophiles). As shown in Figure 1 (b), this basis of comparison yields α effects of 10^2–10^3, increasing with decreasing nucleophile basicity in accord with the general decrease in the α effect with increasing pK_a of oxime nucleophiles in alkylation, acylation, and phosphorylation, as noted by Hudson.[2]

References and Notes

(1) We are indebted to Laporte Industries Ltd. for support of this research and to the Science Research Council for a studentship (D.M.D.).

(2) R. F. Hudson, "Chemical Reactivity and Reaction Paths", G. Klopman, Ed., Wiley, New York, N.Y., 1974, pp 167–252.
(3) J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, **84**, 16 (1962).
(4) W. P. Jencks and J. Carriulo, *J. Am. Chem. Soc.*, **82**, 1778 (1960).
(5) E. J. Behrman, J. E. McIsaac, L. R. Subbaraman, J. Subbaraman, and H. A. Malhausen, *J. Org. Chem.*, **37**, 1037 (1972).
(6) P. Jones and D. N. Middlemiss, *Biochem. J.*, **130**, 411 (1972); **143**, 473 (1974); D. M. Davies, P. Jones, and D. Mantle, *ibid.*, **157**, 247 (1976).
(7) W. P. Jencks and M. Gilchrist, *J. Am. Chem. Soc.*, **90**, 2622 (1968).
(8) A. J. Everett and G. J. Minkoff, *Trans. Faraday Soc.*, **49**, 410 (1953).

The Chemistry of Benzyl Hydroperoxide

William A. Pryor* and W. David Graham

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803

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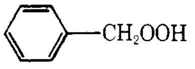
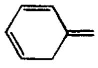
Although benzyl hydroperoxide (BHP) was synthesized a number of years ago,[1] very little data on its stability in solution have been reported.[2] Therefore, we report here the results of a study of BHP, including its rate of decomposition in an inert solvent and in styrene, the rate of polymerization of styrene initiated by benzyl hydroperoxide, and the chain-transfer constant of BHP in styrene.

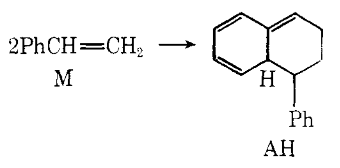


BHP



MCH

Our interest in BHP derives from a study underway in our laboratory of the chemistry of 5-methylene-1,3-cyclohexadiene (MCH). We are studying MCH as a model for the Diels–Alder dimer of styrene, AH, a molecule that is postulated[3] to be responsible for the initiation of the polymerization of styrene by a molecule-assisted homolysis[4] of a C–H bond (eq 1–3).[3b] We have studied the initiation of polymerization



(1)

$$AH + M \longrightarrow A\cdot + HM\cdot \quad (2)$$

$$A\cdot(HM\cdot) + M \longrightarrow M_n\cdot \quad (3)$$

of styrene by MCH,[5] and, since benzyl hydroperoxide is a potential impurity in MCH, we found it necessary to measure the dependence of the rate of polymerization of styrene on BHP as well.

We have observed that BHP is formed by air oxidation of MCH at room temperature in $CHCl_3$ solvent. Although we have not studied this process in detail, the mechanism may proceed with an initiation reaction involving MCH and oxygen

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Table I. Modes of Decomposition of Benzyl Hydroperoxide in 8.35 M Styrene at 60 °C

[PhCH$_2$OOH] × 10^3	$k_d \times 10^5$,[c] s^{-1}	$R_i \times 10^9$,[a] M/s	Fraction consumed: By initiation	Fraction consumed: By chain transfer[b]	Fraction consumed: By other reactions
7.83	0.9	5.0	0.04	0.03	0.93
3.76	1.4	2.7	0.03	0.01	0.96
2.50	1.8	2.0	0.02	0.01	0.97

[a] Calculated from Figure 1 and eq 1. [b] Rate of transfer equals $C[\mathrm{PhCH_2OOH}]R_P/[\mathrm{M}]$. [c] The reaction is assumed to be first order in BHP. The correlation coefficients of the three runs listed here for plots of log [BHP] vs. time are 0.96, 0.99, and 0.99. Correlation coefficients of these data plotted for second-order kinetics in BHP are 0.97, 0.99, and 0.98. See discussion in the text.

