The Iron Salt-Catalyzed Autoxidation of Atactic Polypropylene

S. S. STIVALA and B. R. JADRNICEK,* *Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030* and L. REICH, *Polymer Research Branch, Picatinny Arsenal, Dover, New Jersey 07801*

Synopsis

The iron-catalyzed autoxidation of atactic polypropylene has been studied in the solid phase using infrared spectroscopy. The reaction temperature ranged from 110° to 130° C, the ferric acetylacetonate concentration varied from 0.3×10^{-7} to 90.0×10^{-7} mole per 7.5 mg atactic polypropylene, and the oxygen concentration varied from 5 to 100 vol-%. In the region of relatively low catalyst concentrations, the maximum steady rate varied approximately first order in respect to the catalyst concentration and about zero order at relatively high values of the catalyst concentration. Linear relationships between the maximum steady rate and the oxygen concentration, for both low and high concentrations, were obtained. A general scheme and kinetic expressions derived therefrom previously reported for the uncatalyzed autoxidation of polyolefins and recently modified to account for cobalt-catalyzed autoxidation of atactic polypropylene has been successfully applied to the experimental results.

INTRODUCTION

Salts of transition metals are known to have a strong influence on the autoxidation of hydrocarbons and polyolefins.[1] Several investigators have studied the effects of different metal salt catalysts on oxidizability of polymers.[2-5] The authors have recently extended a kinetic oxidation scheme[1] to the metal salt-catalyzed oxidation of polyolefins to account for the kinetics of cobalt acetylacetonate-catalyzed oxidation of atactic polypropylene.[6-8] Closely related to this work was a study on the effect of oxidation-reduction potential of transition metals on the metal salt-catalyzed oxidation of atactic polypropylene (APP).[9] It was established that cobalt(III) acetylacetonate was the most active catalyst of the metal catalysts studied and that the iron(III) salt was one of the least effective. Iron is commonly found in commercial equipment used for either the preparation or processing of various polymers. Thus, it may be often present as an impurity in polymers such as polypropylene. The purpose of this paper is to report the kinetic behavior of iron salt-catalyzed autoxidation of APP in the solid phase. To explain the experimental results ob-

* Post-doctoral research associate, 1969.

tained, a mechanism proposed earlier, will be applied and derived results will be compared with those for the cobalt-catalyzed reaction.

EXPERIMENTAL

Starting Materials

Atactic Polypropylene (APP).   An uninhibited sample of APP, obtained from Avisun Corp., was purified as described previously.[10]   Upon ignition, the APP sample gave an ash content of 0.008%.   A number-average molecular weight, obtained by osmometry, was 30,000.

Catalysts.   Ferrous and ferric acetylacetonates (2,4-pentanediones) were obtained from J. T. Baker Chemical Co. (the highest purity grade) and were used without further purification.   It was observed that carbon tetrachloride solutions of the ferric salt were unstable upon standing for two to three days (a reddish-brown precipitate formed).   This necessitated continual preparation of fresh solutions.

Apparatus

Infrared spectra were taken on a Perkin-Elmer recording spectrophotometer Model 21.   An oxidation cell used and the other details have been given in an earlier work.[6,10]

Procedure

A film of APP containing a certain amount of either iron(II) or iron(III) acetylacetonate was cast onto optical sodium chloride disk from a solution of purified APP in carbon tetrachloride.   The films (approx. 2.5 mils thick) on the disks were assembled in the oxidation cell and attached to the IR spectrophotometer.   Known amounts of dried oxygen and nitrogen mixtures were passed through the oxidation cell at a constant rate of 30 ml/min after the desired temperature had been reached.   The ratios of oxygen to nitrogen mixtures used were (by volume): 5:95, 10:90, 25:75, 50:50, 75:25, and 100:0.   Reaction temperatures ranged from 110° to 130°C.   The catalyst content in the film was varied from 0.3×10^{-7} to 9.0×10^{-6} mole per 7.5 mg APP.   Infrared spectra of the carbonyl region were recorded as a function of reaction time at a constant catalyst concentration, for different temperatures and oxygen-to-nitrogen ratios (cf. Figs. 1 and 2).   Further, at a constant temperature of 110°C and in pure oxygen, carbonyl concentration was determined as a function of reaction time for various metal catalyst concentrations (Fig. 3).   Apparent weight losses of polymer films during oxidation were found to be low (< 1%).

