

Effect of Concentration of Atactic Polypropylene on its Rate of Autoxidation

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Synopsis

A general scheme previously reported for the autoxidation of polyolefins is further substantiated by results obtained for the uncatalyzed and catalyzed autoxidation of various concentrations of atactic polypropylene (APP) (by admixture with polyisobutylene) under various experimental conditions. Thus, rates of maximum carbonyl formation were measured as a function of APP concentration at 120°C, oxygen concentrations ranging from 0.5%–100% by volume and cobaltic acetylacetonate catalyst concentrations $(3 \text{ and } 17) \times 10^{-7}$ mole/7.5 mg sample. Good agreement was found between experimentally observed and theoretical dependencies of the maximum carbonyl formation rate on APP concentration derived from the combined reaction scheme.

INTRODUCTION

A general kinetic scheme for the autoxidation of various polyolefins,¹ e.g., atactic polypropylene (APP), in the bulk phase under various experimental conditions (temperatures, oxygen concentrations, metal catalyst concentrations) has been applied successfully to explain the rate of formation of volatile products,²⁻⁵ chemiluminescence,⁶⁻⁸ oxygen absorption,⁶⁻⁸ changes in intrinsic viscosity as a function of time,^{9,10} and carbonyl formation.^{2,3,6,11-17} Bawn and Chaudri^{18,19} also successfully used a similar mechanism to both metal catalyzed and uncatalyzed autoxidation of APP in solution in explaining various kinetic dependencies. Their study included the effects of APP concentration, in solution, on autoxidation rate (as measured by oxygen uptake).

The present paper is concerned with a study of the effect of APP concentrations in the bulk phase (by admixture with polyisobutylene, PIB) on the rate of carbonyl formation. Further, this study was carried out both in the presence and absence of metal catalyst, cobalt(III) acetylacetonate.

EXPERIMENTAL

Starting Materials

Atactic Polypropylene (APP). An uninhibited sample of APP, obtained from Avisun Corporation, was purified as described previously.¹² Upon

ignition, the APP sample gave an ash content of 0.008%. Molecular weight of about 30,000 was determined by osmometry.

Polyisobutylene (PIB). An uninhibited sample of PIB, which was obtained from Enjay Chemical Co., was initially purified to yield an ash content of 0.05% and a viscosity-average molecular weight of 1.2×10^6 . The original material was reported to contain processing aids (sodium and zinc stearates) and aluminum residue from polymerization catalyst. To examine the effect of these residues on autoxidation rate, the PIB was further purified (in a manner identical to that used for APP) to give ash content of 0.015% and viscosity-average molecular weight of 0.95×10^6 . Since no appreciable difference in oxidation rate was observed, the earlier material was used primarily in this investigation.

Metal Salt Catalyst. Cobalt(III) acetylacetonate (2,4-pentanedione), mp 210° – 213°C , highest purity grade of J. T. Baker Chemical Co., was used without further purification.

Apparatus

Infrared spectra were taken on a Perkin-Elmer recording spectrophotometer, Model 21. Attached to the spectrophotometer was an oxidation cell with a temperature controller and a potentiometer. A description of the oxidation cell, including other details, have been reported in an earlier work.¹¹

Procedure

APP and PIB were dissolved in carbon tetrachloride and mixed in such proportions that the final solutions contained 0.0, 24.6, 45.0, 62.1, 76.6, 86.7, and 100% of APP by weight. From these solutions, films of about 2.5 mils thick, with and without metal catalyst, were cast onto optical sodium chloride disks. These disks were assembled in the oxidation cell which was attached to the infrared spectrophotometer. Mixtures of oxygen and nitrogen were passed into the oxidation cell at a constant rate of 30 ml/min after the desired reaction temperature (120°C) had been reached. (Prior to reaching this reaction temperature, the system was kept under nitrogen.) Infrared spectra of the carbonyl region were recorded as a function of reaction time and APP concentrations.

For the uncatalyzed oxidation, 10% and 100% oxygen by volume were employed for the various APP concentrations. In the case of the catalyzed oxidation, for the low catalyst concentration (3×10^{-7} mole/7.5 mg sample), 0.5, 10, and 100% oxygen by volume were used. For the relatively high catalyst concentration (17×10^{-7} mole/7.5 mg sample), 10% and 100% oxygen concentrations were used. The catalyzed oxidations were also studied under similar APP concentrations as in the uncatalyzed reactions.

