

## Catalytic Action of Metal Salts in Autoxidation and Polymerization. X. The Effect of Various Metal Stearates on the Thermal Oxidation of 2,6,10,14-Tetramethylpentadecane

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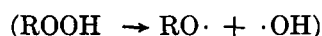
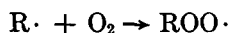
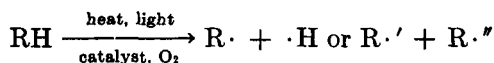
### Synopsis

The various metal stearate-catalyzed thermal oxidations of 2,6,10,14-tetramethylpentadecane (TMPD, a model compound of polypropylene) and the decomposition of TMPD hydroperoxide (TMPD-HPO) were carried out. The results obtained were compared with those of the oxidation of polypropylene reported previously;<sup>18</sup> and the initial reaction process of the oxidation of the polymer is discussed. The catalytic activity of metal stearates in the oxidation of polypropylene differed from that in the oxidation of pure TMPD and was fairly similar to that in the oxidation of TMPD with TMPD-HPO. The more effective the catalyst for the decomposition of TMPD-HPO, the more effective it was for the oxidation of both TMPD with TMPD-HPO and polypropylene. The results apparently indicate that metal catalysts enhance the decomposition of hydroperoxides which presumably contaminate the polymer and form during the oxidation, and also imply that the initiation of the oxidation of polypropylene is primarily affected by the presence of hydroperoxide contamination of the polymer.

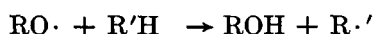
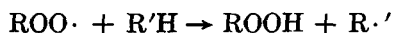
### INTRODUCTION

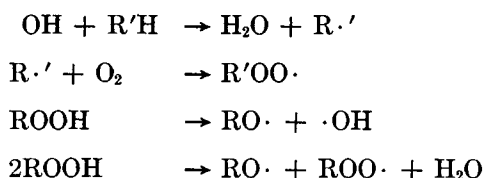
A number of studies on the thermal oxidative degradation of polypropylene have been made.<sup>1-9</sup> In general, the oxidation mechanism of polyolefins is expressed by the following scheme:

Initiation:

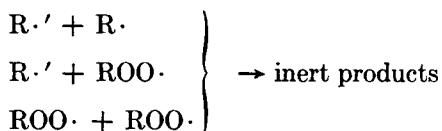


Propagation:

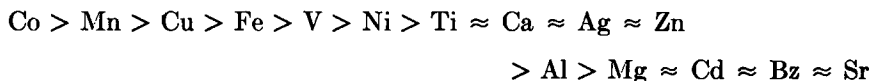




Termination:

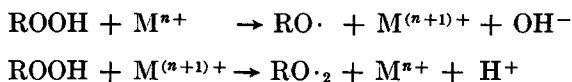


The thermal oxidation reaction is extremely enhanced by the presence of a trace amount of metal or metallic compound.<sup>10-20</sup> In a previous paper,<sup>18</sup> we studied the effects of various metal stearates on the thermal oxidative degradation of polypropylene and the decomposition of *tert*-butyl hydroperoxide and found that the order of decreasing catalytic effect of the fatty acid metal salts was as follows:



We also reported that the catalytic effect for the degradation of the polymer showed a fairly good correlation with that of the decomposition of the hydroperoxide.

One of the main functions of a metallic catalyst during autoxidation is believed to be in promoting the breakdown of hydroperoxides to free radicals, thus continuing chain growth.<sup>1</sup> The reactions can be depicted as follows:



Thus, the metal catalyst activity during the autoxidation of polypropylene should correlate with the oxidation potential.<sup>18</sup> Lately, Reich, Jadrnicsek, and Stivala<sup>19</sup> clearly correlated such catalyst activity of various metal acetylacetonates during oxidation of atactic polypropylene films by measuring carbonyl formation with oxidation-reduction potential. However, the precise initiation process in autoxidation of polyolefins remained unclear. In general, weak points such as tertiary hydrogens, double bonds, branched points, hydroperoxides, and foreign particles are believed to play an important role in the initiation process.

