

Decomposition of Hydroperoxides by Boric Acid Anhydride in Solution. Electrophilic Hydroxylation of the Solvent

By Hiroshi Sakaguchi, Etsuo Niki,* and Yoshio Kamiya, Department of Reaction Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Tokyo 113, Japan

Three kinds of hydroperoxides were decomposed in aliphatic and aromatic hydrocarbons in the presence of boric acid anhydride at 100 °C in order to study the hydroxylation of the solvent. Secondary 1-methylheptyl hydroperoxide was decomposed by boric acid anhydride to give mainly octan-2-ol and its borate ester, and when n-pentane, n-hexane, benzene, and mesitylene were used as solvent they were simultaneously hydroxylated to secondary pentanols, secondary hexanols, phenol, and mesitol respectively. In the decomposition of t-butyl hydroperoxide, the solvent was hydroxylated to the corresponding alcohol or phenol, but t-butyl alcohol formed was dehydrated to isobutene. Acid-catalysed rearrangement of t-butyl hydroperoxide to acetone and methanol also took place. Cumyl hydroperoxide was decomposed exclusively to phenol and acetone and little cumyl alcohol and hydroxylation of solvent were observed. It was suggested that the solvent was hydroxylated not by free atomic oxygen or by a radical process but by an ionic, electrophilic substitution reaction where boron acted as electron acceptor and hydroperoxide oxygen as electron donor, generating an active hydroxonium ion.

THE autoxidation of aliphatic hydrocarbons in the presence of boric acids gives alcohols in high yield¹ and it has been suggested that boric acid decomposes the hydroperoxide selectively to the corresponding alcohol and boric ester and protects alcohol from further oxidation. Interestingly, when hydroperoxide is decomposed by boric acid, the solvent is also hydroxylated. Broich and Grasemann² found that, when cyclododecyl hydroperoxide was decomposed in cyclododecane in the presence of boric acid anhydride, cyclododecanone and cyclododecanol were formed in 120% yield based on hydroperoxide decomposed and they interpreted this result in terms of formation and subsequent attack of atomic oxygen on cyclododecane to give cyclododecanol. Grasemann³ found that aromatic solvents such as toluene and naphthalene were also hydroxylated, and Takamitsu and Hamamoto⁴ observed the formation of decanol from decane in the boric acid-catalysed decomposition of cyclohexyl hydroperoxide. The formation of mesitol from mesitylene in high yield has been found by Wolf and Barnes⁵ in the decomposition of tetralinyl, t-butyl, and cyclohexyl hydroperoxides catalysed by cyclohexyl metaborate. In the oxidation of ethylbenzene with boric acid anhydride, considerable amounts of *o*- and *p*-ethylphenol were observed in addition to 1-phenylethanol.⁶ These results clearly demonstrate the hydroxylation of solvent in the boric acid-catalysed decomposition of hydroperoxide. However, the mechanism of this hydroxylation reaction and the active species are not yet established. The objective of the present work is to study the decomposition of three kinds of hydroperoxides in various solvents in the presence of boric acid anhydride aiming

specifically at elucidating the mechanism of hydroxylation of the solvent.

EXPERIMENTAL

Materials.—1-Methylheptyl hydroperoxide was prepared from octan-2-ol by the method of Williams and Mosher.⁷ It was purified by distillation under reduced pressure, b.p. 42.5 °C at 0.27 Torr (Found: C, 65.7; H, 12.4. Calc. for C₈H₁₈O₂: C, 64.9; H, 12.15%). Iodimetric analysis showed 99.4% purity and little impurity was observed by g.l.c. after reduction with triphenylphosphine. Commercial t-butyl hydroperoxide was purified by fractional distillation, b.p. 40.0 °C at 25 Torr. Cumyl hydroperoxide was purified as described previously.⁸ Other organic materials were purified by conventional method when necessary.

Procedures.—Commercial orthoboric acid (5 × 10⁻⁴ mol) was placed in an ampoule connected to a vacuum line and then heated gradually to 250 °C over ca. 6 h under vacuum. It is reported⁹ that orthoboric acid is dehydrated quantitatively to boric acid anhydride by this treatment and in fact a 44 wt% loss was observed experimentally by thermal gravimetric analysis. The ampoule was cooled and 5 ml of solution containing 5 × 10⁻²M hydroperoxide was introduced into the ampoule by the vacuum transfer technique together with a magnetic stirrer. The ampoule was sealed under vacuum and immersed in a thermostatted oil-bath.

