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# The Autoxidation of $\alpha$-Methylstyrene in the Presence of Metal Salt[1]

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The azobisisobutyronitrile-initiated autoxidation of $\alpha$-methylstyrene in the presence of metal salt was studied from the viewpoints of rate and products. The over-all activation energy was found to be 19.7 kcal./mol. In most cases, metal salts had a retarding effect on the rate of oxidation. With manganese and copper salts, an increase in the concentration of the metal decreased the rate of oxidation monotonously. However, cobalt naphthenate had an accelerating effect within a limited range of concentration, although it also had an inhibiting effect at higher concentrations. The products were acetophenone, formaldehyde, $\alpha$-methylstyrene oxide and $\alpha$-methylstyrene polyperoxide. Metal salt had little effect on the products of oxidation, with the exception of cobalt salt, which gave $\alpha$-methylstyrene oxide in considerable yield even at 760 mmHg of oxygen pressure, where little $\alpha$-methylstyrene oxide was formed in the presence of other metal salts or in the absence of catalysts.

The initiated and metal-catalyzed oxidation of hydrocarbons has received considerable attention in recent years.[2] The functions of the metal salts in the autoxidizing systems are not yet, however, fully understood in detail. Most of the previous work on the metal-catalyzed autoxidation of unsaturated hydrocarbons has been concerned with compounds that have relatively unreactive double bonds. The metal-catalyzed oxidation of unsaturated compounds with reactive and polymerizable double bonds has received little attention. In view of these circumstances, it is a matter of theoretical as well as technological interest to study the autoxidation of olefins with reactive double bonds in the presence of the metal salts.

The purpose of this work is to study the azobisisobutyronitrile-initiated autoxidation of $\alpha$-methylstyrene in the presence of metal naphthenate from the viewpoints of rate and products.

Mayo, Miller and Russell[3] studied the oxidation of unsaturated compounds with reactive double bonds in the presence of azobisisobutyronitrile as a free radical initiator, although in the absence of metal catalysts. They showed that the autoxidation of $\alpha$-methylstyrene by a free radical mechanism gives two simultaneous reactions, a copolymerization of $\alpha$-methylstyrene with oxygen and a cleavage reaction to form acetophenone, formaldehyde and $\alpha$-methylstyrene oxide.

## Experimental

**Materials.**—$\alpha$-Methylstyrene was obtained from Allied Chemical; it was more than 99.8 mol.% pure. Prior to the experiment it was washed with alkali to remove the inhibitor, passed through activated alumina, and stored under nitrogen. Guaranteed reagent-grade azobisisobutyronitrile (hereafter designated as ABN) was stored in an ice box. Metal salt catalysts were obtained from the Dainippon Printing Ink Mfg. Co. and the Nihon Kagaku Sangyo Co. The metals used were cobalt, manganese, copper, lead, zinc, iron, and nickel (10.0, 8.2, 10.2, 30.3, 10.6, 10.0, and 8.0% respectively). The catalysts were used as metal naphthenates. The purity of the oxygen and the nitrogen was more than 99% (as determined by gas chromatography).

**Procedures.**—Two procedures were employed, one for measuring the oxidation rate of the monomer ($R_M$) and the rate of formation of the products, and the other for measuring the rate of oxygen absorption ($-dO_2/dt$). In the former procedure, a catalyst was dissolved in 65 ml. of $\alpha$-methylstyrene in advance; then this solution and ABN were added to a 300-ml., 4-necked flask equipped with ground glass joints. The mixture was stirred vigorously by a Teflon paddle using a magnetic stirrer. All of the reaction was performed under one atmosphere. The reaction gas was sometimes diluted with nitrogen to make a fixed-oxygen partial pressure and was fed in at the rate of 4 cc./sec. The exhaust gas was taken out through a reflux condenser and then a trap cooled by methanol and dry ice to $-50°C$. The reaction mixture was sampled periodically and analyzed. The rate of oxygen absorption was measured by a manometer in a constant-pressure closed system.

**Analyses.**—The oxidation rate of the monomer was measured by following the disappearance of the monomer by gas chromatography A (Apiezon-L column;

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1) Presented in part at 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965.

2) a) J. L. Bolland, *Quart. Revs.*, **3**, 1 (1949); b) L. Bateman, ibid., **8**, 147 (1954); c) H. S. Blanchard, *J. Am. Chem. Soc.*, **82**, 2014 (1960); d) Y. Kamiya and K. U. Ingold, *Can. J. Chem.*, **41**, 2020, 2034 (1963), **42**, 1027, 2424 (1964).