Richters<sup>20</sup> studied the initiation process in the oxidation of polypropylene using a color reaction in detecting early signs of oxidative degradation in thin polypropylene film. He concluded that the oxidation below 110°C is initiated by foreign particles which are believed to originate in the production machines, in particular the pelletizer. The conclusion implies that

the initiation of the oxidation starts with the abstraction of *tert*-hydrogen either directly by metal or activated metal-oxygen complexes.

Bocek<sup>21</sup> and Pokorny<sup>22</sup> reported that the determination of an extremely minor amount of hydroperoxide ( $10^{-7}$  to  $10^{-6}$  mole) in atactic polypropylene was possible. Unfortunately, these methods cannot be successfully applied to the determination of trace amounts of hydroperoxide in unoxidized isotactic polypropylene.

The present paper deals with the initiation process in the oxidation of polypropylene, comparing the catalyst activity of metal stearates in the oxidation of 2,6,10,14-tetramethylpentadecane (a model compound of polypropylene) and that of polypropylene reported previously.<sup>18</sup> The results imply that the initiation of the oxidation of the polymer is extremely influenced by the presence of hydroperoxide, presumably a contaminant of the polymer.

## EXPERIMENTAL

### Reagents

**Metal Stearates.** Each metal stearate was prepared according to the literature<sup>18</sup> by double decomposition of sodium stearate with corresponding metal salts.

**2,6,10,14-Tetramethylpentadecane.** Commercial first-grade reagent 2,6,10,14-tetramethylpentadecane (TMPD, product of the Wako Pure Chemical Ind. Ltd. Co., Japan) was distilled under reduced nitrogen atmosphere at 3 mm Hg, at 126°–127°C. The distillate was kept under nitrogen atmosphere in a refrigerator.

### Thermal Oxidation

In a ca. 20-ml flat-bottomed oxygen absorption cell containing 3.91 mg of each metal stearate (corresponding to 0.5 wt-%), 1 ml TMPD was added. Then oxidation was carried out under atmospheric oxygen pressure, mostly at 120° and 130°C, with a conventional oxygen absorption apparatus prepared in our laboratory. The samples used were pure TMPD and TMPD containing  $9.59 \times 10^{-6}$  mole/l. TMPD hydroperoxide (TMPD-HPO) which was prepared by the oxidation of TMPD.

From the oxygen uptake curves thus obtained, the times required to absorb 10 ml oxygen per 1 ml TMPD were estimated ( $t_{10}$ ), and were compared with the results of the oxidation of polypropylene reported previously.<sup>18</sup>

### Decomposition of TMPD-HPO

A ca. 20-ml two-necked flat bottomed flask equipped with a reflux condenser and a magnetic stirrer was previously flushed with dry nitrogen, and 7.82 mg metal stearate (corresponding to 0.5 wt-%) and 2 ml TMPD-HPO solution (0.20 mole/l.) was successively added. The contents were

stirred and the thermal decomposition of TMPD-HPO was then carried out at 100°C. Decomposition of hydroperoxide was measured by iodometry on 0.2-ml aliquots during the reaction. TMPD-HPO solution was previously frozen by liquid nitrogen and was evacuated to remove dissolved gases.

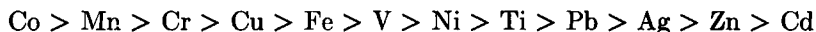
### Infrared Spectra Analysis

Infrared spectra of the oxidized TMPD were measured by a KBr plate sandwich method using a 0.05-mm-thick spacer, and the relative changes in absorption intensity at 3380  $\text{cm}^{-1}$  and 1715  $\text{cm}^{-1}$  were estimated. The absorption intensity at 735  $\text{cm}^{-1}$  was used as an internal standard.