The character of the infrared absorption band (5.4–6.1 μ) was found to be generally the same as those obtained for the uncatalyzed oxidation of APP[10] and the cobalt salts-catalyzed oxidation of APP.[6]   The amount of carbonyl (from aldehydes, ketones, acids, etc.) formed as a function of time was measured in terms of the total absorbance area (cm²) of the carbonyl band as described previously.[10]   Further, based upon work reported
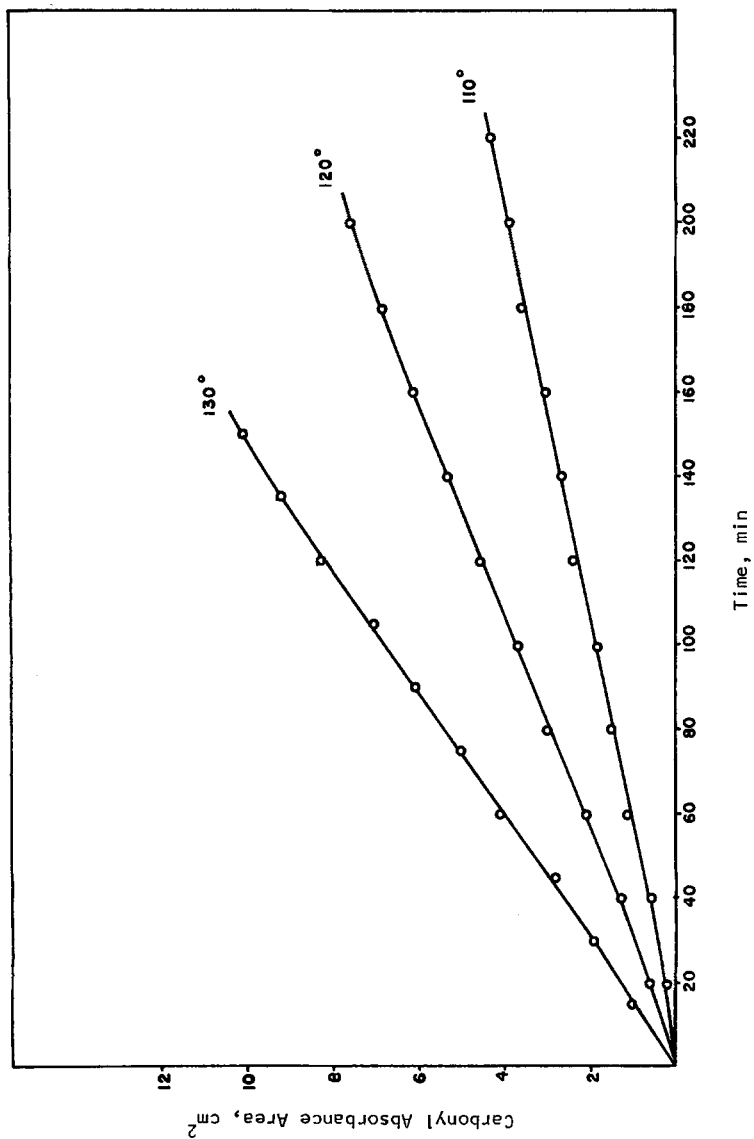
Fig. 1. Carbonyl absorbance area vs. reaction time at oxygen: nitrogen ratio of 25:75 for various temperatures; $[Fe(III)] = 3 \times 10^{-7}$ mole/7.5 mg APP.
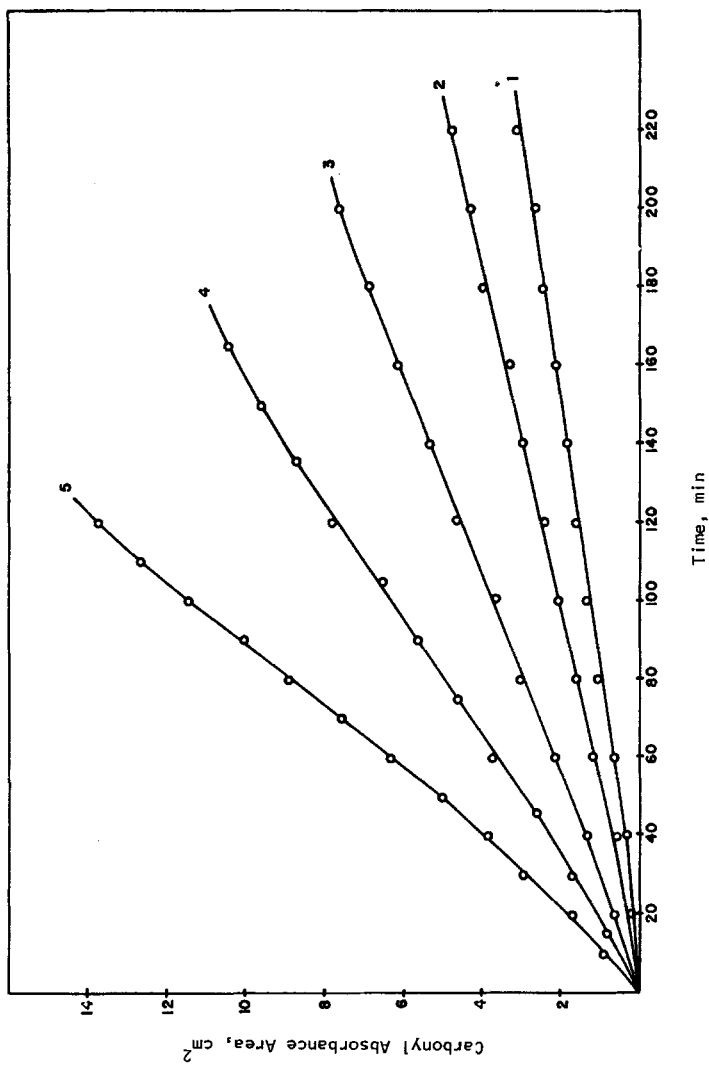
Fig. 2. Carbonyl absorbance area vs. reaction time at 120°C and [Fe(III)] = 3 × 10⁻⁷ mole/7.5 mg APP, for various ratios of oxygen:nitrogen ratios: (1) 5:95; (2) 10:90; (3) 25:75; (4) 50:50; (5) 100:0.
