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REACTIONS OF ATOMS AND FREE RADICALS IN SOLUTION. XXV. THE REACTIONS OF OLEFINS WITH MERCAPTANS IN THE PRESENCE OF OXYGEN[1]

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Mercaptan-induced polymerization and copolymerization reactions are intimately related to one type of olefin-mercaptan addition reaction, and may be interpreted or profitably studied only on the basis of a fundamental understanding thereof. Although such addition reactions may be classified into at least two basically different types, those relevant to the present discussion are free-radical chain reactions yielding products of anti-Markovnikov configuration (1, 2).

Chain reactions of the kind specified may be said to involve three essential steps. The first is the generation from the mercaptan (RSH), by any one of a variety of possible means, of mercaptyl (RS·) free radicals. An applicable method and the one most commonly employed, involves the attack of an oxidant (Ox) upon the mercaptan (Equation 1). The second step consists in the additive reaction of a mercaptyl free radical with an olefin molecule (Equation 2). The third step completes the addition through interaction of the derived free radical formed in the second step and a molecule of mercaptan, at the same time regenerating the chain-initiating mercaptyl free radical (Equation 3).

1. $RSH + Ox \rightarrow OxH + RS\cdot$
2. $R'CH{=}CH_2 + RS\cdot \rightarrow R'(RSCH_2)CH\cdot$
3. $R'(RSCH_2)CH\cdot + RSH \rightarrow R'CH_2CH_2SR + RS\cdot$

Concerning over-all mercaptan-styrene additions it has been established that the relative reaction rates follow the order: $ArylSH > HO_2CCH_2SH >> RCH_2SH > RR'CHSH > RR'R''CSH$, which is the same order observed for corresponding rates of mercaptan oxidation by a variety of oxidants (3).

Whereas type reactions 1 and 3 have much in common, in that both are essentially oxidation-reduction reactions, it may be reasonably inferred that when one is relatively rapid the other will be relatively rapid also, and that when one is relatively slow the other will likewise be relatively slow. Which of these, if either, is the rate-determining step for the over-all addition is impossible to decide upon the basis of available data.

Any *a priori* assumption as to a relationship between the relative rates of type reactions 1 and 2 is more difficult to justify. However, there is some reason to believe, either that type reaction 2 is in most cases sufficiently rapid that the

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actual over-all addition rate is determined by the rate of type reaction 1 and/or the rate of type reaction 3, or that there is a positive correlation between the relative rate of type reaction 2 on the one hand and the relative rates of type reactions 1 and 3 on the other. On the whole, the former assumption would appear the more plausible.

It is also a reasonable inference that, for a given mercaptan, the rate of addition will vary with the relative reactivity of the olefin (with respect to type reaction 2) as has been shown to be the case for olefin-trichloromethyl radical additions (4, 5).

In order that a mercaptan may be induced to serve as an olefin polymerization inductant, rather than as a simple addendum, it is essential so to adjust reaction conditions that the type reaction exemplified by equation 3 shall be as completely as possible superseded by the desired one of various possible potentially competitive chain-branching processes (Equation 4).

4. $R'(RSCH_2)CH\cdot + R'CH{=}CH_2 \rightarrow R'[R'(RSCH_2)CHCH_2]CH\cdot$

5. $R'[R'(RSCH_2)CHCH_2]CH\cdot + x[R'CH{=}CH_2]$
$\rightarrow R'(RSCH_2)CH[—CH_2CHR'—]_xCH_2CHR'\cdot$

6. $R'(RSCH_2)CH[—CH_2CHR'—]_xCH_2CHR'\cdot + XY$
$\rightarrow R'(RSCH_2)CH[—CH_2CHR'—]_xCH_2CHR'X + Y\cdot$

When, under otherwise suitable experimental conditions, the presence of an agent is recognized as inhibitory of the over-all polymerization process a logical approach to the elucidation of its mode of action consists in a study of its effects upon the individual processes exemplified by type reactions 1, 2, 3, 4, 5, and 6. Accordingly, a clue to the causes of oxygen inhibition of mercaptan-induced emulsion copolymerization was sought by the authors in the present study of the effect of oxygen on oxidant-initiated mercaptan-olefin additions.