## RESULTS AND DISCUSSION

### Oxidation of Pure TMPD

Oxygen uptake curves of pure TMPD at 130°C are shown in Figure 1. The order of decreasing catalytic effect of the fatty acid salts for the oxidation of polypropylene at 120°C was as follows<sup>18</sup>:



As shown in Figure 1, almost all metal stearates accelerate more or less the rate of oxygen absorption of pure TMPD; and Cu, Cr, Fe, Ag, and so on, enhance markedly the oxidation of TMPD. However, the order of catalytic effect of the metal stearates differs substantially from that in the polymer. For examples, extremely effective catalysts for the oxidation of the polymer such as Co and Mn remarkably reduce the catalyst activity for the oxidation of pure TMPD, while Ag and Zn accelerate the oxidation of pure TMPD. Therefore, a correlation between the catalytic effect of the metal stearates in the oxidation of polypropylene and that in the oxidation of pure TMPD hardly exists.

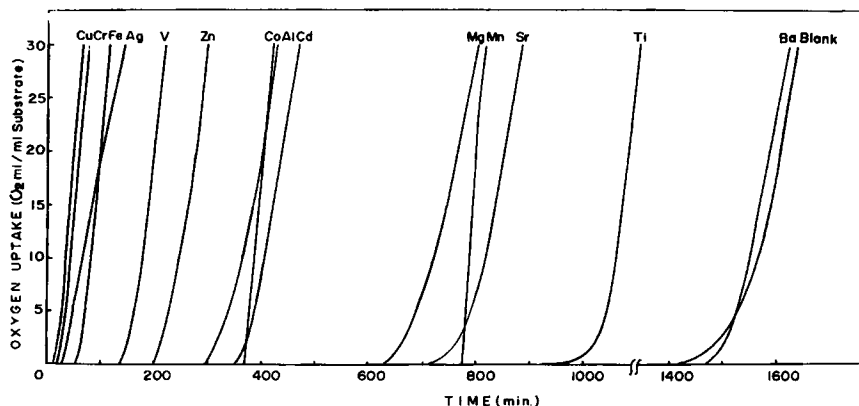
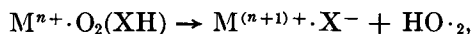


Fig. 1. Oxygen uptake curves of pure TMPD at 130°C.

Since the experimental system was supposed to be free from trace amounts of hydroperoxide, the role of the metal catalysts can be attributed to factors other than hydroperoxide. Betts and Uri<sup>23</sup> postulated a reaction of metal with molecular oxygen via a complex which involves metal, oxygen, and substrate (or solvent) of the type



while Bawn<sup>24</sup> and Kern and Willersinn<sup>25</sup> proposed that the initiation of hydrocarbon oxidation is due to the formation of free radical by the interaction of the metal with substrates. Therefore, the differences in the catalytic effect of metal stearates seem to be dependent upon the mode of the interaction of metal with substrate or molecular oxygen.

For the initiation of the oxidation of pure TMPD in the absence of both metal catalyst and substrate hydroperoxide, explanation remains unclear. However, Dulog<sup>26</sup> presented some evidence for a direct initiation reaction of the substrate with molecular oxygen in the oxidation of tetralin. Semenov<sup>4</sup> also postulated the abstraction of hydrogen by molecular oxygen. Thus, one may assume a similar initiation mechanism for the oxidation of pure TMPD.

