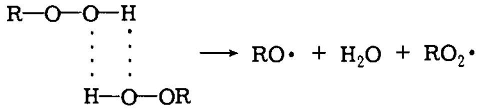
On "Bimolecular Initiation" by Hydroperoxides

R. Hiatt* and Thomas McCarrick

Contribution from the Department of Chemistry, Brock University, St. Catharines, Ontario, Canada. Received October 24, 1974

Abstract: 3-Hydroperoxy-2,3-dimethyl-1-butene has been thermally decomposed in toluene and other solvents. Free radical induced decompositions of this hydroperoxide have been studied using t-Bu_2O_2, Ac_2O_2, and $Ph_3C\cdot$ dimer as radical sources. The hydroperoxide is far more susceptible to radical-induced decomposition than nonolefinic peroxides and by itself in solvents is mainly attacked by the peroxy radical adding to the carbon-carbon double bond. One result of this addition is a chain branching reaction having relatively low activation energy: $RO\cdot + R'O\cdot + \cdot OH$ from $RO_2\cdot + RO_2H$. Kinetic analysis shows that the chain branching step is very nearly second order in RO_2H concentration. This is probably the true mode of initiation in autoxidizing olefins rather than bimolecular initiation by hydroperoxides.

Bimolecular initiation enjoys a well-entrenched position in the lore of hydroperoxide chemistry,[1] mainly due, no doubt, to the classic kinetic studies of Bateman and Hughes[2] but bolstered by unambiguous evidence that hydroperoxides do tend to dimerize in nonpolar solvents,[3] and that the rate of free radical production in autoxidizing olefins greatly exceeds[1a,b] that ascribable to unimolecular homolysis of a hydroperoxide.[4,5] Moreover the presumed bimolecular reaction



$$\begin{matrix} R{-}O{-}O{-}H \\ \vdots \quad \vdots \\ H{-}O{-}OR \end{matrix} \longrightarrow RO\cdot + H_2O + RO_2\cdot \qquad (1)$$

is thermochemically attractive, being less endothermic than the unimolecular homolysis

$$RO_2H \longrightarrow RO\cdot + \cdot OH \qquad (2)$$

However it has always seemed odd to us that the well-documented cases of bimolecular reaction are limited to the initiation of olefin autoxidation or the thermal decompositions of allylic hydroperoxide products of those autoxidations. For the sceptic, some aspects of the bimolecular situation are easily rationalized; kinetic order and accelerated loss of RO_2H can be ascribed to radical-induced decomposition. The rapid rate of radical production has remained, however, as a serious hurdle.

With no great hope of resolving this problem, we thought it still worthwhile to apply the brute force of modern analytical techniques, GLC and GLC-MS, to a determination of what actually goes on when an allylic hydroperoxide decomposes. An exercise required an allylic hydroperoxide which could be prepared in a reasonable state of purity and which might give a tractible product mixture (cyclohexenyl hydroperoxide, for example, fulfills neither of these requirements[1b,6]). The hydroperoxide obtained from singlet O_2 attack on tetramethylethylene,[7,8] 3-hydroperoxy-2,3-dimethyl-1-butene, hereafter referred to as TMEH as an abbreviation of "tetramethylethylene hydroperoxide", seemed to fit the particulars.

Since TMEH is a tertiary hydroperoxide and a close analog to t-BuO_2H, we rather expected that it would be equally well behaved. The intimate nature of its ill manners has proved so complex as to make a definitive analysis of dubious value. What has clearly emerged is an alternative to bimolecular initiation that is rather compelling.

Experimental Section

Materials. TMEH was prepared by the irradiation of an oxygenated solution of tetramethylethylene and Rose Bengal in methanol after the procedure of Schenck and Schulte-Elte.[7] Products from several runs were combined and fractionally distilled to give hydroperoxide of better than 98% purity by iodometric titration.

t-Bu_2O_2 and Ac_2O_2 were used as obtained from Lucidol Division, Pennwalt Corp., the latter as a 25% solution in dimethyl phthalate.