3) a) A. A. Miller and F. R. Mayo, *J. Am. Chem. Soc.*, **78**, 1017 (1956); b) G. A. Russell, ibid., **78**, 1035 (1956); c) F. R. Mayo, ibid., **80**, 2465 (1958); d) F. R. Mayo and A. A. Miller, ibid., **80**, 2480 (1958); e) F. R. Mayo, ibid., **80**, 2497 (1958); f) F. R. Mayo, A. A. Miller and G. A. Russell, ibid., **80**, 2500 (1958).

column temperature, 180°C; nitrogen carrier gas, 30 cc./min.). The oxidation products were analyzed by gas chromatography A, a study of the infrared spectra and by chemical analysis. The internal standard method was employed for the gas chromatographic analyses of the reaction mixture, using styrene as an internal standard. Infrared spectra analyses were made as well, because there was some possibility that peroxide decomposed in the gas chromatography to form the decomposition products. It was found, however, that the decomposition of peroxides in the gas chromatographic column was negligible. Acetophenone was sometimes determined gravimetrically with 2, 4-dinitrophenylhydrazine. In a few experiments, formaldehyde was measured as a dimethone derivative. However, its quantitative analysis was extremely difficult since most of the formaldehyde formed in the oxidation became attached to the wall as paraformaldehyde. Several iodometric methods were employed in an attempt to determine the peroxide, but no satisfactory procedure could be found. Carbon monoxide and carbon dioxide were measured by gas chromatography with a column of Molecular Sieve-13X and Acetonyl Acetone-S respectively. The formation of both gases was found to be negligible. The water content was measured by Karl Fisher titration; its formation was very small, below 0.1% of the products. Moreover, no other products could be detected either by gas chromatography or by a study of the infrared spectra. It was assumed, therefore, that formaldehyde was formed in an amount equivalent to acetophenone and that the only product other than acetophenone, formaldehyde and $\alpha$-methylstyrene oxide was $\alpha$-methylstyrene polyperoxide.

**The Preparation of $\alpha$-Methylstyrene Oxide.**—$\alpha$-Methylstyrene oxide was prepared as follows for use as the standard of the gas chromatographic analyses. A mixture of 102 g. of acetic anhydride and 2.4 g. of sulfuric acid was vigorously stirred into 57 g. of 30% hydrogen peroxide at room temperature and then reacted for an hour. Fifty grams of $\alpha$-methylstyrene was then dropped into the solution, with the temperature kept at 0°C, and stirred for two hours. After the reaction, *t*-butylcathecol, an inhibitor, was added, the reaction mixture was extracted with benzene, and acetic acid was removed by 5% sodium bicarbonate, washed with water and dehydrated. The products thus obtained were distilled in vacuo.

**The Preparation of $\alpha$-Methylstyrene Polyperoxide.**—The reaction was carried out like the other experiments. The final reaction mixture was poured into twice as much cold methanol to precipitate the methanol-insoluble polyperoxide. The polymer was then washed with methanol until it became stiff. It was dissolved in benzene, precipitated, and washed with methanol. This operation was repeated twice. Finally it was dried in vacuo to remove the methanol.

## Results and Discussion

The products of the oxidation of $\alpha$-methylstyrene are acetophenone, formaldehyde, $\alpha$-methylstyrene oxide and $\alpha$-methylstyrene polyperoxide. A typical example of the reaction of $\alpha$-methylstyrene with oxygen is shown in Fig. 1.

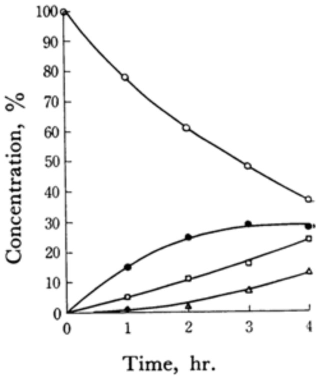

Fig. 1. Oxidation of $\alpha$-Methylstyrene at 70°C, ABN 0.030 mol./l., Co-N $3.4\times10^{-3}$ mol./mol. and oxygen pressure 760 mmHg.
○: $\alpha$-methylstyrene
●: $\alpha$-methylstyrene polyperoxide
□: acetophenone
△: $\alpha$-methylstyrene oxide