(eq 4), followed by a chain sequence (eq 5 and 6).[6]

$$\mathrm{MCH} + \mathrm{O_2} \longrightarrow \mathrm{PhCH_2\cdot} + \mathrm{HO_2\cdot} \tag{4}$$

$$\mathrm{PhCH_2\cdot} + \mathrm{O_2} \longrightarrow \mathrm{PhCH_2OO\cdot} \tag{5}$$

$$\mathrm{PhCH_2OO\cdot} + \mathrm{MCH} \longrightarrow \underset{\mathrm{BHP}}{\mathrm{PhCH_2OOH}} + \mathrm{PhCH_2\cdot} \tag{6}$$

A number of reports on other hydroperoxides demonstrate that hydroperoxides undergo a decomposition in olefins like styrene at a rate that is greatly accelerated over that observed in "inert" solvents such as alkanes.[7] The rate of polymerization of monomers like styrene also is greater than would be predicted from the rate of decomposition of hydroperoxides measured in nonolefin solvents. Several proposals that rationalize these accelerated rates have been published.[7b–d,8]

We observed that the rate of decomposition of an approximately 0.02 M solution of BHP in octane is slow at 100 °C. The apparent first-order rate constant is 5.4×10^{-7} s^{-1}, corresponding to a half-life of 15 days. The rates of decomposition of hydroperoxides are often reported to be of a kinetic order in hydroperoxide greater than unity.[7] However, first-order kinetic plots of the logarithm of the BHP concentration vs. time for our data have correlation coefficients greater than 0.99, whereas second-order plots show slight but noticeable curvature. Thus, our data do not require the postulation of a decomposition that is more complex than first order for BHP in octane.

As expected, the rate of decomposition of BHP in styrene is accelerated over that observed in octane. The data could be plotted with virtually equal precision in plots that are either first or second order in BHP.[9] (Data in styrene were less precise than in octane because the polystyrene precipitates during the iodometric titration.) From analogy with our results in octane, we have assumed that the decomposition of BHP in styrene is first order in BHP, and Table I shows the rate constants calculated in this way at 60 °C. The rate constant of approximately 1×10^{-5} s^{-1} at 60 °C is approximately 20 times faster than the rate in octane at 100 °C.

Benzyl hydroperoxide initiates the polymerization of styrene. The rate of polymerization, R_p, due to an initiator I is given by eq 7,[8,10]

$$R_p = \frac{k_p[\mathrm{M}]R_i^{0.5}}{(2k_t)^{0.5}} = \frac{k_p[\mathrm{M}](k_d f[\mathrm{I}])^{0.5}}{k_t^{0.5}} \tag{7}$$

where k_d is the rate constant for decomposition of I and f is the efficiency of the decomposition in producing free radicals. Figure 1 shows a plot of the rate of polymerization vs. the square root of the BHP concentration, and it can be seen that eq 7 is obeyed. If the value of $2k_t/k_p^2$ is taken as 1722 at 60 °C,[11] then the value of R_i for BHP is calculated to be 5.1×10^{-9} M s^{-1} for 8×10^{-3} M BHP. The value of $k_d f$, therefore, is 6.4×10^{-7} s^{-1} at 60 °C.