Triphenylmethyl dimer was obtained by the action of silver metal on Ph_3CCl in benzene.[9] The solution was filtered and used as such.

2,3-Dimethyl-2,3-epoxypentane was prepared by m-chloroperbenzoic acid epoxidation of the olefin.

Analyses were carried out by GLC, employing a Varian Aerograph 1200 flame ionization instrument for liquid samples and an F & M Model 700 (thermal conductivity) for gases. For monitoring TMEH concentration, the column used was 6 ft × $\frac{1}{8}$ in. Pyrex, packed with 5% SE-30 on Chromosorb WAW. At 80° and a flow rate of 30 ml/min, retention time was 230 sec.

GLC-mass spectrograph analyses utilized an AEI MS-30 double-beam, double-focusing instrument.

Rate Measurements. Samples were degassed and sealed in Pyrex ampoules and heated for an appropriate length of time in a constant-temperature bath. Eight samples were used for each run, and the contents of each ampoule was analyzed in triplicate by GLC.

Results and Discussion

Products. TMEH was thermally decomposed in a variety of solvents including toluene, benzene, hexadecane, and Nujol. The products (Table I) are remarkable both in the material not accounted for and in the nondependence on solvent of methane and 2,3-dimethyl-3-buten-1-ol (TMEA) yields. Products from decomposition in toluene are more conspicuous by absences; not present in identifiable amounts were: xylenes, $PhCH_2OH$, $PhCHO$, $PhCO_2H$, and $(PhCH_2)_2$. Clearly under these conditions, benzyl radicals, if produced, are not dimerized or oxidized. Analysis of the mixture by GLC-MS indicated the presence of small amounts of product having the benzyl fragment in a somewhat larger molecule, but the separation could not be refined sufficiently to permit analysis of individual components.

Production of TMEA implicates $CH_2{=}CMeCMe_2O\cdot$ as an intermediate, with methane resulting from β-scission of a methyl radical. The ketone resulting from this scission was not found, but addition of $CH_2{=}CMe{-}CO{-}Me$ to the reaction mixture under thermolysis conditions showed that it was very rapidly consumed.

The hydroperoxide was exposed to free radicals under conditions where it was thermally stable; $Ph_3C\cdot$ at 29° in benzene gave a 40% yield of Ph_3COH and no Ph_3CH. The preference for a SH2 reaction under these conditions is interesting but not particularly informative.[10]

Acetyl peroxide at 90° in benzene produced a 10% yield

---

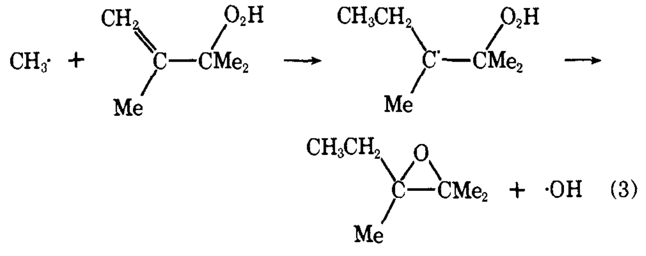
* Author to whom correspondence should be addressed.

Table I. Products from the Decomposition of TMEH

	Mol/mol of RO_2H decomposed				
Conditions	ROH[a]	CH_4	CO	Ph_3COH	Epoxide[b]
Thermolysis[c]	0.24	0.16	0.02		
$Ph_3C\cdot$[d]				0.40	
Ac_2O_2[e]		NA[g]			0.10[f]

[a] $CH_2{=}CMe{-}CMe_2OH$. [b] 1. [c] 0.2 *M* RO_2H in either benzene, toluene, *m*-xylene, hexadecane, or mineral oil at 150° for 6 half-lives. [d] 0.1 *M* RO_2H, 0.025 *M* $[Ph_3C]_2$ in benzene, 5 hr at 25°. [e] 0.1 *M* RO_2H, 0.01 *M* Ac_2O_2 in benzene at 90° for 30 hr. [f] Also 0.3–0.04 mol/mol of MeOH. [g] Not applicable.

of an expected product, the epoxide resulting from alkyl radical addition to the double bond.