**The Effect of ABN on the Rate and Products of Oxidation.**—The rates of oxygen absorption at 0.003, 0.005 and 0.010 mol./l. of ABN were 0.29, 0.36 and 0.51 mol./l./hr. respectively, when $\alpha$-methylstyrene was oxidized at 70°C in the absence of the metal salt. These results show that the rate of oxidation is proportional to the square root of the ABN concentration. This suggests that, at a sufficiently high oxygen pressure, termination is a bimolecular reaction of two radicals. The reaction sequence must be as follows[2a,b]:

$$\mathrm{ABN} \xrightarrow{k_i} 2\mathrm{R}'\cdot \rightarrow 2e\mathrm{M}\cdot \qquad (1)$$

$$\mathrm{M}\cdot + \mathrm{O}_2 \rightarrow \mathrm{MOO}\cdot \qquad (2)$$

$$\mathrm{MOO}\cdot + \mathrm{M} \rightarrow \mathrm{M}\cdot \qquad (3)$$

$$2\mathrm{MOO}\cdot \rightarrow \text{non-radical products} \qquad (4)$$

where $\mathrm{R}'\cdot$ is the dimethylcyanomethyl radical, $e$ is the efficiency of ABN, and M is the $\alpha$-methylstyrene monomer. M· and MOO· represent free radicals of an unspecified length and ending in monomer and peroxide units respectively. In this paper, M· and MOO· correspond to $\sim\mathrm{CH_2C(CH_3)(C_6H_5)}\cdot$ and $\sim\mathrm{CH_2C(CH_3)(C_6H_5)OO}\cdot$. In fact, this mechanism is simplified; for example, the alkoxy radical MO·, i. e., $\sim\mathrm{CH_2C(CH_3)(C_6H_5)O}\cdot$, which may arise from the depolymerization of the polyperoxy radical, is left out of consideration, and also consumption of oxygen in reaction 1 is disregarded. Under steady state conditions, the rate of oxidation is given by Eq. 5;

$$-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t = \frac{k_3}{(2k_4)^{1/2}}[\mathrm{M}](R_i)^{1/2} \qquad (5)$$

where $R_i = 2ek_i[\mathrm{ABN}]$. The experimental data coincide with this rate equation provided $e$ is constant independent of the concentration of the initiator. It was also confirmed that the rate was first-order with respect to $\alpha$-methylstyrene

TABLE I. OXIDATION OF $\alpha$-METHYLSTYRENE AT 70°C, ABN 0.030 mol./l. AND OXYGEN PRESSURE 760 mmHg

| Catalyst | | Conv.[a] | Rate ($R_M$)[b] | Products Yields in mol. %[c] | | |
|---|---|---|---|---|---|---|
| | mol./mol. | % | mol./l./hr. | $AcC_6H_5$ | $C_9H_{10}O$ | $(C_9H_{10}O_2)_n$ |
| Ni-N[d] | $3.0\times10^{-4}$ | 65 | 1.93 | 52 | — | 48 |
| Zn-N | $3.0\times10^{-4}$ | 61 | 1.74 | 53 | — | 47 |
| Pb-N | $4.2\times10^{-4}$ | 60 | 1.69 | 53 | — | 47 |
| Fe-N | $3.1\times10^{-4}$ | 57 | 1.66 | 43 | — | 57 |
| Co-N | $3.4\times10^{-4}$ | 53 | 1.39 | 55 | 7 | 38 |
| Mn-N | $3.0\times10^{-4}$ | 38 | 0.89 | 26 | — | 74 |
| Cu-N | $3.2\times10^{-4}$ | 32 | 0.71 | 43 | — | 57 |
| None | — | 62 | 1.79 | 56 | — | 44 |

a) (Reacted $\alpha$-methylstyrene/initial $\alpha$-methylstyrene)$\times 10^2$ Reactions were carried out for 4 hr.
b) Observed rate of oxidation of monomer.
c) Based on $\alpha$-methylstyrene reacted.
d) N represents naphthenate.

(shown in Fig. 5).