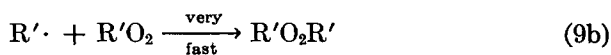
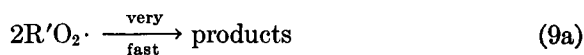
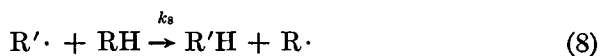
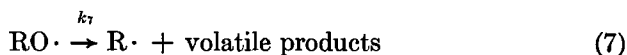
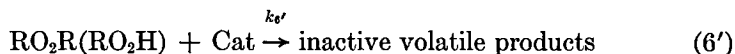
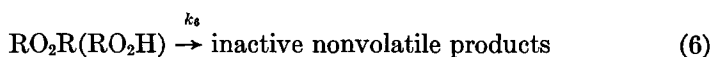
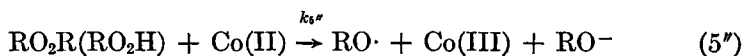
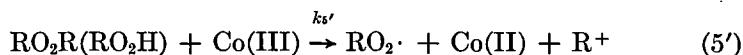
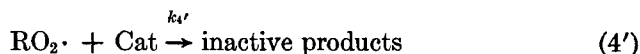
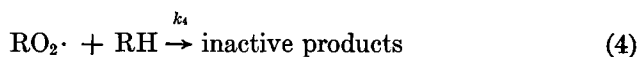
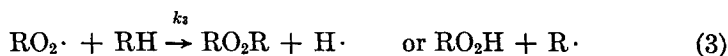
Conditions for evaluation of carbonyl absorbance areas, the validity of the Lambert-Beer law, and the fact that the diffusion control did not apply to the 2.5-mil-thick polymer film were established earlier.¹¹ Further, the

amount of total active oxygen, present as peroxides and hydroperoxides, and the amount of the hydroperoxide alone were determined iodometrically.^{20,21} The peroxide present was calculated by difference.

The PIB alone was found to be much more resistant to oxidation, in the presence and absence of metal catalysts, than APP by itself. Thus, under the experimental conditions used, the PIB began to oxidize long after the maximum rate of oxidation of the APP had been reached.

THEORY

In the following is shown a general kinetic scheme which is a combination of previously reported schemes for both uncatalyzed and catalyzed oxidations of APP.^{11,12}



As demonstrated previously, various kinetic expressions could be derived for uncatalyzed and catalyzed autoxidations from the above scheme. For

the former reaction, steps (1), (2) to (4), (5), (6), and (7) through (9b) were used, whereas for the latter oxidation, steps (1'), (2) to (4), (4'), (5'), (5''), (6), (6') and (7) through (9b) were employed.

Uncatalyzed Oxidation^{11,22}

In this case, the following expression was derived for the maximum rate of carbonyl formation, $\rho_{m,0}$, at constant temperature:

$$\rho_{m,0} = \frac{K_1'[\text{O}_2][\text{RH}]}{1 - \frac{K_2'[\text{RH}]}{K_3'[\text{RH}] + [\text{O}_2]}} \quad (10)$$

where $[\text{RH}] \equiv \text{APP concentration (substrate)}$,

$$K_1' = \frac{Ck_1k_3k_8}{(k_3 + k_4)(k_5 + k_6)}$$

$$K_2' = \frac{2k_3k_5k_8}{k_9(k_3 + k_4)(k_5 + k_6)}$$

$$K_3' = \frac{k_8}{k_9}$$

and C is a constant.

From eq. (10), simpler expressions could be derived depending upon various experimental conditions used, as indicated in the following.