1

It is tentatively assumed that the benzyl analog was one of the minor products from the thermal decomposition in toluene.

The presence of water in product mixtures resulting from thermolyses and from Ac_2O_2-induced decomposition was inferred from the opalescence of the product solution, but water content was not measured quantitatively.

Allylic rearrangement, shown by Brill[11] to be very facile for some hydroperoxides of this type, appeared not to be a problem either before or during decomposition:

$$CH_2{=}CMe{-}CMe_2O_2H \nleftrightarrow HO_2CH_2CMe{=}CMe_2 \qquad (4)$$

NMR spectra of the neat TMEH after standing at room temperature for several weeks showed no detectable primary hydroperoxide. Analyses of decomposition products revealed none of the primary alcohol nor any H_2 expected from primary hydroperoxide decomposition.[12]

Rate Studies. Thermal decompositions were conducted in three solvents, hexadecane, toluene, and Nujol, over the temperature range of 130–190° with initial concentrations of TMEH varied from 0.01 to 0.20 *M*. Kinetic analysis showed poor fits to either simple first or simple second order; plots for either mode were reasonably linear for the first 60–70% decomposition (correlation coefficients for least-squares plots = 0.98–0.99), but k_1's and k_2's so determined were dependent on $[TMEH]_0$.

Consequently computer analysis was used to fit the data to an expression

$$-d[RO_2H]/dt = k[RO_2H] + k'[RO_2H]^n \qquad (5)$$

where $0 < n < 3$. The results were not completely definitive, but best fits were obtained when $k \simeq 0$ and $1.3 < n < 1.7$. Since eq 5 where $n = 1.5$ is easily developed for a radical-induced decomposition[13] and has been frequently observed for this phenomenon,[5,14,15] the rate constants and activities parameters were calculated on this basis and are shown in Table II. The method does not give a value for *k*, of course, since the contribution from the first-order term was negligible.

The thermal decomposition thus appears to be very largely a radical-induced chain reaction. The complex rate constant k' (equals $k_2^{1/2}(k_1/k_3)$) is mildly affected by the solvent, but E_a''s and A''s (Table II) are all about the same. (Subscripted rate constants refer to ref 13.)

E_a' and A' can be estimated from known values for similar reactions. Assuming E_{a_1} = 44 kcal, log A_1 = 16.1,[5] E_{a_2} = 1.5 kcal, log A_2 = 8.0,[16] E_{a_3} = 0, log A_3 = 10,[17] then E_a' = 29.5 kcal and log A' = 11.0. The agreement with experimental values (Table II) is close enough to convince us that radical initiation in this system is via unimolecular homolysis of TMEH at a rate very similar to that found for *t*-BuO_2H.[5]

As a further test, a mixture of TMEH (0.10 *M*) and *t*-Bu_2O_2 (0.10 *M*) was decomposed at 150°. The hydroperoxide disappeared much faster than in the absence of *t*-Bu_2O_2, of course. Since the rate constant (k_d) for *t*-Bu_2O_2 homolysis at 150° is 100 to 1000 times greater than that for the hydroperoxide, we might write as a good approximation

$$-d[RO_2H]/dt = k''[t\text{-}Bu_2O_2]^{1/2}[RO_2H] \qquad (12)$$

where $k'' = k_2(k_d/k_3)^{1/2}$. Upon integration

$$\ln[RO_2H]_0/[RO_2H] = 2k''/k_d[t\text{-}Bu_2O_2]_0^{1/2}[1 - e^{-k_dt/2}] \qquad (13)$$

Taking $k_d = 2.29 \times 10^{-4}$ sec^{-1},[19] eq 13 gave a straight line with $k'' = 2.2 \times 10^{-3}$ $M^{-1/2}$ sec^{-1}. (The reaction was carried to 70% conversion and had chain lengths of five or greater.)