Analyses.—After reaction, the ampoule was opened and analysed as follows. Unchanged hydroperoxide was determined by iodimetric titration. Products were analysed by g.l.c. using two different columns at three temperatures: polyethylene glycol 20M at 200 °C for cumyl alcohol, acetophenone, and phenol; Porapak Q at 200 °C for cumyl alcohol, acetophenone, and phenol, mesitol, hexan-1-, -2-, and -3-ol, octan-2-one, octan-2-ol, and pentan-1-

¹ A. N. Bashkurov, *Khim. Nauka i Prom.*, 1956, **1**, 273; V. V. Kamzolkin, A. N. Bashkurov, M. I. Khotimskaya, N. M. Grozhan, and G. M. Yezhenkina, *Neftekhimiya*, 1961, **1**, 244.

² F. Broich and H. Grasemann, *Erdoel Kohle, Erdgas, Petrochem.*, 1965, **18**, 360.

³ H. Grasemann, *Erdoel Kohle, Erdgas, Petrochem.*, 1969, **22**, 751.

⁴ N. Takamitsu and T. Hamamoto, *Nippon Kagaku Kaishi*, 1973, 1156.

⁵ P. F. Wolf and R. K. Barnes, *J. Org. Chem.*, 1969, **34**, 3441.

⁶ A. Masuda and Y. Yamazaki, 30th Annual Meeting of Chem. Soc. Japan, Osaka, 1974.

⁷ H. R. Williams and H. S. Mosher, *J. Amer. Chem. Soc.*, 1954, **76**, 2987.

⁸ H. Sakaguchi, Y. Kamiya, and N. Ohta, *Bull. Jap. Petrol. Inst.*, 1972, **14**, 71.

⁹ K. Othmer, 'Encyclopedia of Chemical Technology,' Wiley, New York, 1964, 2nd edn., vol. 3, p. 602.

-2-, and -3-ol; and Porapak Q at 130 °C for acetone, methanol, t-butyl alcohol, and isobutene.

RESULTS

Decomposition of 1-Methylheptyl Hydroperoxide.—1-Methylheptyl hydroperoxide was selected as a model secondary aliphatic hydroperoxide. The results of decomposition of 1-methylheptyl hydroperoxide by boric acid anhydride at 100 °C in several solvents are summarized in Table 1. As solvents, n-pentane and n-hexane were chosen as model aliphatic hydrocarbons, benzene as the

from the hydroperoxide was octan-2-ol. The material balance for octan-2-ol was not satisfactory; however, this may be mainly because of the formation of the boric ester of the alcohol formed. The formation of octan-2-one in the presence of boric acid anhydride was small. The products distribution in Table 1 suggests that the contribution of thermal and Lewis acid-catalysed decompositions are small under the conditions employed.

In the presence of boric acid anhydride, every solvent was oxidized and gave the corresponding alcohol or phenol. Table 1 implies that the rate of decomposition of hydroperoxide and reactivity of solvent are closely correlated.

TABLE 1

Decomposition of 1-methylheptyl hydroperoxide (0.050M) by boric acid anhydride under vacuum at 100 °C for 2 h

[B ₂ O ₃]/M	Solvent	Conversion (%)	10 ³ [Product]/M (%) ^a			
			Octan-2-ol	Octan-2-one	From solvent	
0.25	n-Pentane	30.6		0.4 (2)	s-Pentanol ^b	3.5 (21)
0.25	n-Hexane ^d	68.6	12 (33)	0.3 (0.8)	s-Hexanol ^c	6 (17)
	Benzene ^d				Phenol	9 (23)
0.25	Benzene	81.2	27 (60)	0.9 (2)	Phenol	25 (57)
0.25	Mesitylene	99.4	35 (63)	0 (0)	Mesitol	51 (92)
0	Benzene	10.9	8	0 (0)	Phenol	0 (0)
0 ^e	Benzene	82.4	15 (33)	22 (49)	Phenol	0 (0)

^a Numbers in parentheses are percentages based on hydroperoxide decomposed. ^b Total pentan-2- and -3-ols. ^c Total hexan-2- and -3-ols. ^d n-Hexane-benzene (3 : 2 v/v). ^e At 150 °C.

most stable aromatic hydrocarbon, and mesitylene as an aromatic hydrocarbon reactive toward both radical and electrophilic reagents. The results of thermal decomposition in the absence of boric acid anhydride at 100 and 150 °C are also shown for comparison in Table 1.