When equimolecular quantities of styrene and propyl mercaptan (in heptane solution) are shaken at room temperature in an atmosphere of oxygen, very little, if any, of the usual free-radical addition product ($C_6H_5CH_2CH_2S$-*n*-C_3H_7) is formed. An amount of oxygen molecularly equivalent to the amount of mercaptan consumed is absorbed, and the major product formed (*ca.* 89%) gives an elementary analysis corresponding to a combination of one molecule each of styrene, propyl mercaptan, and oxygen. This product has been shown to be a mixture of the racemic forms of the hydroxylated sulfoxide, $C_6H_5CH(OH)CH_2S(\rightarrow O)$-*n*-$C_3H_7$. Analogous compounds are formed when other olefin-mercaptan mixtures are allowed to absorb oxygen.

It is noteworthy that the rate of oxygen absorption by an olefin-mercaptan mixture is much greater than the rate of oxygen absorption by either the corresponding olefin or the corresponding mercaptan alone. For a series of mixtures containing in common a given olefin the rate of oxygen absorption increases with the ease of oxidation of the mercaptan present (Table I). The fact that a mixture of propyl mercaptan with styrene absorbs oxygen much more rapidly than a similar mixture of the same mercaptan with 1-octene (see experimental part) suggests that, for a series of mixtures containing in common a given mercaptan, the rate of absorption varies directly with the relative reactivity of the olefin.

The general characteristics of these reactions, as well as the principal products formed, are consistent with a generalized reaction scheme in which oxygen operates both as a mercaptan oxidant and an addition-chain interrupter (see equations 7, 8, 9, and 10).

7. $RSH + O_2 \rightarrow RS\cdot + HO_2\cdot$

8. $HO_2\cdot + RSH \rightarrow RS\cdot + H_2O_2$

9. $RS\cdot + R'CH{=}CH_2 \rightarrow R'(RSCH_2)CH\cdot$

10. $R'(RSCH_2)CH\cdot + O_2 \rightarrow R'(RSCH_2)CHO_2\cdot$

TABLE I

Relative Rates of Oxygen Absorption by Styrene-Mercaptan Mixtures[a] in Heptane Solution

MERCAPTAN	TIME	MOLE-% O_2 ABSORBED
tert-Butyl	7 weeks	2
n-Propyl	14 hours	15
Anisyl	8 minutes	50

[a] Equimolar amounts (0.012 mole) of styrene and mercaptan in 10 ml. of solvent.

The exact mode of formation of the observed products is still a matter of speculation. Fairly credible possibilities which suggest themselves are:

11a. $R'(RSCH_2)CHO_2\cdot + RSH \rightarrow R'(RSCH_2)CHO_2H + RS\cdot$

12a. $R'(RSCH_2)CHO_2H \rightarrow R'CH(OH)CH_2S(\rightarrow O)R$

and/or

11b. $R'(RSCH_2)CHO_2\cdot \rightarrow R'[RS(\rightarrow O)CH_2]CHO\cdot$

12b. $R'[RS(\rightarrow O)CH_2]CHO\cdot + RSH \rightarrow R'CH(OH)CH_2S(\rightarrow O)R + RS\cdot$

Because a mixture of styrene and *tert*-butyl mercaptan absorbs oxygen very slowly (2 mole-% in seven weeks), the preparation by this method of the corresponding hydroxylated sulfoxide is not practical. That the slowness of oxygen absorption by mixtures of olefin and a tertiary mercaptan is attributable primarily to the slow rate of type reaction 1 rather than to failure of type reaction 2 (which may, however, still be relatively slow)[2] is indicated by the formation of the desired adduct when a positive method of free radical initiation was invoked. Thus, the addition of a small quantity of α-cumyl hydroperoxide