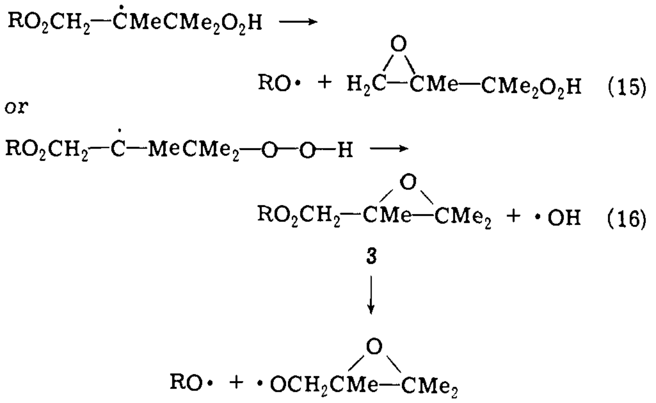
If the induced chain is not modified by the character of the initiating radical, as seems reasonable, $k'/k'' = (k_1/k_d)^{1/2}$. From the values of k' and k'', k_d appears to be only 65 times greater than k_1. This is somewhat less than we predicted, (i.e., 10^2 to 10^3), but the discrepancy may arise from the initial approximation that all initiation was due to *t*-Bu_2O_2[20] or it may be due to another factor with which we shall deal below.

Rates of Radical Production

An obvious clue to what is going on in the thermal decomposition of TMEH is the solvent-independent yield of ROH and CH_4. Both must arise from RO· (via hydrogen abstraction and scission, respectively), yet the source of RO· in these quantities cannot be unimolecular homolysis nor SH2 attach by solvent radicals. It must be

$$RO_2\cdot + CH_2{=}CMeCMe_2O_2H \longrightarrow RO_2CH_2{-}\dot{C}MeCMe_2O_2H \qquad (14)$$

followed by either



$$RO_2CH_2{-}\dot{C}MeCMe_2O_2H \longrightarrow RO\cdot + H_2C{-}CMe{-}CMe_2O_2H \qquad (15)$$

or

$$RO_2CH_2{-}\dot{C}{-}MeCMe_2{-}O{-}O{-}H \longrightarrow RO_2CH_2{-}CMe{-}CMe_2 + \cdot OH \qquad (16)$$

3

$$\downarrow$$

$$RO\cdot + \cdot OCH_2CMe{-}CMe_2$$

Clearly each RO· produced by these reactions renders another RO_2H incapable of producing RO·. Thus a 40% yield of ROH + CH_4 is equivalent to 80% of hydroperoxide destroyed, at very least (to the extent that some RO·'s and CH_3·'s will add to C=C rather than abstracting hydrogen, this is an underestimate), and these reactions must be the major route for hydroperoxide destruction.

Now reaction 15 is a straight one-radical-for-one-radical induced decomposition. It does not, of course, reduce the

Hiatt, McCarrick / On "Biomolecular Initiation" by Hydroperoxides

Table II. Rate Data for Thermal Decomposition of TMEH[18]

Solvent	T, °C	[TMEH], M	10^5k, $M^{-1/2}$ sec^{-1} [a]	r[b]	Log A	E_a
Hexadecane	130	0.01	6.80	0.993		
Hexadecane	130	0.10	6.06	0.983		
Hexadecane	150	0.01	37.6	0.990		
Hexadecane	150	0.10	27.7	0.991		
Hexadecane	170	0.01	178	0.991	12.06	30.0
Hexadecane	170	0.05	139	0.996		
Hexadecane	170	0.10	128	0.989		
Hexadecane	170	0.20	155	0.993		
Hexadecane	190	0.01	1010	0.983		
Hexadecane	190	0.10	753	0.988		
Nujol	150	0.10	94.9	0.985		
Nujol	170	0.10	329	0.991	12.25	29.7
Nujol	190	0.10	1900	0.987		
Toluene	150	0.04	10.6	0.998		
Toluene	170	0.04	47.5	0.994	11.26	29.5
Toluene	190	0.04	206	0.996		

[a] Calculated as $-d[RO_2H]/dt = k[RO_2H]^{3/2}$. [b] Correlation coefficient for least-squares slope of rate vs. $[RO_2H]^{3/2}$.