### Oxidation of TMPD Containing TMPD-HPO

The metal-catalyzed thermal oxidation of TMPD containing TMPD-HPO ( $9.59 \times 10^{-6}$  mole/l.) was carried out at 120°C. The oxygen uptake curves of TMPD with TMPD-HPO are shown in Figure 2. This figure shows that the order of decreasing catalytic effect of the metal stearates in the oxidation of TMPD with TMPD-HPO at 120°C is as follows:

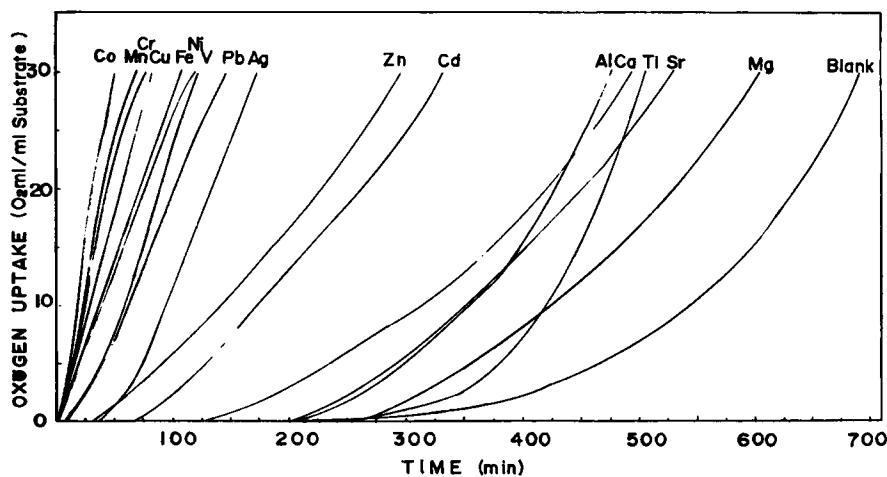


Fig. 2. Oxygen uptake curves of TMPD with TMPD-HPO at 120°C.

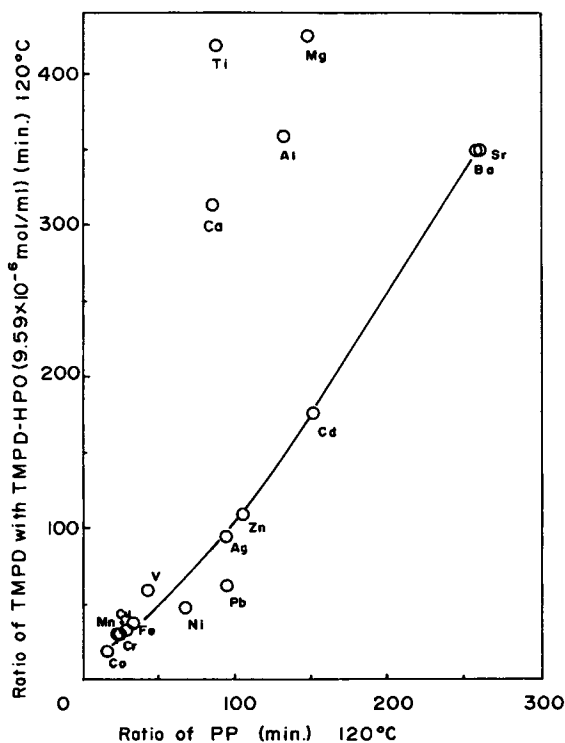


Fig. 3. Correlation between  $t_{10}$  of TMPD with TMPD-HPO and  $t_{10}$  of polypropylene. (Data of polypropylene were taken from ref. 18).

In the thermal oxidation of polypropylene at 120°C, the order was as follows:



Thus, the order of catalyst activity of metal stearates in the oxidation of TMPD with TMPD-HPO is fairly similar to that in the oxidation of polypropylene. From Figure 2 the times required to absorb 10 ml oxygen per 1 ml TMPD with TMPD ( $t_{10}$ ) were estimated and compared with those of  $t_{10}$  in the oxidation of polypropylene.

The values of  $t_{10}$  for TMPD with TMPD-HPO were plotted against those of polypropylene (data were taken from Osawa et al.<sup>18</sup>) and are shown in Figure 3. It clearly demonstrates that Co, Mn, Cr, Cu, Fe, and so on, remarkably enhance the oxidation of both TMPD with TMPD-HPO and polypropylene. In the case of the oxidation of TMPD containing *tert*-butyl hydroperoxide ( $8.33 \times 10^{-6}$  mole/l.), an almost similar order of catalytic effect was observed.