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[2] It should be recognized that reactions of type 2 require an appreciable activation energy, and various observations suggest that the reaction velocity-temperature gradient may be rather steep. This might well account for the fact that mercaptan-induced copolymerizations that proceed satisfactorily at 50° are too slow for practical consideration at or near 0°.

and a ferrous salt to a mixture of styrene and *tert*-butyl mercaptan caused a rapid uptake of oxygen and formation of the corresponding hydroxylated sulfoxide. The function of the hydroperoxide and of the iron may be formulated as follows:

13. $C_6H_5(CH_3)_2COOH + Fe^{++} \rightarrow C_6H_5(CH_3)_2CO\cdot + FeOH^{++}$

14. $C_6H_5(CH_3)_2CO\cdot + tert\text{-}C_4H_9SH \rightarrow C_6H_5COCH_3 + tert\text{-}C_4H_9S\cdot + CH_4$

The reactions 9 to 12b then follow.

It is noteworthy that when styrene-mercaptan addition experiments are conducted in the absence of oxygen, even when equimolecular quantities of olefin and mercaptan are used, there is a considerable yield of product containing two molecules of hydrocarbon per molecule of mercaptan, together with a high-boiling residue with a hydrocarbon-mercaptan ratio greater than two to one.[3] These observations indicate that for the reactant pairs investigated type reaction 4, and even type reactions 5 and 6, are favored over type reaction 3. In heptane solution and in the presence of oxygen as the sole oxidant, neither the usual one-to-one styrene-mercaptan addition product nor any product containing more than one molecule of olefin per molecule is formed. It may therefore be inferred that type reaction 10 is favored over both type reactions 3 and 4. The nature of the role of oxygen as an inhibitor of mercaptan-induced polymerization and copolymerization thus becomes obvious.

EXPERIMENTAL

Reagents. Styrene (Dow) was freed of inhibitors by distillation at reduced pressure (15 mm.) immediately before use.

1-Octene (Humphrey, Wilkinson Co.) was distilled through an efficient column, and a fraction with physical properties in agreement with the best literature values (b.p. 121°, n_D^{20} 1.4088) was accepted. The material was redistilled from sodium immediately before use.

n-Heptane (Phillips pure grade) was distilled from sodium immediately before use.

n-Propyl mercaptan (Eastman white label) was distilled immediately before use, and fractions boiling at 67–68° were accepted.

tert-Butyl mercaptan (Eastman white label) was distilled immediately before use, and fractions boiling at 66–67° were accepted.

p-Anisyl mercaptan was prepared by the method of Suter and Hansen (6), and was distilled immediately before use (b.p. 69–70°/1.0 mm.).

All reagents were "peroxide-free" to the extent that they reacted negatively to the ferrothiocyanate test.

Absorption of oxygen by a heptane solution of styrene and n-propyl mercaptan. A heptane (100 ml.) solution of styrene (20.8 g., 0.2 mole) and *n*-propyl mercaptan (15.2 g., 0.2 mole) was shaken in an atmosphere of oxygen at room temperature. At 1.5 hours oxygen absorption amounted to 0.0089 mole; at 7.25 hours 0.0292 mole of oxygen had been absorbed, and crystals began to separate from the reaction mixture. The rate of oxygen absorption then underwent a slow progressive decrease and became negligible at 100 hours, at which time total absorption amounted to 0.157 mole.

The crystals which separated were washed several times with ligroin and dried. The filtrate contained 0.045 mole of *n*-propyl mercaptan, phenethyl *n*-propyl sulfide (0.001 mole), and propyl disulfide (0.002 mole).

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[3] Incidentally, the same statement is true of butadiene-mercaptan addition experiments.