hydroperoxidic content but destroys a molecule of TMEH. Reaction 16 is more interesting since from one radical it produces *three*! This degenerative chain-branching process is no doubt responsible for the explosions we encountered in attempts to decompose TMEH in concentrations of 1 M or greater. More importantly it represents a source to the system of radicals produced by homolysis having activation energy no greater than 37.5 kcal.[4]

Kinetic analysis of this revised situation yields an algebraic expression too complicated to be useful if all possibilities are included. However, simplifying in what seems a reasonable way, the following set of equations obtain. (All RO·'s and ·OH are considered kinetically equivalent, as are all RO·'s. RO_2R = **3**.)

$$RO_2H \xrightarrow{k_a} RO\cdot + \cdot OH \tag{a}$$

$$RO\cdot + RO_2H \xrightarrow{k_b} RO_2\cdot + ROH \tag{b}$$

$$RO_2\cdot + RO_2H \xrightarrow{k_c} RO_2R + \cdot OH \tag{c}$$

$$RO_2R \xrightarrow{k_d} 2RO\cdot \tag{d}$$

$$2RO_2\cdot \xrightarrow{k_e} \text{termination} \tag{e}$$

Assuming steady states in RO·, RO_2·, and RO_2R, an expression for RO_2R concentration is obtained:

$$[RO_2R] = \frac{k_c^2k_d/k_e[RO_2H]^2 \pm \{k_c^4k_d^2/k_e^2[RO_2H]^4 + 4k_ak_c^2k_d^2/k_e[RO_2H]^3\}^{1/2}}{2k_4^2}$$

This rather pleasing result indicates that, to the extent that radical production results from the homolysis of RO_2R, its rate will be dependent on two terms, one second order in $[RO_2H]$ and one having an order of $[RO_2H]$ dependence between 1.5 and 2. It may be noted, parenthetically, that initiation of autoxidation is seldom experimentally dependent on the square of $[RO_2H]$; "2" is simply the closest integer to the decimal dependence observed.

These results may seem to obviate our earlier kinetic and thermochemical analyses of TMEH-induced decomposition, but we think not. Considering what the radical $RO_2CH_2\dot{C}MeCMe_2O_2H$ would be expected to do, biting back on the peroxy linkage yielding RO· is thermodynamically advantageous to the alternative of attacking the hydroperoxidic bond to give ·OH. Hence in TMEH decomposition, the sequence of reactions 14 and 15 probably prevails over sequence 14, 16. A small contribution from reaction 16 presumably accounts for the somewhat greater-than-expected rate of initiation found for TMEH initiated induced decomposition when t-Bu_2O_2 and TMEH initiated decompositions are compared.

In the presence of oxygen, the situation becomes quite different. $RO_2CH_2\dot{C}MeCMe_2O_2H$ adds O_2 to give $RO_2CH_2C(-O_2\cdot)Me\text{-}CMe_2O_2H$ which then abstracts a hydrogen from solvent (or hydroperoxide) to produce $RO_2CH_2C(-O_2H)Me\text{-}CMe_2O_2H$ (**2**). Thus the uninteresting sequence of reactions 14, 15 is eliminated from the competition. Transposition of **2** for **3** does no violence to the kinetic analysis.

To summarize, we suggest that the initiator in olefin autoxidation is not the allylic hydroperoxide but a peroxide produced in the course of induced decomposition of the hydroperoxide. It has been shown that the concentration of that peroxide is nearly second order in the concentration of the allylic hydroperoxide. Not all the questions are answered, of course. For instance, in an autoxidizing olefin, there are many more C=C—C's than C=C—CO_2H's. The species $RO_2C(—O_2H)—C—C$ might be considered the main initiator, but this would give a different kinetic result; RO_2H would appear to a fractionally less than first power.[21]

Likewise reducing the theoretical activation energy for radical production from 42-44 kcal/mol for a hydroperoxide to 37 kcal/mol for an alkyl peroxide does not go quite far enough to account for the rapid rate of radical formation observed in olefin autoxidation.