These results imply that a minor amount of hydroperoxide initially contaminating the polymer plays an extremely important role in the oxidation of the polymer. The hydroperoxide presumably formed during the manufacturing process or storage of the polymer.

### Decomposition of TMPD-HPO

To examine the catalytic activity of the metal stearates for the decomposition of TMPD-HPO, the metal-catalyzed decomposition of TMPD-HPO was carried out in TMPD solution. The decomposition curves are shown in Figure 4. Again, the rate of the decomposition of TMPD-HPO was extremely enhanced in the presence of Co, Mn, V, Cr, Cu, and so on. However, as shown in Figure 4, the concentration of hydroperoxide increases at the very beginning of the reaction in some systems where the rate of the decomposition of hydroperoxide is fairly slow. Since gaseous substances dissolved in TMPD were supposed to be removed by a freeze-vacuum method, the oxygen absorbed in TMPD-HPO solution might additionally form new hydroperoxide, while in the other systems, where the rate of the decomposition of hydroperoxide is fast, the concentration of hydroperoxide decreases only with time. In such systems, the decomposition of TMPD-HPO seems to be too fast to accumulate newly formed hydroperoxide.

From Figure 4 the per cent decomposed TMPD-HPO after 50 min was estimated. The values obtained were compared with  $t_{10}$  of the oxidation of TMPD with TMPD-HPO and with  $t_{10}$  of the oxidation of polypropylene. These correlations are shown in Figures 5 and 6, respectively. As shown, the more effective the catalyst in the decomposition of TMPD-HPO is, the more effective the catalyst is either in the oxidation of TMPD with TMPD-HPO or in the oxidation of polypropylene.

Since availability of pure polypropylene which is completely free from contaminated hydroperoxide seems to be doubtful at present, we used TMPD as a model compound of the polymer. It may be questionable to discuss directly the initiation process of the oxidation of the polymer by the results of the low molecular weight compound. Assuming a similar initiation process for the oxidation of both polymers and low molecular weight compounds, the results mentioned above indicate the importance of a minor amount of hydroperoxide for the initiation process of the oxida-

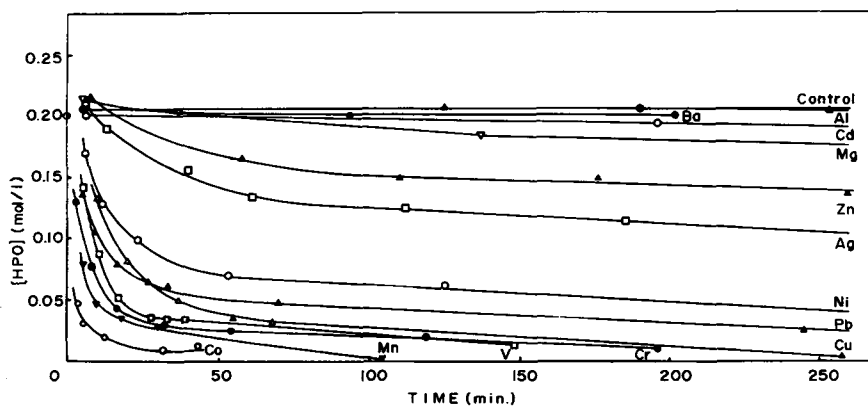


Fig. 4. Decomposition of TMPD-HPO by various metal stearates at 100°C.