Nitrogen evolution by the decomposition of the initiator must be taken into consideration in some cases. The fragments from ABN are assumed to either take up oxygen to produce the dimethylcyanomethyl peroxy radical or recombine in the "cage." The resulting peroxy radicals can initiate the chains. This situation is indicated by the following eqautions;

$$\text{ABN} \xrightarrow{k_i} 2\text{R}'\cdot + \text{N}_2 \qquad (1')$$

$$2\text{R}'\cdot \xrightarrow{\text{O}_2} 2e\text{R}'\text{OO}\cdot + (1-e)(\text{R}'-\text{R}') \qquad (1'')$$

$$2e\text{R}'\text{OO}\cdot \xrightarrow{\text{M}} 2e\text{M}\cdot \qquad (1''')$$

Hence, the net oxygen absorption by the monomer is given by the observed value plus $(1-e)k_i[\text{ABN}]$. However, the kinetic chains in this reaction are long enough so that the consumption of oxygen and the monomer, and the nitrogen evolution in reaction 1 may be disregarded. As a matter of fact, $(1-e)k_i[\text{ABN}]$ is equal to $1.5\times10^{-3}$ mol./l./hr. at 70°C and with 0.030 mol./l. of ABN, assuming $e$ to be 0.7. This value is less than 1% of the observed value.

As for the products, an increase in the concentration of ABN increases the cleavage products, acetophenone, formaldehyde and $\alpha$-methylstyrene oxide. These results may probably be attributed to the increase in the rate of termination.

**The Effect of Metal Salt on the Rate and Products of Oxidation.**—The rates and the products of the oxidation of $\alpha$-methylstyrene in the presence and in the absence of various metal salts are shown in Table I.

As Table I shows, manganese and copper salts retard the oxidation significantly. However, the activity of the catalyst cannot be compared directly in Table I, since it depends on the concentration of the catalyst. The effect of the concentration of the metal salts on the rate of oxidation is shown in Fig. 2. Manganese and copper naphthenates act as retarders independent of their concentrations, and an increase in the concentration of these salts decreases the rate of oxidation monotonously. The inhibiting effect of metal salt catalysts is observed in some cases at a high concentration of catalysts,[4] but it is seldom observed that manganese and copper salts show an inhibiting effect independent of their concentrations. The effect of the cobalt naphthenate catalyst differs from that of manganese and copper catalysts.

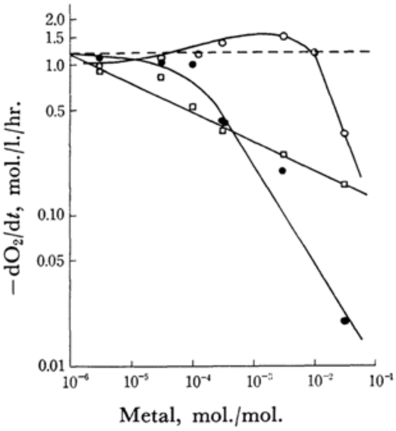

Fig. 2. Effect of the metal concentration on the rate of oxidation at 70°C, ABN 0.030 mol./l. and oxygen pressure 760 mmHg.
○: Co, ●: Mn, □: Cu
The broken line illustrates the rate of oxidation in the absence of metal catalysts.

The rate of oxidation increases gradually with an increase in the concentration of the cobalt salt catalyst, reaches a maximum at $3.4\times10^{-3}$ mol./mol. of cobalt naphthenate, and then falls rapidly with a further, small increase in the catalyst.

It is assumed that these inhibiting effects of

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[4] For example, N. Ohta, *J. Chem. Soc. Japan, Ind. Chem. Sect.* (*Kogyo Kagaku Zasshi*), **65**, 1353 (1962).

TABLE II. EFFECT OF TEMPERATURE ON RATE OF OXIDATION OF $\alpha$-METHYLSTYRENE WITH ABN 0.030 mol./l., Co-N $3.4\times10^{-3}$ mol./mol. AND OXYGEN PRESSURE 760 mmHg

| Expt. No. | Reaction temp., °C | $R_i$ 1) mol./l./hr. | Rate const. $\mathrm{sec}^{-1}$ | $R_M$ mol./l./hr. | Chain length 2) |
|---|---|---|---|---|---|
| 242 | 60 | 0.0018 | $3.20\times10^{-5}$ | 0.85 | 470 |
| 214 | 70 | 0.0070 | $7.00\times10^{-5}$ | 1.85 | 260 |
| 241 | 80 | 0.024 | $1.85\times10^{-4}$ | 4.90 | 200 |
| 228 | 90 | 0.068 | $3.56\times10^{-4}$ | 9.43 | 140 |

1) Rate of initiation. Calculated from Ref. 5. $R_i=2ek_i[\mathrm{ABN}]$ $e$ was assumed to be 0.7.
2) Chain length$=R_M/R_i$

the catalyst may be attributed to the direct termination and/or the deactivation of active radicals, for example, the transfer reaction between radicals and metal ions or the formation of an inactive complex, by the metal salt catalyst.