Fractional crystallization of the crystalline precipitate (29.3 g.) from benzene (150 ml.) effected its separation into two fractions: fraction *A* (12.4 g., m.p. 105–107°), relatively insoluble in cold benzene, and fraction *B* (13.6 g., m.p. 64–70°), very soluble in cold benzene. Recrystallization of fraction *A* from benzene yielded 10.2 g. of material melting at 108–109°; further recrystallization did not affect the melting point. Recrystallization of fraction *B* from ether-ligroin raised the melting point to 68–70°; neither further recrystallization nor low-temperature sublimation affected the melting point.

Anal. Calc'd for $C_{11}H_{16}O_2S$: C, 62.2; H, 7.6; S, 15.1.
Found (Fraction *A*): C, 62.2; H, 7.6; S, 15.7.
Found (Fraction *B*): C, 62.1; H, 7.4; S, 15.3.

Reduction of 4.0 g. of product *A* with the aid of Raney nickel in aqueous alcohol (7) yielded a 1.7-g. (75%) mixture of acetophenone (29%), (identified by the melting point and mixture melting point, 240°, of its 2,4-dinitrophenylhydrazone) and α-phenylethanol (identified by the melting point and mixture melting point, 89–90°, of its carbanilic ester).

Oxidation of 1.17 g. (0.005 mole) of product *A* in 25 ml. of glacial acetic acid with aqueous potassium permanganate (0.6 g. of $KMnO_4$ in 20 ml. of H_2O) yielded the corresponding sulfone, m.p. 101–102°. The melting point of this material was not altered by admixture with either the analogous oxidate of product *B* or authentic specimens of *n*-propyl β-hydroxyphenethyl sulfone independently prepared in other ways.

Anal. Calc'd for $C_{11}H_{16}O_3S$: C, 57.9; H, 7.0.
Found: C, 57.7; H, 6.8.

Upon treatment with phenyl isocyanate the hydroxylated sulfone yielded a carbanilic ester melting at 116–117°, and otherwise identical with the analogous derivative of the oxidate of product *B* and of samples of independently synthesized sulfone.

Anal. Calc'd for $C_{18}H_{21}NO_4S$: N, 4.0. Found: N, 4.3.

Like independently synthesized specimens of the high-melting raceme of *n*-propyl β-hydroxyphenethyl sulfoxide, product *A* was soluble in water, acetic acid, and ethanol, and relatively insoluble in benzene, ligroin, heptane, and carbon tetrachloride. Its melting point (108–109°) underwent no depression upon admixture of the material with specimens of the high-melting raceme of *n*-propyl β-hydroxyphenethyl sulfoxide independently synthesized as hereinafter described.

Identification of product B [low-melting raceme of $C_6H_5CH(OH)CH_2S(\rightarrow O)n\text{-}C_3H_7$*].* Reduction of 4 g. of product *B* with the aid of Raney nickel in aqueous alcohol (7) yielded a 1.2-g (53%) mixture of acetophenone (identified by the melting point and mixture melting point, 240°, of its 2,4-dinitrophenylhydrazone) and α-phenylethanol (identified by the melting point and mixture melting point, 89–90°, of its carbanilic ester).

Oxidation of 0.42 g. of product *B* in 2 ml. of acetone with 0.3 ml. of 30% hydrogen peroxide yielded the corresponding sulfone which, upon crystallization from benzene, melted at 101–102°. The melting point of this material was not altered by admixture with either the analogous oxidant of product *A* or authentic specimens of *n*-propyl β-hydroxyphenethyl sulfone independently prepared in other ways.

Like independently synthesized specimens of the low-melting raceme of *n*-propyl β-hydroxyphenethyl sulfoxide, product *B* was relatively soluble in benzene. Its melting point (68–70°) underwent no depression upon admixture of the material with independently synthesized specimens of the low-melting raceme of *n*-propyl β-hydroxyphenethyl sulfoxide.

It is of interest to note that the molecular weight of the low-melting form (68–70°) of the racemate of β-hydroxyphenethyl sulfoxide in benzene is 425. The calculated molecular weight is 212.