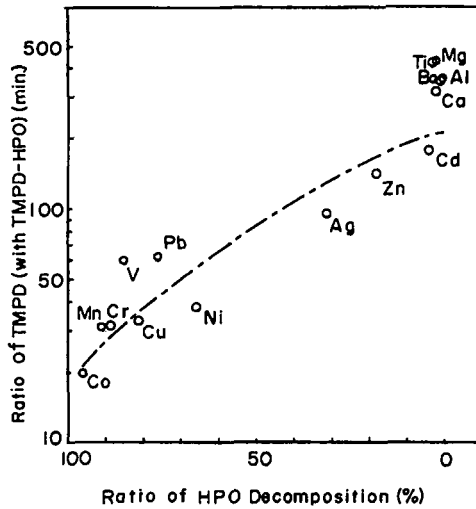


Fig. 5. Correlation between decomposition of TMPD-HPO (decomposed % after 50 min) and oxygen uptake of TMPD with TMPD-HPO.

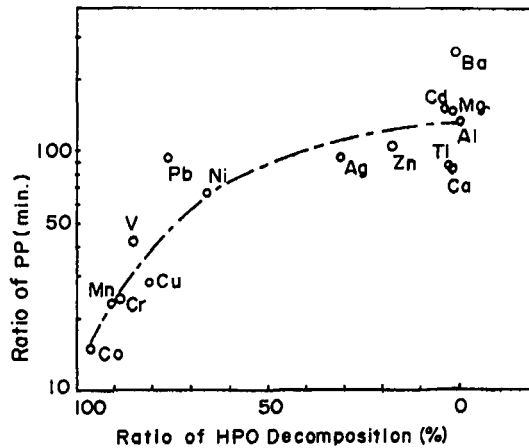


Fig. 6. Correlation between decomposition of TMPD-HPO (decomposed % after 50 min) and oxygen uptake of polypropylene ( $t_{10}$ ). (Data of polypropylene were taken from ref. 18).

tion of polypropylene. In other words, from the various correlations between the oxidation of TMPD (both in the absence and in the presence of TMPD-HPO) and that of polypropylene, or the decomposition of TMPD-HPO, the initiation process in the oxidation of polypropylene is likely to start by the catalytic decomposition of a minor amount of hydroperoxide contaminating the polymer, and then the hydroperoxide accumulates gradually by the successive oxidation. Thus, the more effective the metal catalyst in the decomposition of TMPD-HPO is, the more effective the catalyst is either in the oxidation of TMPD containing TMPD-HPO or in the oxidation of polypropylene.



This apparently means that the metal catalyst acts effectively both in the decomposition of hydroperoxide contaminating the polymer and in the decomposition of hydroperoxide formed during the oxidation. Furthermore, the order of catalytic effect of various metal stearates in the oxidation of polypropylene differed from that in the oxidation of pure TMPD, and was similar to that in the oxidation of TMPD with TMPD-HPO. Therefore, we propose that a minor amount of hydroperoxide contaminating the polypropylene plays an extremely important role in the initiation process of the oxidation of the polymer.

Thus, one should take into account the role of a minor amount of hydroperoxide contaminating the polymer for the initiation process of the polymer degradation.

### Effect of Temperature

The dependence of the rate of oxygen absorption on temperature was examined for pure TMPD and TMPD with TMPD-HPO. Arrhenius plots obtained from the oxygen uptake curves are shown in Figure 7. The apparent activation energies for the oxidation estimated from the Arrhenius plots shown in Figure 7 were 29.7 and 29.5 kcal/mole for pure TMPD and

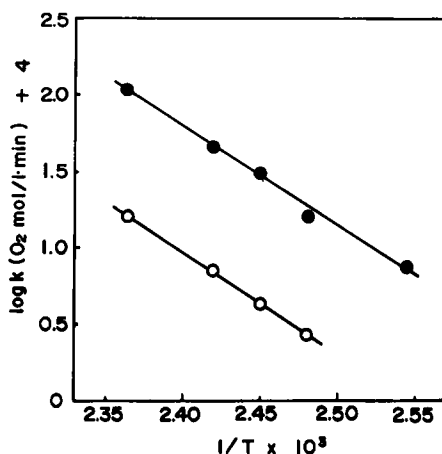


Fig. 7. Arrhenius plots of oxidation of pure TMPD and TMPD with TMPD-HPO ( $1.07 \times 10^{-4}$  mole/l.): (O) pure TMPD; (●) TMPD with TMPD-HPO.