Table 1 shows that the rates of decomposition of 1-methylheptyl hydroperoxide in the presence of boric acid anhydride were much faster in every solvent than those of the uncatalysed thermal decomposition. Therefore, the

No other products such as pentan-1-ol, hexan-1-ol, or 3,5-dimethylphenol were observed. It is worth pointing out that phenol was not formed in the thermal decomposition in benzene.

Decomposition of t-Butyl Hydroperoxide.—As a model tertiary aliphatic hydroperoxide, t-butyl hydroperoxide was decomposed in several solvents at 100 °C in the presence of boric acid anhydride. The results are summarized in Table 2. As observed with 1-methylheptyl hydroperoxide,

TABLE 2

Decomposition of t-butyl hydroperoxide (0.050M) by boric acid anhydride under vacuum at 100 °C for 2 h

[B ₂ O ₃]/M	Solvent	Conversion (%)	t-Butyl alcohol	10 ³ [Product]/M (%) ^a			From solvent	
				Isobutene	Acetone	Methanol	s-Hexanol ^b	
0.25	n-Hexane	43.5	1 (5)	3 (11)	Trace	1.2 (5)	s-Hexanol ^b	0.9 (4)
0.25	Benzene	78.8	0 (0)	4 (9)	1.6 (4)	8 (21)	Phenol	4 (11)
0.25	Mesitylene	72.6	1 (3)	12 (33)	1 (3)	2 (6)	Mesitol	40 (108)
0	Benzene	0	0	0	0	0		
0 ^c	Benzene	11.6	5 (89)	0.4 (7)	3 (58)	0.2 (3)	Phenol	0 (0)

^a Numbers in parentheses are percentages based on hydroperoxide decomposed. ^b Total hexan-2- and -3-ol. ^c At 150 °C.

contribution of thermal decomposition can be assumed to be quite small at 100 °C. The aromatic solvents yielded higher conversions. The major decomposition product

* The polymerization of isobutene was confirmed by the following independent experiments. When t-butyl alcohol was heated in the presence of boric acid anhydride, a decrease in t-butyl alcohol and formation of isobutene were observed and isobutene then decreased at higher conversions. In addition, when isobutene was treated with boric acid anhydride, the formation of 2,4,4-trimethylpent-1-ene and -2-ene was observed, which then decreased with time. These results and our previous work¹⁰ on the decomposition of t-butyl hydroperoxide under vacuum indicate that isobutene formed by the dehydration of t-butyl alcohol polymerizes in the presence of boric acid anhydride.

boric acid anhydride accelerated the decomposition of t-butyl hydroperoxide and the thermal decomposition was negligibly small at 100 °C. As observed previously,¹⁰ the major product from t-butyl hydroperoxide was isobutene formed by the dehydration of t-butyl alcohol. In contrast to 1-methylheptyl hydroperoxide, the formation of acetone and methanol suggest that acid-catalysed rearrangement of t-butyl hydroperoxide also took place. Much of the missing product from t-butyl hydroperoxide is probably a polymer formed from isobutene.*

¹⁰ H. Sakaguchi, E. Niki, and Y. Kamiya, *Nippon Kagaku Kaishi*, 1975, 596.

The product distribution in the decomposition of *t*-butyl hydroperoxide was considerably different from that of 1-methylheptyl hydroperoxide. However, the solvent was similarly hydroxylated in the presence of boric acid anhydride. This implies that much of the primary product from *t*-butyl hydroperoxide is *t*-butyl alcohol and that the decomposition of *t*-butyl hydroperoxide to *t*-butyl alcohol and the hydroxylation of the solvent proceed simultaneously by a concerted mechanism.