Synthesis of the high- and low-melting racemes of n-propyl β-hydroxyphenethyl sulfoxide [$C_6H_5CH(OH)CH_2S(\rightarrow O)\text{-}n\text{-}C_3H_7$]. β-Hydroxyphenethyl bromide (0.05 mole), prepared by the method of Read and Reid (8), was converted to the *n*-propyl thio ether [$C_6H_5CH(OH)CH_2S\text{-}n\text{-}C_3H_7$] (b.p. 117–118°/1 mm.) by warming at 60° for one hour with the sodium salt of *n*-propyl mercaptan (0.05 mole) in absolute alcohol. The sulfide (0.5 g.) was oxidized to the corresponding sulfoxide in glacial acetic acid (10 ml.) by treatment at room temperature with an equimolecular quantity of 30% hydrogen peroxide. Removal of the solvent and crystallization of the residue from benzene yielded the high-melting raceme of *n*-propyl β-hydroxyphenethyl sulfoxide, m.p. 107.5–108.5°. This material, when mixed with product *A*, previously described, melted at 108.5°. Upon evaporation of the benzene mother-liquor a solid melting at 64–70° was obtained. This was the crude low-melting raceme of *n*-propyl β-hydroxyphenethyl sulfoxide, which, upon crystallization from ether-ligroin, melted at 68–70°, and upon admixture did not depress the melting point of product *B*, previously described.

Synthesis of DL-*n-propyl β-hydroxyphenethyl sulfone.* Oxidation of the high-melting raceme of *n*-propyl β-hydroxyphenethyl sulfoxide (0.98 g.) with aqueous potassium permanganate (1.4 g. of $KMnO_4$ in 45 ml. of H_2O) yielded the corresponding sulfone, m.p. 101°. Admixture of this material with the analogous oxidates of the low-melting raceme of *n*-propyl β-hydroxyphenethyl sulfone or of products *A* or *B*, previously described, did not depress the melting point.

Absorption of oxygen by a styrene-n-propyl mercaptan mixture in the absence of solvent. A mixture of styrene (10.4 g., 0.1 mole) and *n*-propyl mercaptan (7.6 g., 0.1 mole) was shaken in an atmosphere of oxygen at room temperature. After 40 hours 0.062 mole of oxygen had been absorbed, and crystals began to separate from the reaction mixture. The rate of oxygen absorption gradually decreased up to 64 hours at which time it approximated zero at a total oxygen uptake of 0.064 mole. The resultant crystal mush was thinned with ligroin; the crystals were separated and thoroughly washed with ligroin. The ligroin washings gave a strong positive peroxide test with ferrothiocyanate reagent. By titration of an aliquot portion of combined washings and filtrate it was established that 0.094 mole (94%) of mercaptan had been consumed.

The excess of mercaptan consumed over oxygen absorbed is readily understood in view of the products formed and the conditions of the experiment.

The products isolated were a mixture of the racemic forms of *n*-propyl β-hydroxyphenethyl sulfoxide (12 g., 60% on the basis of mercaptan consumed, 88% on the basis of oxygen absorbed) and a yellow liquid (4.3 g.) which contained *n*-propyl phenethyl sulfide. The latter was identified by oxidation to the corresponding sulfone (m.p. 50–52°.)

Absorption of oxygen by a styrene-n-propyl mercaptan aqueous emulsion. Styrene (10.4 g., 0.1 mole) and *n*-propyl mercaptan (7.6 g., 0.1 mole) were added to 200 ml. of redistilled water in which 0.8 g. of potassium laurate had been dispersed, and the resultant mixture was shaken in an atmosphere of oxygen at room temperature. When all the mercaptan charged had been consumed a total of 0.0515 mole of oxygen had been absorbed at an average rate of 35 ml. per hour. Soap was precipitated by the addition of calcium chloride (0.3 g.), and the reaction mixture was extracted with ether. From the 15 g. of residue remaining after removal of ether from the dried extract were isolated: 2.5 g. (0.017 mole) of *n*-propyl disulfide, 2.86 g. (0.0135 mole) of racemic *n*-propyl β-hydroxyphenethyl sulfoxides, and 2.5 g. (0.013 mole) of *n*-propyl β-hydroxyphenethyl sulfide. From the aqueous extract was obtained, after removal of the water at reduced pressure, an additional portion (1.08 g., 0.0051 mole) of the racemes of *n*-propyl-β-hydroxyphenethyl sulfoxide. The disulfide and the sulfide are attributed to the reactions:

15. $2\ n\text{-}C_3H_7S\cdot \rightarrow (n\text{-}C_3H_7S\text{—})_2$

16. $(n\text{-}C_3H_7S\text{-})_2 + C_6H_5(n\text{-}C_3H_7SCH_2)CHO_2H \rightarrow n\text{-}C_3H_7S(\rightarrow O)S\text{-}n\text{-}C_3H_7 + C_6H_5CH(OH)CH_2S\text{-}n\text{-}C_3H_7$

Absorption of oxygen by a heptane solution of 1-octene and n-propyl mercaptan. A solution of 1-octene (5.6 g., 0.05 mole) and *n*-propyl mercaptan (3.8 g., 0.05 mole) in heptane (25 ml.) was shaken in an atmosphere of oxygen. Oxygen absorption was negligible during the first 24 hours and slow thereafter. At 50.5 hours, when 0.0045 mole of oxygen had been absorbed, crystals began to separate from the reaction mixture. At 263 hours 0.038 mole of mercaptan had been consumed and 0.0218 mole of oxygen had been absorbed.

The precipitated crystals were recrystallized from benzene; m.p 106.0–106.5° (1.1 g.). Admixture of this material with specimens of *n*-propyl β-hydroxy-*n*-octyl sulfoxide, independently prepared as herein after described, did not depress the melting point.

Anal. Calc'd for $C_{11}H_{24}O_2S$: C, 60.0; H, 10.9.

Found: C, 60.0; H, 11.1.

Oxidation of the *n*-propyl β-hydroxy-*n*-octyl sulfoxide with hydrogen peroxide in acetic acid resulted in the formation of the corresponding sulfone, m.p. 60–62°.

The filtrate remaining after removal of the hydroxylated sulfoxide was freed of heptane under reduced pressure. Further distillation yielded the following fractions: (a) 40–80°/0.04 mm., 1.0 g.; (b) 85–100°/0.04 mm., 0.2 g.; (c) residue, which crystallized, m.p. 38–40°, 1.23 g.

Fraction c, after recrystallization from benzene-ligroin, melted at 40°. This material is presumably the low-melting raceme of *n*-propyl β-hydroxy-*n*-octyl sulfoxide.

Anal. Calc'd for $C_{11}H_{24}O_2S$: C, 60.0; H, 10.9.

Found: C, 59.9; H, 10.6.

The material, m.p. 40°, when treated with hydrogen peroxide in acetic acid, was converted to the corresponding sulfone, which, after crystallization from a mixture of benzene and petroleum ether, melted at 57–58°; mixture with sulfone from high-melting raceme, m.p. 58–60°.

Fraction a on redistillation (0.85 g.) was separated into the following cuts: (*a*) 45–47°/0.03 mm., 0.4 g.; (*b*) 67–70°/0.03 mm., 0.39 g. Cut *a* was treated with 30% hydrogen peroxide in acetic acid, yielding *n*-propyl-*n*-octyl sulfone (m.p. and mixture m.p. 57°). Cut *b* on treatment with 30% hydrogen peroxide in acetic acid yielded the hydroxylated sulfone, $n\text{-}C_6H_3CH(OH)CH_2SO_2\text{-}n\text{-}C_3H_7$, m.p. 59–61°, which when mixed with an independently prepared sample melted at 61–63°. Cut *a* is therefore *n*-propyl *n*-octyl sulfide and *b* is the hydroxylated sulfide, $n\text{-}C_6H_{13}CH(OH)CH_2S\text{-}n\text{-}C_3H_7$.