TMPD with TMPD-HPO, respectively. The results indicate that the oxidation of both systems proceeds via an almost similar mechanism in the absence of metal catalyst, and that the presence of a minor amount of hydroperoxide at the initial stage is essential in the rate determining the hydrocarbon oxidation.

### Effect of TMPD-HPO Concentration

The dependence of the rate of the oxidation of TMPD on the initial hydroperoxide concentration was also examined in the range of  $1.07 \times$

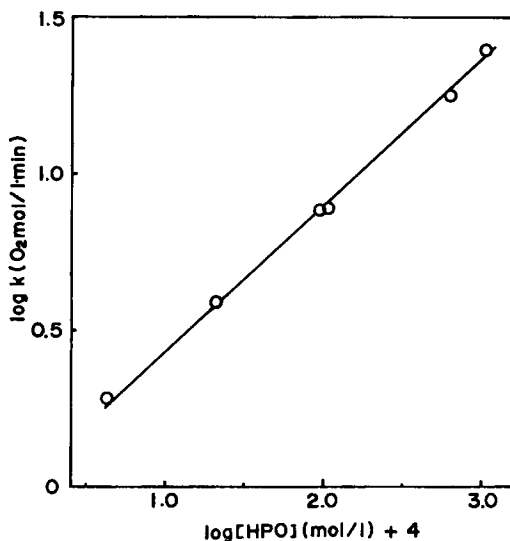


Fig. 8. Dependence of rate of oxygen absorption on initial TMPD-HPO concentration.

$10^{-4}$  to  $4.27 \times 10^{-7}$  mole/l. The results obtained are shown in Figure 8. From the slope of the linear curve shown in this figure, it was estimated that the rate of TMPD oxidation was dependent on the power of 0.46 of the concentration of the initial substrate hydroperoxide. In a conventional hydrocarbon oxidation, the rate of oxidation is dependent on the square root of the initial hydroperoxide concentration.<sup>1</sup> Thus, the value obtained is relatively close to the conventional value and also implies the important role of the initially contaminated hydroperoxide in the polymer.

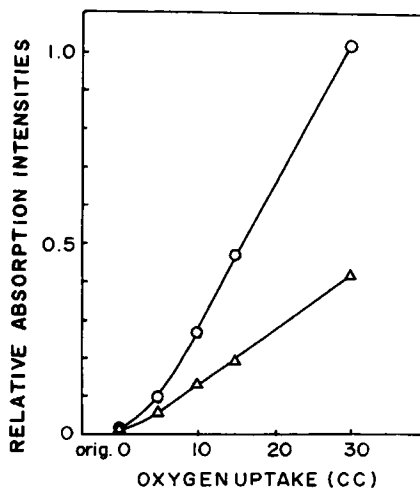


Fig. 9. Relative absorption intensities of infrared spectra against amount of oxygen uptake: (O)  $1517 \text{ cm}^{-1}/735 \text{ cm}^{-1}$ ; ( $\Delta$ )  $3380 \text{ cm}^{-1}/735 \text{ cm}^{-1}$ .

### Infrared Spectra

The relative absorption intensities of infrared spectra at  $1715\text{ cm}^{-1}$  due to carbonyl groups and  $3380\text{ cm}^{-1}$  due to hydroxyl groups<sup>27</sup> against the amount of oxygen uptake are plotted in Figure 9. An increase in oxygenated groups in TMPD oxidation is apparent, as usual.

As mentioned above, the catalyst activity of various metal stearates in the oxidation of polypropylene differs from that of pure TMPD, and is quite similar to that in the oxidation of TMPD with TMPD-HPO. Therefore, we propose that a minor amount of hydroperoxide presumably contaminating the polymer plays an extremely important role in the initiation process in the oxidation of the polymer.

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