In styrene, BHP decomposes partly by an induced process in which polystyryl radicals attack the peroxide (eq 8).

$$\mathrm{M}_n\cdot + \mathrm{PhCH_2OOH} \rightarrow \mathrm{M}_n\mathrm{H} + \mathrm{PhCH_2OO\cdot} \tag{8}$$

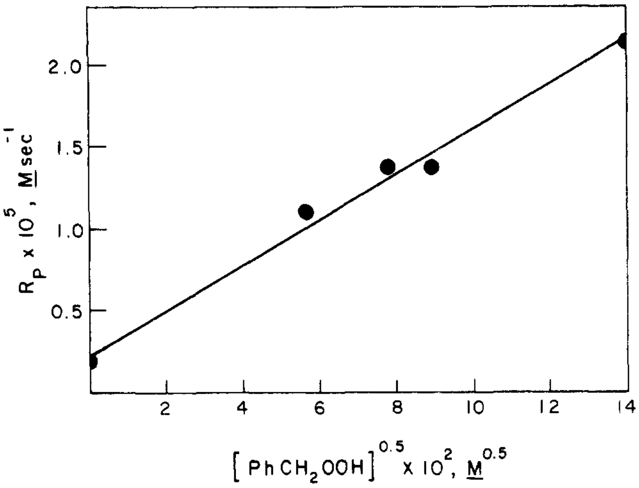

Figure 1. A plot of the rate of polymerization vs. the square root of the concentration of benzyl hydroperoxide at 60 °C.

The rate constant for this process can be obtained from the chain-transfer constant, $C = k_{tr}/k_p$. Using standard techniques,[12] we have determined the transfer constant of BHP to be 0.15 at 60 °C in styrene, a value that is consistent with values reported for other hydroperoxides.[13] Despite the large transfer constant, only a small fraction of the BHP decomposes by chain transfer (see Table I).

By comparing the total rate of decomposition of BHP in styrene (determined by iodometric titration) with values of R_i, the efficiency of initiation can be determined; our data give f, the efficiency, as 0.04. Thus only about 4% of BHP disappears in styrene to give free radicals that initiate polymerization. The majority of the BHP decomposes by other than radical pathways or by cage processes that do not produce free radicals.[7] Table I summarizes the importance of various modes of decomposition observed for BHP in styrene.

Finally, some comment seems appropriate concerning our observation of the rapid oxidation of 5-methylene-1,3-cyclohexadiene (MCH) to benzyl hydroperoxide. We have not optimized the conditions for this oxidation, but it is dependent both on the solvent, being much faster in chloroform than in octane or benzene, and on the method of preparation (and presumably the impurities) in MCH.[14] It is clear that the oxygenation reaction occurs with MCH and not toluene, since attempts to prepare BHP by autoxidation of toluene have failed.[15] The secondary hydrogens in MCH are very labile,[4] and it seems reasonable that reaction 4 would be fast for MCH if it occurs at all.[6,16]

Experimental Section

Solvents. Heptane and octane were first washed with a mixture of concentrated H_2SO_4 and HNO_3, dried, distilled, and passed through a silica gel column. Styrene was commercial material which was purified by first washing with 10% NaOH to remove inhibitor, fractionating under reduced pressure, and then refractionating and filtering through alumina just before use: bp 46–47 °C (15 mmHg).

Benzyl hydroperoxide (BHP) was prepared in low yield by the method of Walling and Buckler[1] and purified by column chromatography (silica gel, CH_2Cl_2) and vacuum transfer to give material 96% pure by iodometric titration.[17] The NMR spectrum in $CDCl_3$ is δ 4.83 (s, 2 H, CH_2), 7.28 (m, 5 H, phenyl), 8.6 (br s, variable with temperature, 1 H, OOH).[18] The BHP prepared in this way is identical in all respects with the product of oxidation of 5-methylene-1,3-cyclohexadiene.

Samples were prepared in 10-mL drying ampules fitted with "O" ring seals for attachment to a vacuum line. The ampules were cleaned by soaking in concentrated HNO_3, washing thoroughly with water, and drying at 110 °C. The appropriate amount of hydroperoxide was dissolved in solvent and samples were pipetted into the reaction vessels. The ampules were degassed by at least three freeze-thaw cycles and then sealed at 5×10^{-5} mmHg.

Decomposition in octane was carried out by immersion of ampules containing 1-mL samples in a 100.2 °C oil bath. Concentration of hydroperoxide was followed through 80% reaction by titration[17] of samples removed at regular intervals.