When Concentration of Oxygen Is Constant and Low. Under these conditions, eq. (10) can be reduced to

$$\rho_{m,0} = \frac{K_1'[\text{O}_2][\text{RH}]}{K_3' - K_2'} = f([\text{RH}]^1). \quad (11)$$

When Concentration of Oxygen Is Constant and High. For this case, eq. (10) reduces to

$$\rho_{m,0} = K_1'([\text{O}_2][\text{RH}]^1 + K_3'[\text{RH}]^2) = f([\text{RH}]^1 + [\text{RH}]^2). \quad (12)$$

Catalyzed Oxidation^{12,22}

In this case, the following expression was obtained for a net maximum rate formation, $\rho_{m,net}$ (the difference between observed catalyzed rate, $\rho_{m,tot}$, and the maximum uncatalyzed rate, $\rho_{m,0}$) at constant temperature:

$$\rho_{m,net} = \frac{\alpha\varphi(K_3 + [\text{O}_2])}{K_3(1 - 2\beta) + [\text{O}_2](1 - \beta)} \quad (13)$$

where

$$\alpha \equiv \frac{k_3[\text{RH}]C'}{(k_3 + k_4)[\text{RH}] + k_4'[\text{Cat}]} \left(\frac{k_8'}{2k_5' + k_6'} \right)$$

$$\beta \equiv \frac{k_3[\text{RH}]}{(k_3 + k_4)[\text{RH}] + k_4'[\text{Cat}]} \left(\frac{k_5'}{2k_5' + k_6'} \right)$$

where $[\text{Cat}] \equiv$ metal salt catalyst concentration and C' is a constant.

From eq. (13) simpler expressions could be derived depending upon various experimental conditions used, as indicated in the following.

When Concentration of Catalyst Is Low. For low catalyst concentrations it is readily observed that α and β should be independent of $[\text{RH}]$ (substrate concentration). Two cases may now be considered.

(a) *When oxygen concentration is very low:*

Under these conditions, $K_3(1 - 2\beta) \gg [\text{O}_2](1 - \beta)$, and, providing $[\text{O}_2] \ll K_3$, eq. (13) becomes

$$\rho_{m,net} = f([\text{RH}]^1). \quad (14)$$

At this point, it should be noted that from previous work¹¹ $K_3(120^\circ\text{C}) = 44$ and $\beta(120^\circ\text{C}) = 0.48$. Thus, in order for $K_3(1 - 2\beta) \gg [\text{O}_2](1 - \beta)$, the oxygen concentration must be much lower than 4% (for APP alone). When $K_3(1 - 2\beta) \approx [\text{O}_2](1 - \beta)$, as for about 10% oxygen, then, from eq. (13),

$$\rho_{m,net} = f\left(\frac{[\text{RH}]^{1-2}}{[\text{RH}]^{0-1}}\right) \quad (15)$$

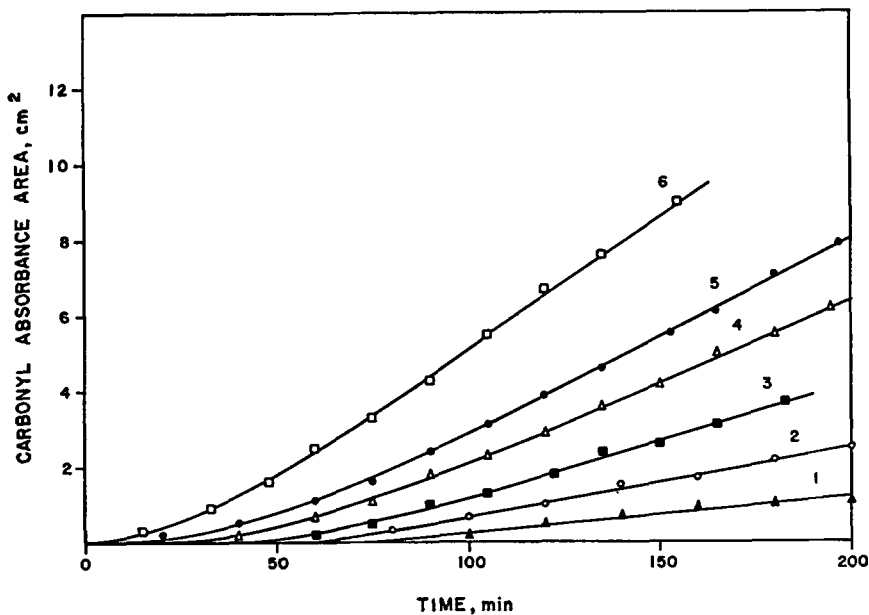


Fig. 1. Carbonyl absorbance area vs. reaction time at 120°C and for pure oxygen, at various concentrations of APP: (1) 24.6%; (2) 45.0%; (3) 62.1%; (4) 76.6%; (5) 86.7%; (6) 100%.