One of the authors previously proposed the following chain termination in the oxidation of tetralin2d);

$$\mathrm{ROO}\cdot + \mathrm{Me} \rightarrow \text{inactive products} \qquad (6)$$

or, alternatively:

$$\mathrm{ROO}\cdot + \mathrm{Me}^{2+} \rightarrow (\mathrm{ROO}\text{-}\mathrm{Me}^{3+}) \qquad (7)$$

$$(\mathrm{ROO}\text{-}\mathrm{Me}^{3+}) + \mathrm{ROO}\cdot \rightarrow \text{inactive products} \qquad (8)$$

If the chain termination is assumed to be reaction 6, or reactions 7 and 8 instead of reaction 4, they give the following rate equations:

$$-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t = \frac{k_3[\mathrm{M}](R_i)}{k_8[\mathrm{Me}]} \qquad (9)$$

or

$$-\mathrm{d}[\mathrm{O}_2]/\mathrm{d}t = \frac{k_3[\mathrm{M}](R_i)^{1/2}}{(2K_8k_9[\mathrm{Me}])^{1/2}} \qquad (10)$$

respectively. Indeed, these chain terminations by the catalyst are competitive with the reaction 4, but at a sufficiently high concentration of the metal salt the former reactions may well be predominant, while at the utmost limit Eq. 5 must be replaced by Eq. 9 or 10.

In Fig. 2 it may be seen that the rate of oxidation is approximately inversely proportional to $[\mathrm{Cu\text{-}N}]^{0.2}$. In the presence of manganese naphthenate, the rate decreases slowly as the metal concentration is increased, but when it exceeds $10^{-4}$ mol./mol., the rate decreases sharply and is inversely proportional to $[\mathrm{Mn\text{-}N}]^{0.7}$. These results may well be attributed to the chain termination reaction by metal salt in addition to reaction 4; probably in the case of copper salt, reactions 7 and 8, and in the case of manganese salt, reaction 6.

Cobalt showed quite a different effect, as has been stated above, which must now be discussed in connection with the products. The yields of the products are shown in Table I. A distinctive feature is that a considerable amount of $\alpha$-methylstyrene oxide is formed in the presence of the cobalt naphthenate catalyst, although in the presence of other salts, as well as in the absence of the metal salt, little epoxide was formed under these reaction conditions. The effect of the concentration of cobalt salt on the yield of $\alpha$-methylstyrene oxide was found to be analogous to that on the rate of oxidation. The results, shown in Fig. 3, indicate that the increase in the rate of oxidation and the formation of epoxide are closely related. Cobalt naphthenate, unlike manganese and copper salts, is assumed to be able to increase the rate of oxidation and to form $\alpha$-methylstyrene oxide as well. However, it also terminates chains as it is increased above a critical concentration, i. e., $3.4\times10^{-3}$ mol./mol. The decrease in the rate of oxidation is very sharp, and, in Fig. 2, it may also be seen that the rate is inversely proportional to $[\mathrm{Co\text{-}N}]^{1.0}$, suggesting that the reaction 4 is replaced by the reaction 6.

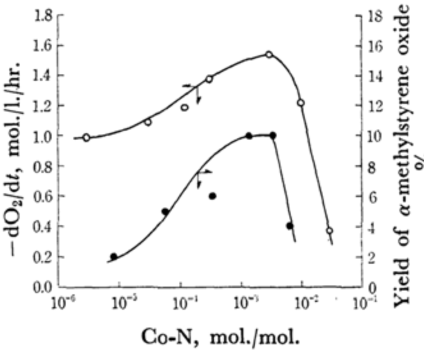


Fig. 3. Effect of Co-N concentration on the rate of oxidation and the yield of $\alpha$-methylstyrene oxide (at conv.=50%) at 70°C, ABN 0.030 mol./l. and oxygen pressure 760 mmHg.

The apparent order of the oxidation on the metal, however, is complex. Moreover, the proportions of the two valence states of the metal and the nature of the ligands probably change during the oxidation, further complicating the apparent order.

Other metal naphthenate catalysts had little effect on the products of the oxidation.

**The Effect of the Temperature on the Rate and Products of Oxidation.**—Reactions were carried out over the temperature range from 50 to 90°C. The results are summarized in Table II. From Table II the over-all activation energy of the oxidation of $\alpha$-methylstyrene in the presence of ABN and cobalt naphthenate may be found to be 19.7 kcal./mol. The effect of the temperature on the formation of acetophenone is shown in Fig. 4. Polyperoxide was supposed to decompose more rapidly at higher temperatures, causing an increase in the yields of the cleavage products. On the contrary, the yield of acetophenone became lower as the reaction temperature rose. The new broad band near 3500 cm$^{-1}$, probably due to the polymeric hydroxy group, appeared in the infrared spectrum of the products more significantly at higher temperatures.