Decomposition in styrene was carried out as above on 5-mL samples through 40% reaction at 60.0 °C. Due to the increase in viscosity of the styrene solutions and probably the trapping of hydroperoxide in the polymer (which precipitates during analysis), the precision is less than in octane.

Polymerization rates at 60.0 °C were determined gravimetrically by precipitation of the polymer in cold methanol. The styrene solution (5 mL) was first diluted with a small amount of toluene (2–3 mL) and then very slowly pipetted into 400 mL of reagent-grade methanol at 10 °C. The precipitated polymer was filtered on a sintered glass funnel and brought to constant weight under vacuum. Rates were determined for the first 5% conversion of monomer.

Chain-transfer constant of benzyl hydroperoxide was determined by standard methods[12] from the intrinsic viscosity of polymer solutions in benzene. Concentrations of hydroperoxide from 9×10^{-4} to 8×10^{-3} M were used.

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Registry No.—BHP, 3071-34-9; octane, 111-65-9; styrene, 100-42-5.

References and Notes

(1) C. Walling and S. A. Buckler, *J. Am. Chem. Soc.*, **77,** 6032 (1955).
(2) A study of *p*-methylbenzyl hydroperoxide was concerned with product formation: W. J. Farrissey, Jr., *J. Am. Chem. Soc.*, **84,** 1002 (1962).
(3) (a) F. R. Mayo, *J. Am. Chem. Soc.*, **75,** 6133 (1953); **90,** 1280 (1968); (b) for a review, see W. A. Pryor and L. D. Lasswell, "Advances in Free Radical Chemistry", Vol. V, Academic Press, New York, N.Y., 1975, pp 27–99; (c) W. A. Pryor, M. Iino, and G. R. Newkome, *J. Am. Chem. Soc.*, **99,** 6003 (1977).
(4) W. A. Pryor, J. H. Coco, W. H. Daly, and K. N. Houk, *J. Am. Chem. Soc.*, **96,** 5591 (1974).
(5) W. A. Pryor, W. D. Graham, and J. G. Green, *J. Org. Chem.*, **43,** 527 (1978).
(6) W. A. Pryor and R. A. Patsiga, *Spectrosc. Lett.*, **2,** 61 (1969); S. W. Benson, "*Thermochemical Kinetics*", 2nd ed, Wiley, New York, N.Y., 1976, pp 237–243.
(7) (a) A. Farkas and E. Passaglia, *J. Am. Chem. Soc.*, **72,** 3333 (1950); (b) C. Walling and Y. W. Chang, *Ibid.*, **76,** 4878 (1954); (c) S. W. Benson, *J. Chem. Phys.*, **40,** 1007 (1964); (d) C. Walling and L. Heaton, *J. Am. Chem. Soc.*, **87,** 38 (1965); (e) E. V. Tobolsky and L. R. Martin, *J. Polym. Sci.*, **55,** 49 (1961).
(8) W. A. Pryor, "Free Radicals", McGraw-Hill, New York, N.Y., 1966.
(9) The reaction was followed to 55–80% decomposition of the BHP.
(10) M. S. Matheson, E. E. Auer, E. B. Bevilaqua, and E. J. Hart, *J. Am. Chem. Soc.*, **73,** 1700 (1951).
(11) A. V. Tobolsky and J. Offenbach, *J. Polym. Sci.*, **16,** 311 (1955).
(12) E. A. Collins, J. Bares, and F. W. Billmeyer, Jr., "Experiments in Polymer Science", Wiley, New York, N.Y., 1973, p 398; G. Odian, "Principles of Polymerization", McGraw-Hill, New York, N.Y., 1970, pp 205–212; F. R. Mayo, R. A. Gregg, and M. S. Matheson, *J. Am. Chem. Soc.*, **73,** 1691 (1951).
(13) The transfer constant, *C*, for *tert*-butyl hydroperoxide is 0.035–0.066; *C* for cumyl hydroperoxide is 0.052–0.1; cf. J. Brandrup and E. H. Immergut, "Polymer Handbook", Interscience, New York, N.Y., 1966, p II-87.
(14) K. R. Kopecky has made similar observations (private communication to W. A. Pryor).
(15) H. Hock and S. Lang, *Ber.*, **76,** 169 (1943).
(16) Rapid, room temperature air oxidation of hydrocarbons has been observed: cf. W. Parker, R. L. Tranter, C. I. F. Watt, L. W. K. Chang, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96,** 7121 (1974); A. Bromberg, K. A. Muszkat, and E. Fisher, *Chem. Commun.*, 1352 (1968).
(17) C. D. Wagner, R. H. Smith, and E. D. Peters, *Anal. Chem.*, **19,** 979 (1947).
(18) E. J. Y. Scott, *J. Chem. Phys.*, **74,** 1174 (1970); G. A. Ward and R. D. Mair, *Anal. Chem.*, **31,** 538 (1969).