At least two directions for further work are obvious: the behavior of peroxy radicals toward allylic hydroperoxides in general needs to be tested, and tendencies for addition vs. H abstraction elucidated. Isolation of intermediates such as the postulated $RO_2CH_2C(-O_2H)MeCMe_2O_2H$ is feasible, and their properties should be determined.

While work is proceeding along these lines and others, it still seems worth while at this time to raise the question over "bimolecular initiation" and to argue the possibility of alternatives.

Acknowledgments. We gratefully acknowledge the financial support of the National Research Council of Canada which made this work possible, also the assistance of Mr. B. I. Shushan in performing some of the gas analyses, and the generous donation of acetyl peroxide by Lucidol Division, Pennwalt Corp.

Supplementary Material Available. The data for typical kinetic runs in hexadecane [TMEH] vs. time will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number JACS-75-5234.

References and Notes

(1) For reviews, see: (a) L. Riech and S. S. Stivala, "Autoxidation of Hydrocarbons and Polyolefins", Marcel Dekker, New York, N.Y., 1969; (b) R. Hiatt, "Organic Peroxides", Vol. II, D. Swern, Ed., Wiley, New York, N.Y., 1971, Chapter 1; (c) J. A. Howard, "Free Radicals", Vol. II, J. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 1.

(2) L. Bateman and H. Hughes, *J. Chem. Soc.*, 4594 (1952).

(3) C. Walling and L. Heaton, *J. Am. Chem. Soc.*, **87**, 48 (1965).

(4) S. W. Benson, *J. Chem. Phys.*, **40**, 1007 (1964).

(5) R. Hiatt and K. C. Irwin, *J. Org. Chem.*, **33**, 1436 (1968).

(6) R. Hiatt and L. Zikmund, unpublished work.

(7) G. O. Schenck and K. H. Schulte-Elte, *Justus Liebigs Ann. Chem.*, **618**, 185 (1958).

(8) C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *J. Am. Chem. Soc.*, **90**, 975 (1968).

(9) M. Gomberg and L. H. Cone, *Ber.*, **39**, 3286 (1906).

(10) The alternate route to Ph_3COH, via $Ph_3C\cdot + RO_2H \rightarrow Ph_3CH + RO_2\cdot$, $2RO_2\cdot \rightarrow O_2 + 2\ RO\cdot$, $Ph_3C\cdot + O_2 \rightarrow Ph_3COH$ is precluded not only by the absence of Ph_3CH, but by the tendency of $Ph_3CO\cdot$ to rearrange.

(11) W. F. Brill, *J. Am. Chem. Soc.*, **87**, 3286 (1965).

(12) L. J. Durham and H. S. Mosher, *J. Am. Chem. Soc.*, **84**, 2811 (1962), and references therein.

(13) In the simplified treatment

$$RO{-}OH \xrightarrow{k_1} RO\cdot + HO\cdot \tag{6}$$

$$RO\cdot\ (\text{or } HO\cdot) + SH \longrightarrow S\cdot + ROH\ (\text{or } H_2O) \tag{7}$$

where SH = solvent

$$S\cdot + RO_2H \xrightarrow{k_2} S'\cdot\ (\text{or } SH + RO_2\cdot) \tag{8}$$

where S′• in this case might be

$$S{-}CH_2{-}\dot{C}MeMe_2O_2H$$

$$RO_2\cdot + RO_2H \xrightarrow{k_2'} S''\cdot \tag{9}$$

where $S''\cdot = RO_2CH_2\dot{C}MeCMe_2O_2H$

$$S\cdot + S\cdot\ (\text{or } S'\cdot \text{ or } S''\cdot) \xrightarrow{k_3} \text{nonradical products} \tag{10}$$

If $k_2 \simeq k_2'$ and k_3 is about the same for all terminations, then steady state gives

$$-d[RO_2H]/dt = k_1[RO_2H] + k_2(k_1/k_3)^{1/2}[RO_2H]^{3/2} \tag{11}$$

(14) E. R. Bell, J. H. Raley, F. F. Rust, F. H. Seubold, and W. E. Vaughan, *Discuss. Faraday Soc.*, **10**, 246 (1951).