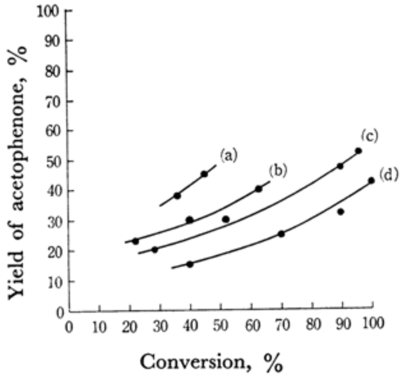
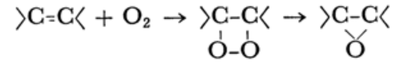


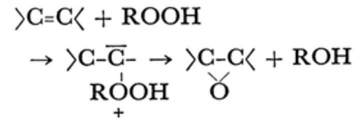
Fig. 4. Effect of temperature on the yield of acetophenone in the oxidation of $\alpha$-methylstyrene with ABN 0.030 mol./mol., Co-N $3.4\times 10^{-3}$ mol./mol. and oxygen pressure 760 mmHg. (a) 60°C, (b) 70°C, (c) 80°C, (d) 90°C

**The Effect of the Oxygen Pressure on the Rate and Products of Oxidation.**—This effect had been studied in detail by Mayo and Miller[3d] in the absence of the metal catalysts. We obtained similar results in the presence of catalysts. At low oxygen pressures, the rate of oxidation increased with the oxygen pressure, becoming independent of it above 365 mmHg. These results indicate that, at low oxygen pressures, chain termination reactions involve the monomer radicals in addition to the peroxy radicals. The yield of $\alpha$-methylstyrene oxide varied considerably with the oxygen pressure, although the formation of acetophenone was not influenced so much. The yields of $\alpha$-methylstyrene oxide under 175, 365, and 760 mmHg of oxygen pressure were 20, 13, and 9%, while those of acetophenone were 30, 33, and 33%, respectively, when 50% of the initial $\alpha$-methylstryene was oxidized at 70°C with 0.030 mol./l. of ABN and $3.4\times 10^{-3}$ mol./mol. of cobalt naphthenate. An increase in the oxygen partial pressure decreases the yield of $\alpha$-methylstyrene oxide.

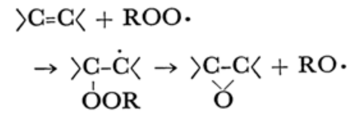
Three mechanisms have been proposed for the formation of epoxides[6]; (a) the direct addition of oxygen to a double bond via a cyclic peroxide; (b) the addition of hydroperoxide to a double bond, and (c) the addition of peroxy radicals to a double bond.



$$\text{(a)}\quad \rangle C{=}C\langle + O_2 \rightarrow \rangle\underset{\text{O--}}{C}{-}\underset{\text{O}}{C}\langle \rightarrow \rangle\underbrace{C{-}C}_{O}\langle \qquad (11)$$

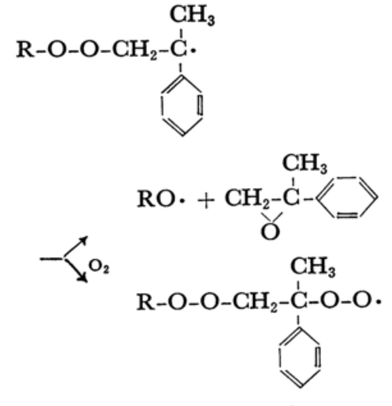


$$\text{(b)}\quad \rangle C{=}C\langle + ROOH \rightarrow \rangle\underset{\underset{+}{ROOH}}{C}{-}\overline{C}{-} \rightarrow \rangle\underbrace{C{-}C}_{O}\langle + ROH \qquad (12)$$



$$\text{(c)}\quad \rangle C{=}C\langle + ROO\cdot \rightarrow \rangle\underset{OOR}{C}{-}\dot{C}\langle \rightarrow \rangle\underbrace{C{-}C}_{O}\langle + RO\cdot \qquad (13)$$

The effect of oxygen pressure on the yield of $\alpha$-methylstyrene oxide supports the reaction 13. The decomposition of the intermediate radical, in this case a free radical of an unspecified length ending in the monomer unit $ROOCH_2C(CH_3)$-$(C_6H_5)\cdot$, into epoxide and alkoxy radical is competitive with reaction 2, the addition of oxygen to the monomer radical. Therefore, the more slowly the intermediate $\beta$-peroxy alkyl radical reacts with oxygen, the more chance the radical has to decompose unimolecularly.[3d,7] The formation of epoxide is thereby increased by lowering the oxygen partial pressure.