Direct α-Lithiation of Phenoxyacetic Acid and Electrophilic Substitution

Waldemar Adam*[1] and Hans-Heinrich Fick

Department of Chemistry, University of Puerto Rico,
Rio Piedras, Puerto Rico 00931

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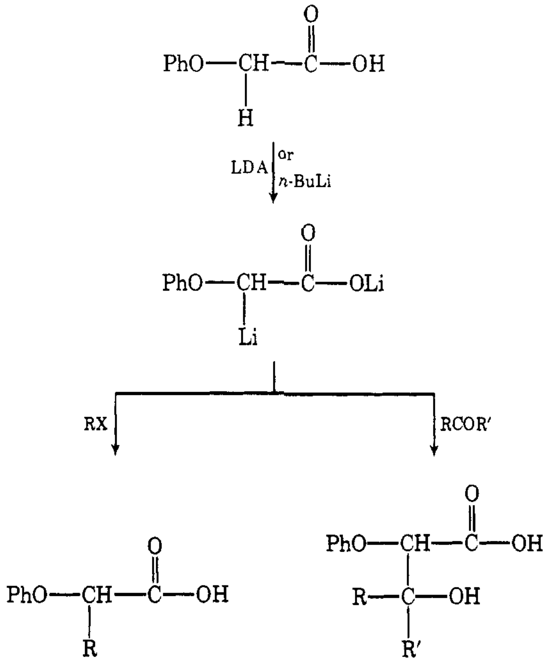
The destabilization exerted by juxtaposed oxygen atoms on carbanionic centers is well recognized.[2] This effect is most dramatically accentuated in the side-chain metalation of thioanisole vs. ring metalation of anisole by *n*-butyllithium.[3] A powerful synthetic utilization has been the Corey–Seebach reagent,[4] prepared by direct metalation of 1,3-dithiane with *n*-butyllithium, conditions which fail to produce the corresponding 2-carbanion from 1,3-dioxane.[2a] However, allylic ethers were recently[5] converted efficiently into allyloxy carbanions with *sec*-butyllithium, and α-alkoxynitrile carbanions[6] have been used as synthons, showing that the destabilizing influence of the α-oxygen atom can be moderated by conjugation. In fact the enolate ion of 2-carbomethoxy-1,3-dioxolane was formed only fivefold slower than that of the carbocyclic analogue, i.e., 2-carbomethoxycyclopentane, in the methoxide-catalyzed deuterium exchange.[7]

These facts suggested that it should be possible to prepare stable solutions of the hitherto unknown enolate **2** by metalation of phenoxyacetic acid with strong bases such as *n*-butyllithium or lithium diisopropylamide (LDA).[8] The potential usefulness of such a α-lithiocarboxylate **2** as synthon encouraged us to explore the direct lithiation of phenoxyacetic acid (**1**). Presently we report our successful generation of this enolate and its reaction with electrophiles.

Treatment of phenoxyacetic acid (**1**) in THF with stoichiometric amounts (2 mol) of *n*-BuLi at −78 °C generated



3a, R = CH_3
b, R = $PhCH_2$

3c, R = H; R′ = Ph
d, R = R′ = CH_3