On the basis of mercaptan consumed (0.038 mole), therefore, the reaction of octene with *n*-propyl mercaptan yielded *ca.* 0.005 mole (13%) of the high-melting raceme of *n*-propyl β-hydroxy-*n*-octyl sulfoxide, *ca.* 0.0055 mole (14%) of the corresponding low-melting raceme, < 0.0021 mole (5.5%) of the usual olefin-mercaptan addition product, *n*-propyl *n*-octyl sulfide, and 0.0019 mole (5%) of hydroxylated sulfide.

Neither the total amount of oxygen absorbed nor the total amount of mercaptan consumed is accounted for in the products isolated. Competing reactions for oxygen in which octenyl hydroperoxide, $n\text{-}C_5H_{11}CH(OOH)CH{=}CH_2$, is formed, and/or conversion of mercaptan to disulfide may take place. Because the addition of mercaptyl radical to 1-octene is relatively slow the probability of such competing reactions is increased. The procedure used in working up the reaction mixture would not have detected the compounds suggested or their further reaction products. This study is being continued.

That the usual olefin-mercaptan addition product is here formed whereas none was detected as resulting from the analogous styrene reaction, may be attributed to the greater reactivity (with respect to type reaction 3) of the $n\text{-}C_6H_{13}(n\text{-}C_3H_7SCH_2)CH\cdot$ radical as compared to that of the $C_6H_5(n\text{-}C_3H_7SCH_2)CH\cdot$ radical.

Synthesis of n-propyl β-hydroxy-n-octyl sulfoxide. A. 1-Octene secondary bromohydrin (b.p. 60–62°/0.4 mm.), prepared by treatment of 1-octene with bromine in aqueous potassium bromide solution, was converted to the *n*-propyl thio ether by treatment with a slight excess of the sodium salt of *n*-propyl mercaptan in ethanol. To 2.5 g. of the resulting *n*-propyl β-hydroxy-*n*-octyl sulfide (b.p. 92–93°/0.25 mm.), dissolved in 1 ml. of glacial acetic acid, was added 0.13 ml. of 30% hydrogen peroxide in 5 ml. of water, and the reaction mixture was allowed to stand at room temperature for several hours. After removal of solvents under reduced pressure, the residue was thrice crystallized from benzene-ligroin solution, when it melted at 105–106°. Its melting point was not depressed by admixture with the high-melting product of the 1-octene-mercaptan-oxygen reaction.

B. The hydroxylated sulfide was also prepared by treatment of 1,2-epoxyoctane (b.p. 43°/10 mm.) with the sodium salt of *n*-propyl mercaptan. Hydrogen peroxide in acetic acid yielded the high-melting hydroxylated sulfoxide (m.p. 105–106°).

Absorption of oxygen by a heptane solution of styrene and p-anisyl mercaptan. A solution of 1.25 g. (0.012 mole) of styrene and 1.69 g. (0.012 mole) of *p*-anisyl mercaptan in 10 ml. of heptane was shaken in an atmosphere of oxygen. Oxygen absorption was rapid and exothermic, and the reaction mixture became turbid after 30 seconds. Absorption amounted to 0.003 mole in 2 minutes, 0.0062 mole in 8 minutes, and 0.0079 mole in 42 minutes, at which time shaking was discontinued. The reaction mixture separated into two layers; neither layer contained mercaptan. From the lower layer (2.8 g.) was obtained a white solid (0.66 g., after washing with ether and drying) which melted at 105–113°, and, after several crystallizations from benzene-ligroin, at 128–129°.

Anal. Calc'd for $C_{15}H_{16}O_3S$: C, 65.2; H, 5.8.

Found: C, 65.3; H, 5.9.

Presumably this is the hydroxylated sulfoxide, $C_6H_5CH(OH)CH_2S(\rightarrow O)C_6H_4$-*p*-$OCH_3$, corresponding to the identified *n*-propyl mercaptan product.