where the exponents in the numerator and denominator refer to kinetic orders ranging from 1 to 2, and 0 to 1, respectively:

(b) *When oxygen concentration is very high:*

Under these conditions, $[O_2](1 - \beta) \gg K_3(1 - 2\beta)$, and eq. (13) becomes

$$\rho_{m.net} = f([RH]^{1-2}). \quad (16)$$

When Catalyst Concentration Is High. Equation (13) may also be written in the following form:¹²

$$\rho_{m.net} = \frac{C_1[Cat]}{k_{4'}[Cat] + C_2[RH]} \quad (13a)$$

where

$$C_1 \equiv k_1 k_3 [O_2] [RH]^2 C' \left(\frac{k_{6'}}{2k_{5'} + k_{6'}} \right)$$

$$C_2 \equiv (k_3 + k_4) - k_3 \left(\frac{k_{5'}}{2k_{5'} + k_{6'}} \right) \left(\frac{2K_3 + [O_2]}{K_3 + [O_2]} \right)$$

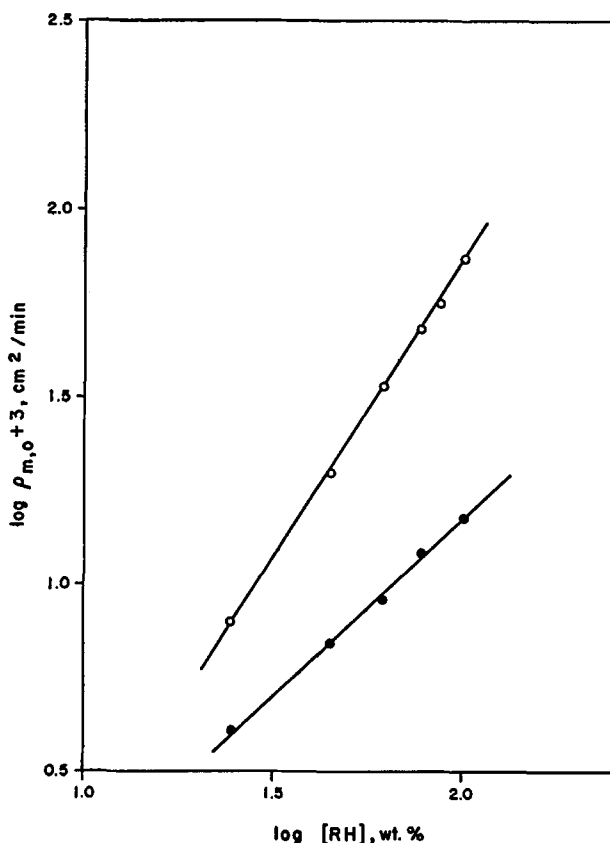


Fig. 2. Dependence of maximum rate, $\rho_{m,0}$, on concentration of APP at 120°C: (●) 10% O₂; (O) 100% O₂.

From eq. (13a), at high catalyst concentration, $k_4[\text{Cat}] \gg C_2[\text{RH}]$ (regardless of $[\text{O}_2]$), and therefore

$$\rho_{m,\text{net}} = f([\text{RH}]^2). \quad (17)$$

RESULTS AND DISCUSSION

Initially, we shall consider the uncatalyzed oxidation results. Accordingly, Figure 1 shows typical plots of carbonyl absorbance as a function of time for various $[\text{RH}]$ at 120°C for 100% oxygen concentration. It is noted that as $[\text{RH}]$ increases, the rate of carbonyl formation increases as anticipated, cf. eq. (2). In Figure 2 are depicted plots of $\log \rho_{m,0}$ versus $\log [\text{RH}]$ for 10% and 100% oxygen. In the former case, a slope of 0.94 was obtained, whereas in the latter case, a slope of 1.58 was obtained. These values indicate the kinetic dependencies of $\rho_{m,0}$ upon $[\text{RH}]$, in accordance with eqs. (11) and (12), respectively. Thus, orders of 1 and between 1 and 2 were obtained for the low and high oxygen concentrations, respectively, as predicted.