(13)

(2)

**The Effect of the Reaction Time on Rate and Products of Oxidation.**—As is shown in Fig. 5, the rate of oxidation is first-order with respect to $\alpha$-methylstyrene, confirming Rate Eq. 5. The yield of the products depends on the time; the yield of polyperoxide decreases, and that of the cleavage products increases, with time. As will be discussed later, $\alpha$-methylstyrene polyperoxide is quite stable under the reaction conditions employed; hence, these results do not arise from the

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[5] C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York (1957).

[6] Reviewed in the paper by G. H. Twigg, *Chem. & Ind.*, 4 (1962); W. F. Brill, *J. Am. Chem. Soc.*, **85**, 141 (1963).

[7] G. A. Russell, *J. Chem. Educ.*, **36**, 111 (1959).

TABLE III. $\alpha$-METHYLSTYRENE POLYPEROXIDE[a)]

| | C, % | H, % | O, %[b)] | N, % | mol. wt. |
|---|---|---|---|---|---|
| Calcd.[c)] | 71.98 | 6.71 | 21.31 | 0 | |
| Found | 73.37 | 6.75 | 19.88 | 0.0 | 1530[d)] |
| | 73.35 | 6.54 | 20.11 | 0.0 | |
| $H-(C_9H_{10}O_2)_{10}-H$ | 71.90 | 6.79 | 21.31 | 0 | 1502 |
| $H-(C_9H_{10}O_2)_{10}-CH=C(CH_3)(C_6H_5)$ | 73.42 | 6.80 | 19.78 | 0 | 1618 |

a) Prepared at 70°C, ABN 0.010 mol./l. and oxygen pressure 760 mmHg.
b) Calcd. by the difference.
c) Calcd. for $(C_9H_{10}O_2)_n$.
d) Determined by osmometry.

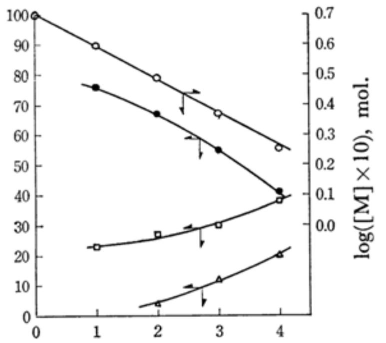


Fig. 5. Effect of the reaction time on the rate and products of oxidation at 70°C, ABN 0.030 mol./l., Co-N $3.4\times10^{-3}$ mol./mol. and oxygen pressure 760 mmHg.
○: $\alpha$-methylstyrene
●: $\alpha$-methylstyrene polyperoxide
□: acetophenone
△: $\alpha$-methylstyrene oxide

decomposition of polyperoxide. The reason for this is not definitely known. One possibility is the decrease in the concentration of $\alpha$-methylstyrene, a strong radical scavenger itself. The peroxy radical reacts competitively in two ways; one is the addition to the double bond of $\alpha$-methylstyrene (reaction 3), while the other is the cleavage reaction to form the cleavage products (reaction 14):

$$RO_2CH_2C(CH_3)(C_6H_5)O_2\cdot \rightarrow$$
$$RO_2\cdot + CH_2O + C_6H_5C(O)CH_3 \qquad (14)$$

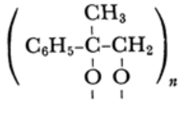
This must be also applied to the alkoxy radical. The decrease in the concentration of $\alpha$-methylstyrene, as a result, presumably increases the life time of peroxy and alkoxy radicals and gives these radicals more chance to decompose into the cleavage products.

**$\alpha$-Methylstyrene Polyperoxide.**—The polymer prepared by the method described in the experimental part was colorless, transparent and a little gummy. The composition of methanol-insoluble $\alpha$-methylstyrene polyperoxide was determined by elementary analyses. The results are illustrated in Table III.