Removal of solvents from the combined filtrate and washings remaining from the crystal separation yielded a residual oil which was not further investigated. In view of the relatively low oxygen uptake (as compared with total mercaptan consumption) this oil probably contained, in addition to the low-melting hydroxylated sulfoxide, a substantial amount of the ordinary olefin-mercaptan addition product, *p*-$CH_3OC_6H_4SCH_2CH_2C_6H_5$.

When the reaction is carried out with higher heptane dilutions the rate of oxygen absorption is slower.

Oxygen absorption by a heptane solution of styrene and tert-butyl mercaptan. A solution of 4.3 g. (0.041 mole) of styrene and 3.7 g. (0.041 mole) of *tert*-butyl mercaptan in 20 ml. of heptane was shaken in an atmosphere of oxygen. Oxygen absorption was extremely slow. After seven weeks about 50 mg. of white needle-like crystals had separated from the reaction mixture. This material, after recrystallization from benzene-ligroin, melted at 135.5–136.5°.

Anal. Calc'd for $C_{12}H_{18}O_2S$: C, 63.7; H, 8.0.

Found: C, 63.5; H, 8.0.

Presumably the product isolated is the hydroxylated sulfoxide, $C_6H_5CH(OH)CH_2S(\rightarrow O)$-*tert*-$C_4H_9$, corresponding to the identified high-melting *n*-propyl mercaptan product. The filtrate from this reaction mixture was not further investigated.

Absorption of oxygen by styrene and tert-butyl mercaptan in the presence of α-cumyl hydroperoxide and catalytic quantities of ferrous ion. A mixture of 2.6 g. (0.025 mmole) of styrene, 2.25 g. (0.025 mole) of *tert*-butyl mercaptan, 0.036 g. (0.025 mole) of α-cumyl hydroperoxide, and 0.036 g. (0.013 mmole) of ferrous sulfate heptahydrate was shaken in an atmosphere of oxygen. After 51 hours 0.0184 mole of oxygen (73% on the basis of mercaptan consumed) had been absorbed.

The partially crystalline reaction mixture was treated with ligroin, which removed 1.6 g. of a total of 5.6 g. of material present. From the ligroin solution was obtained benzaldehyde (0.5 g.) and 0.5 g. of the ordinary olefin-mercaptan addition product, $C_6H_5CH_2CH_2S$-*tert*-C_4H_9, identified by the melting point and mixture melting point of the corresponding sulfone (108°). The small amount of higher-boiling residue was not further investigated.

From the solid product remaining after ligroin and ether washing two fractions were obtained by benzene crystallization: (*a*) m.p. 133–135°, 0.54 g.; (*b*) m.p. 92–101°, 0.2 g. Presumably these consisted substantially of the high- and low-melting racemes of the hydroxylated sulfoxide, $C_6H_5CH(OH)CH_2S(\rightarrow O)$-*tert*-$C_4H_9$, corresponding to the identified *n*-propyl mercaptan products.

The results of experiments of this kind indicate that the extreme slowness of oxygen absorption by styrene-*tert*-butyl mercaptan mixtures when oxygen is the sole mercaptan oxidant present is due primarily to the slow rate of type reaction 1 rather than to failure of type reaction 2 (which may, however, still be relatively slow.)

SUMMARY

In the presence of oxygen, olefins react with primary mercaptans to give a mixture of the two racemic forms of an hydroxylated sulfoxide [$RCHOHCH_2S(\rightarrow O)R'$]. *tert*-Mercaptans react with olefins and oxygen extremely slowly, but when a positive method of free radical initiation is invoked a rapid uptake of oxygen takes place and the hydroxylated sulfoxides are formed. A mechanism is suggested which accounts for the formation of these hydroxylated sulfoxides. This mechanism also accounts for the inhibitory effect of oxygen in copolymerization reactions which are initiated with the aid of a mercaptan and an oxidant.

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