In the case of the catalyzed autoxidation, it may be seen from Figure 3 (low catalyst concentration), a typical plot, that as $[\text{RH}]$ increases, the observed rate of carbonyl formation increases, cf. eq. (16). Figure 4 shows a plot of $\log \rho_{m,\text{net}}$ versus $\log [\text{RH}]$ for relatively low concentration of the catalyst and for oxygen concentrations of 0.5%, 10%, and 100%. The slopes

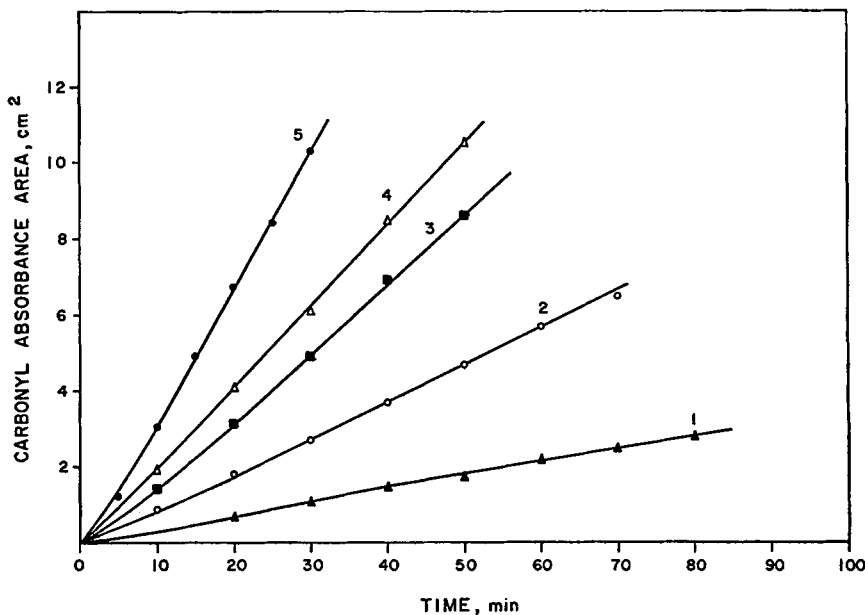


Fig. 3. Carbonyl absorbance area vs. reaction time at 120°C , for pure oxygen and $[\text{Co(III)}] = 3 \times 10^{-7}$ mole/7.5 mg of sample, at various concentrations of APP: (1) 24.6%; (2) 45.0%; (3) 62.1%; (4) 76.6%; (5) 100%.

of the plots are 0.92, 1.17, and 1.75 for 0.5%, 10%, and 100% $[O_2]$, respectively. (In order to correct $\rho_{m,net}$ for various values of $[RH]$ at 0.5% oxygen concentration, $\rho_{m,0}$ was obtained by extrapolation from a plot of $\log \rho_{m,0}$ versus $\log [O_2]$.¹¹) An order of unity with respect to $[RH]$ for 0.5% oxygen would be expected from eq. (14), (observed, 0.92). From eq. (15), it would be anticipated that at moderate concentrations of oxygen (10%),