Since the observed selectivity for *s*-hexanol was quite low, product (3 ml) was stirred with water (0.5 ml) at room temperature for several hours. The amount of *s*-hexanol

corresponding alcohol, the solvent is hydroxylated at the same time.†

Contribution from an Oxygen Atom.—Broich and Grasmann² first proposed the formation of an active oxygen atom in the boric acid catalysed decomposition of hydroperoxide and they suggested that this atomic oxygen was responsible for hydroxylation of the solvent. An oxygen atom which may give alcohol selectively is the singlet O(¹D). However, the formation of O(¹D) is not probable at 100 °C in solution and moreover it has been reported¹¹ that O(¹D) attacks the carbon-hydrogen

TABLE 3

Decomposition of cumyl hydroperoxide (0.050M) by boric acid anhydride under vacuum at 100 °C for 2 h

[B ₂ O ₃]/M	Solvent	Conversion (%)	10 ³ [Product]/M (%) ^a				From solvent	
			Cumyl alcohol	Aceto-phenone	Phenol	Acetone	<i>s</i> -Hexanol	
0.25	<i>n</i> -Hexane	100	0.2 (0.5)	0(0)	14 (28)	41 (83)	<i>s</i> -Hexanol	0 (0)
0.25	Benzene	99.8	0 (0)	0.7 (1.3)	38 (73)	54 (105)		
0.25	Mesitylene	99.7	0 (0)	0 (0)	44 (87)	44 (89)	Mesitol	0 (0)
0	Benzene	4.5	0 (0)	0 (0)	0 (0)	0 (0)		
0 ^b	Benzene	46.7	7 (29)	7 (29)	3 (12)	5 (19)		

^a Numbers in parentheses are percentages based on hydroperoxide decomposed. ^b At 150 °C.

increased about two-fold. Therefore, considerable amounts of alcohol must have been present as boric ester which could not be analysed by g.l.c. No other product from solvent was observed and the formation of phenol was not observed at all during thermal decomposition without boric acid anhydride.

Decomposition of Cumyl Hydroperoxide.—The results of decomposition of cumyl hydroperoxide, a model for aromatic hydroperoxides, are shown in Table 3. Like 1-methylheptyl and *t*-butyl hydroperoxides, the rate of thermal decomposition of cumyl hydroperoxide was quite slow, whereas it decomposed almost completely in 2 h in the presence of boric acid anhydride. A little cumyl alcohol was observed among the products, and phenol and acetone were formed exclusively in every solvent studied, which indicates that acid-catalysed decomposition proceeded predominantly.⁸ This is because of the high acidity of boric acid anhydride as a Lewis acid⁸ and also because of the ready migration of a phenyl group.^{5,8}

A more interesting feature of Table 3 is that the solvent was not hydroxylated at all. The phenol observed in the decomposition of cumyl hydroperoxide in benzene with boric acid anhydride must arise from the hydroperoxide and not from benzene since acetone was formed almost quantitatively and since mesitol was not formed at all from mesitylene.

DISCUSSION

Although the material balance was not always satisfactory, the results show convincingly that, when hydroperoxide is decomposed by boric acid anhydride to the

bond of aliphatic hydrocarbons statistically to give alcohol regardless of primary, secondary, or tertiary hydrogen. Since only secondary alcohols were formed from both *n*-pentane and *n*-hexane in this study, the contribution of O(¹D) must be negligible.

The reactions of the triplet oxygen atom O(³P) with hydrocarbons have been studied by many workers and it was reported that phenol was formed from aromatic hydrocarbons.¹² On the other hand, O(³P) is reported to abstract hydrogen exclusively and give aldehyde or oxygenated products with a smaller carbon number.¹³ Therefore it can be concluded that O(³P) is not responsible for the hydroxylation of the solvent.

Contribution from a Radical Process.—A contribution from a radical process has been proposed¹⁴ where alkoxy and/or peroxy radicals are presumed to be the chain carrier. However, the major reaction of mesitylene with these radicals must be hydrogen atom abstraction from benzylic hydrogen instead of homolytic aromatic substitution and the high yield of mesitol (Tables 1 and 2) cannot be explained by a radical process. More convincing evidence for the incompatibility of the radical process may be the results of thermal decomposition of hydroperoxide where the reaction undoubtedly proceeds by a radical process. As shown in Tables 1–3, no phenol was observed at both 100 and 150 °C in the uncatalysed thermal decomposition of 1-methylheptyl,

¹¹ R. J. Cvetanovic, *J. Chem. Phys.*, 1964, **41**, 3703; 1969, **50**, 590; 1970, **52**, 5821.