(15) G. H. Twigg, *Discuss. Faraday Soc.*, **15**, 240 (1953).

(16) J. A. Kerr and M. J. Parsonage, "Evaluated Rate Data on Gas Phase Addition Reactions", Chemical Rubber Publishing Co., Cleveland, Ohio, 1972, p 214.

(17) K. U. Ingold, "Free Radicals", Vol. I, J. Kochi, Ed., Wiley, New York, N.Y., 1973, Chapter 2.

(18) See paragraph concerning supplementary material at the end of this paper.

(19) L. Batt and S. W. Benson, *J. Chem. Phys.*, **36**, 895 (1962).

(20) Fortuitously the decrease in $[RO_2H]$ closely paralleled the decrease in $[t\text{-}Bu_2O_2]$ so that a 10% contribution of radicals from RO_2H would not have altered the fit to eq 13.

(21) In general, peroxy radicals prefer to abstract an allylic hydrogen from olefins rather than add to the double bond. However, 1,1-disubstituted olefins, and tetramethylethylene particularly, tend to be exceptional in this regard. Thus TMEH may be considered an unrepresentative hydroperoxide vastly different in behavior from, say, cyclohexenyl hydroperoxide. Our unpublished work with cyclohexenyl hydroperoxide indicates otherwise. The products are a very complex mixture, but there is ample evidence that *addition to*, not abstraction from, the hydroperoxide's allylic system predominates. A driving force for addition to allylic hydroperoxides, absent in the case of simple olefins, is the generation of a free valence on carbon next to oxygen. One has, in effect, the free radical analog to the Michael reaction. This hypothesis needs further testing, of course.

Oxidation of Thioureas in Protic Media. The Structures of Hector's, Dost's, and Hugershoff's Bases

C. Christophersen,*[1a] T. Øttersen,*[1b] K. Seff,[1c] and S. Treppendahl[1d]

Contribution from the H. C. Ørsted Institute and the Institute for Chemistry,
University of Copenhagen, DK-2100 Copenhagen, Denmark,
the Department of Pharmacy, University of Oslo, Oslo 3, Norway,
and the Department of Chemistry, University of Hawaii, Honolulu, Hawaii 96822.

Received September 3, 1974

Abstract: The products arising from oxidation of some *N*-alkyl-*N′*-arylthioureas are shown to be 2,4-dialkyl-3,5-bis(arylimino)-1,2,4-thiadiazolidines. In the case of 2,4-dimethyl-3,5-bis(phenylimino)-1,2,4-thiadiazolidine, a three-dimensional single-crystal X-ray structure determination has been carried out. The compound crystallizes in the orthorhombic space group *Pccn* with cell dimensions $a = 15.469\ (7)$, $b = 23.813\ (7)$, $c = 8.114$ Å (4). There are eight molecules per unit cell. The positional and anisotropic thermal parameters of the nonhydrogen atoms have been refined to a conventional *R* index of 4.8% for 1683 reflections. Acid-catalyzed rearrangements were found in two cases to lead to substituted 2-aminobenzothiazole derivatives, the structures of which were assigned partly on the basis of their ^{13}C NMR spectra. From these results, new and conclusive evidence has been brought into the 85 year long discussion of the structures of the so-called Hector's, Dost's, and Hugershoff's bases.

One of the most confusing oxidation reactions in organic chemistry is the oxidation of thioureas. Depending on the substitution pattern of the thiourea, the oxidizing agent, the polarity of the medium, and the conditions used, a variety of products have been isolated.[2] A few examples will suffice to show the complexity and versatility of the reaction which, under certain conditions, leads to ureas, formamidine disulfides, formamidinesulfinic acids, formamidinesulfonic acids, 1,2,4-thiadiazoles, and various benzothiazole derivatives.

Monoarylthioureas are known to give rise to heterocyclic compounds on oxidation under certain conditions. The structures of these compounds have been the subject of several reviews.[3-5] The compounds are usually named after their discoverer as "Hector's bases".[6] A variety of structures have been advanced, but the most favored representa-

Christophersen, Ottersen, et al. / Oxidation of Thioureas in Protic Media