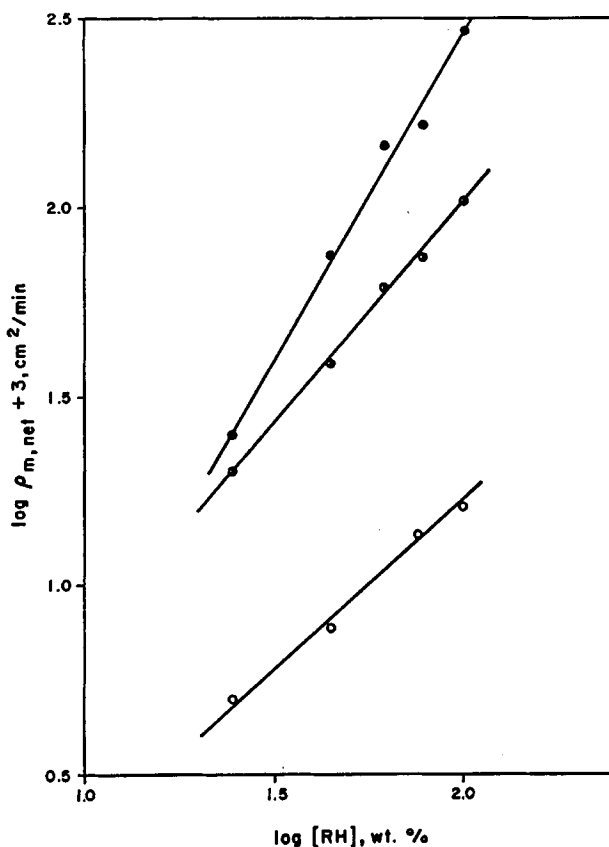


Fig. 4. Dependence of maximum rate, $\rho_{m,net}$, on concentration of APP at 120°C and $[Co(III)] = 3 \times 10^{-7}$ mole/7.5 mg sample: (○) 0.5% O_2 ; (◐) 10% O_2 ; (●) 100% O_2 .

an order of between 1 and 2 could be expected. Although a similar kinetic dependency should be anticipated at very high oxygen concentrations (100%) from eq. (16), it should be noted here that in the former case the kinetic dependency should be of lower order (observed, 1.17 and 1.75 for 10% and 100% oxygen, respectively.)

Figure 5 shows a plot of $\log \rho_{m,net}$ versus $\log [RH]$ at relatively high catalyst concentration and for oxygen concentration of 10% and 100%. For the lower oxygen concentration, a slope of 2.00 was obtained, whereas a

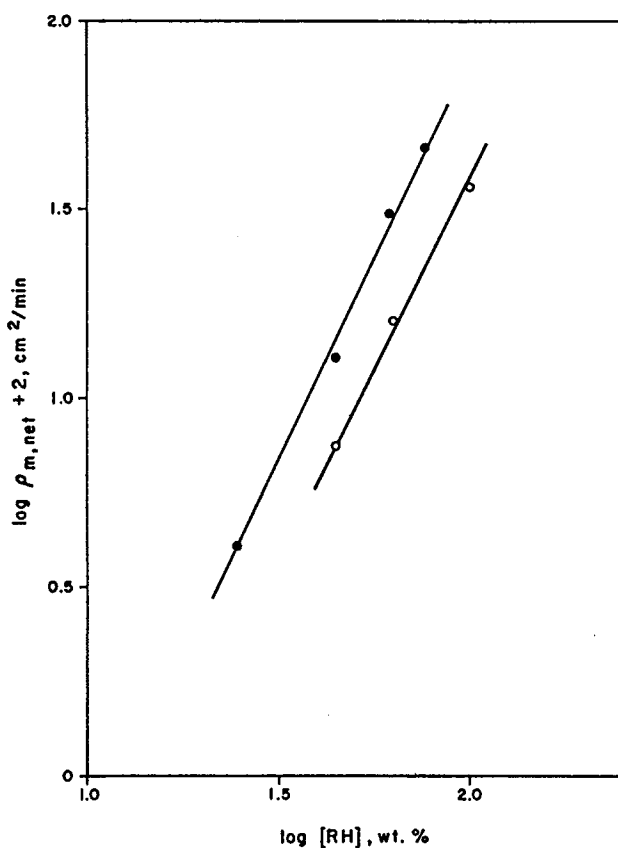


Fig. 5. Dependence of maximum rate, $\rho_{m,net}$, on concentration of APP at 120°C and $[\text{Co(III)}] = 1.7 \times 10^{-6}$ mole/7.5 mg of sample: (○) 10%; (●) 100% O₂.

slope of 2.14 was obtained for the higher oxygen concentration. A slope of 2 would be expected from eq. (17) for various oxygen concentrations.

It can be seen from the preceding that kinetic dependencies, as experimentally obtained, are in very good agreement with the values predicted from theoretical considerations, which therefore further supports the validity of the kinetic scheme previously proposed for polyolefin autoxidation. (However, it should be realized that other schemes may predict similar behavior.)

Finally, we would like to note that we have experimentally observed the presence of peroxides, which offers support for step (9b). However, the formation of hydroperoxides appears to be of greater importance, cf. step (3), since the ratio of hydroperoxides to peroxides was found to be of the order of 10:1 and 24:1 for uncatalyzed and catalyzed oxidations ($[\text{Cat}] = 3 \times 10^{-7}$), respectively (at 120°C and 100% oxygen for both cases).

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