¹² E. Grovenstein, jun., and A. J. Mosher, *J. Amer. Chem. Soc.*, 1970, **92**, 3810.

¹³ J. T. Herron and R. E. Huie, *J. Phys. Chem.*, 1969, **73**, 3327.

¹⁴ L. Lena and J. Metzger, *Kinetika i Kataliz*, 1973, **14**, 136.

† Note added in proof: Wolf, Mckeeon, and Cannell have recently published work on the mechanisms of borate ester induced decomposition of alkyl hydroperoxides (*J. Org. Chem.*, 1975, **40**, 1875). The conclusions of this work are at variance with our own.

t-butyl, and cumyl hydroperoxides in benzene.* This excludes a contribution from a radical process for the hydroxylation of solvent in the decomposition of hydroperoxide by boric acid anhydride at 100 °C.†

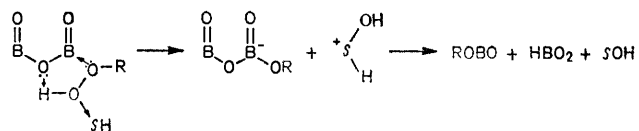
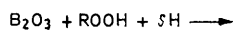
Possibility of Electrophilic Substitution.—The most probable reaction scheme must be an electrophilic substitution reaction where boron acts as electron acceptor and the hydroperoxide oxygen as electron donor. Interactions between the boron and oxygen of boric acid and hydroperoxide oxygen and hydrogen were suggested by Lena and Metzger¹⁴ from an n.m.r. study. Since the rate of decomposition is dependent on the nature of solvent, the solvent must contribute in the decomposition of hydroperoxide and the solvent must be hydroxylated simultaneously with the decomposition of hydroperoxide. It was observed previously by Takamitsu and Hamamoto⁴ that the rate of decomposition of cyclohexyl hydroperoxide by metaboric acid was faster in toluene and ethylbenzene than in dodecane by a factor of 7–8. Electrophilic attack by OH⁺ or O⁺ formed in the decomposition of peroxide by Lewis acid is known for several cases such as epoxidation⁵ and phenol formation.^{5,17,18} In the boric acid catalysed decomposition of hydroperoxide, a stable boric ester is

* Hiatt and Irwin¹⁵ observed the formation of cyclohexanol in the thermal decomposition of t-butyl hydroperoxide in cyclohexane, whereas no phenol was observed in benzene.

† As a referee has pointed out, under free radical conditions considerably higher yields of *ortho*-compounds are obtained than under electrophilic conditions.¹⁶ No information on the partial rate factors in this study can be obtained from either mesitylene or benzene. However, the absence of phenol in the thermal decomposition of hydroperoxide in benzene and also the absence of products derived from the 3,5-dimethylbenzyl radical must indicate that the contribution of free radical hydroxylation is very small.

formed instead of free alcohol and this may be an important driving force for the formation of an active electrophilic species such as hydroxonium ion.

This electrophilic substitution mechanism implies that there should be a 1:1 correspondence between the hydroxylated solvent and alcohol (and boric ester and olefin). However, the data in the Tables show that this is not the case. This must be ascribed mainly to difficulties in the analyses of the products, which probably arise largely because some of the alcohols and phenols are present as boric ester and some boric acid anhydride is precipitated from the reaction mixture. Still the results strongly suggest that the electrophilic substitution mechanism is a predominant reaction path in the



SCHEME

hydroxylation of solvent. The most probable mechanism is shown in the Scheme, where SH represents solvent.

[5/1385 Received, 14th July, 1975]

¹⁵ R. Hiatt and K. C. Irwin, *J. Org. Chem.*, 1968, **33**, 1436.

¹⁶ W. A. Pryor, 'Free Radicals,' McGraw-Hill, New York, 1966, ch. 16.

¹⁷ H. Hart, C. A. Buehler, and A. J. Waring, 'Selective Oxidation Processes, No. 51,' ed. R. F. Gould, Amer. Chem. Soc., Columbus, 1965, p. 1.

¹⁸ M. E. Kurz and G. J. Johnson, *J. Org. Chem.*, 1971, **36**, 3184.