The effects of the end groups are not taken into consideration in the values calculated from $(C_9H_{10}O_2)_n$. The difference between the data obtained and the calculated value is evidently due to the end groups. Mayo and Miller[3d)] reported that $HO_2CH_2C(CH_3)(C_6H_5)-$, $O=CHC(CH_3)(C_6H_5)-$ and H- were good possibilities. However, the data indicate that the end groups do not contain oxygen. Here two end groups, H- and $(C_6H_5)(CH_3)C=CH-$, are presumed; the values calculated from these end groups are also listed in Table III.

From these data $H-(C_9H_{10}O_2)_{10}-CH=C(CH_3)-(C_6H_5)$ may be expected to be most plausible. The infrared spectra show the disappearance of the double bond and the formation of peroxide (at 1030 cm$^{-1}$). $\alpha$-Methylstyrene polyperoxide is believed to be rather clear compared with styrene polyperoxide. In the absence of oxygen, no reaction at all was observed. This absence of the homopolymerization of $\alpha$-methylstyrene practically eliminates the excess monomers from the polymer and reduces irregularities in the polymer. It may be presumed, however, that the composition of $\alpha$-methylstyrene polyperoxide is not always uniform but has some irregularities, and that the molecular weight has a wide distribution.

Mayo and Miller[3d)] reported that the structure of $\alpha$-methylstyrene polyperoxide was substantially $(-OOCH_2C(CH_3)(C_6H_5))_n-$; they based their conclusion on the experimental findings that the pyrolysis of it gave acetophenone and formaldehyde in yields up to 93% and its reduction to $\alpha$-methylstyrene glycol in a 60% yield. On the other hand, Hock and Siebert[8)] proposed the following structure:



$$\left( C_6H_5-\overset{CH_3}{\underset{O}{C}}-\underset{O}{CH_2} \right)_n$$

They also proposed the reaction mechanism shown in Fig. 6. However, the effect of oxygen pressure on the yield of $\alpha$-methylstyrene oxide cannot be illustrated in this sequence.

The decomposition of $\alpha$-methylstyrene polyperoxide in the presence of a metal salt catalyst

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8) H. Hock and M. Siebert, *Chem. Ber.*, **87**, 546 (1954).

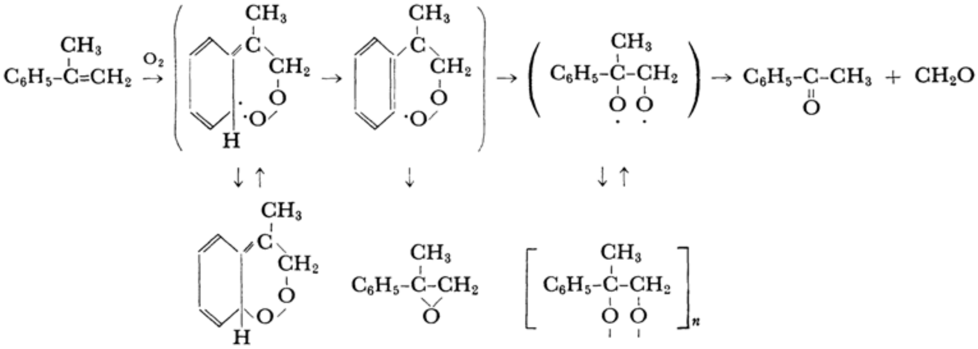

Fig. 6. Reaction mechanism by Hock and Siebert.[8]

was also studied. Some examples of the experiments are given blow.

*Expt. A.*—The product of oxidation at 70°C, ABN 0.030 mol./l. and oxygen pressure 760 mmHg was distilled in vacuo in order to remove both unreacted $\alpha$-methylstyrene and cleavage products. The residue was dissolved in chlorobenzene (a guaranteed reagent was shaken with sulfuric acid, washed with water, and distilled). Cobalt naphthenate was added to the solution, and the reaction was carried out for 2 hr.

*Expt. B*—The oxidation of $\alpha$-methylstyrene was carried out for 2 hr. at 70°C, ABN 0.030 mol./l., and oxygen pressure 760 mmHg, and in the absence of a metal salt catalyst. Then the stream was converted from oxygen to nitrogen, cobalt naphthenate was added to the reaction mixture, and the reaction was continued for another 3 hr.

These experiments demonstrated that $\alpha$-methyl styrene polyperoxide is surprisingly stable under these reaction conditions, and no depolymerization was observed. After all, the cleavage products are expected to be formed not by the depolymerization of polyperoxide, but by the decomposition of the peroxy radicals and/or alkoxy radicals which are produced from peroxy radicals or by reaction 13, the splitting off of epoxide from a polyperoxy radical ending in a monomer unit.

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