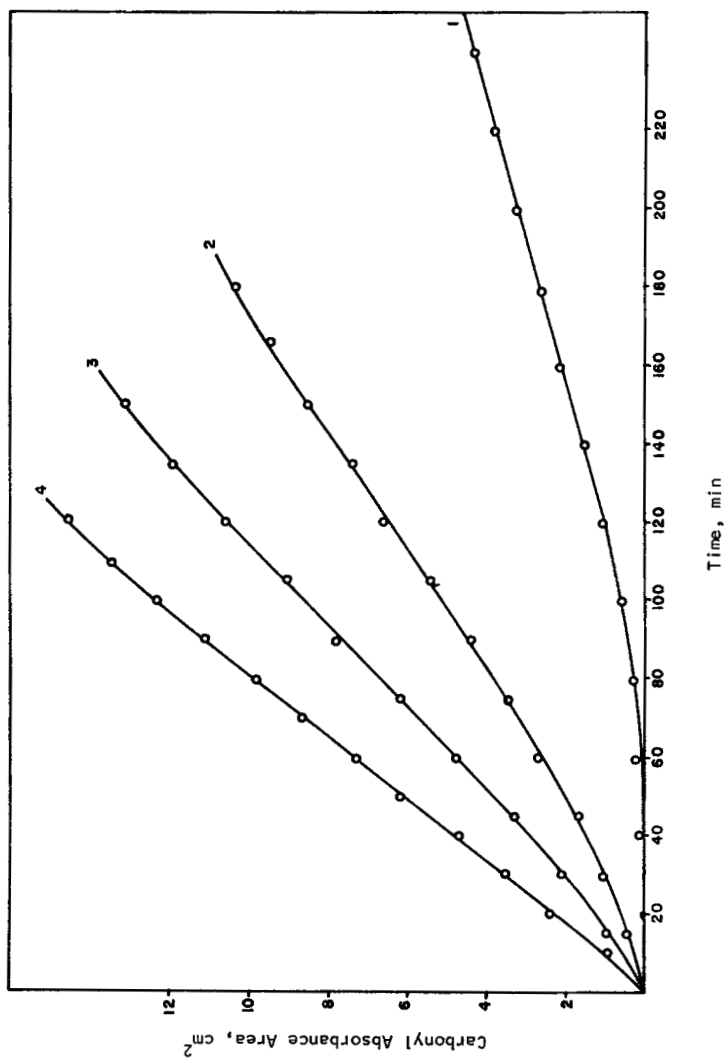
Fig. 3. Carbonyl absorbance area vs. reaction time at 110°C in pure oxygen, for various concentrations of ferric acetylacetonate (per 7.5 mg APP): (1) 0.3×10^{-7} mole; (2) 3.0×10^{-7} mole; (3) 9.0×10^{-7} mole; (4) 15.0×10^{-7} mole.

for the uncatalyzed oxidation of APP,[10] the following should be valid for the iron salt-catalyzed oxidation of APP: (1) The Lambert-Beer's law holds. (2) Diffusion control does not apply to the 2.5-mil-thick APP film under the experimental conditions. (3) No oxidation products containing ester carbonyl group could be detected; this implies that alkoxy radicals (RO·) are not important in the formation of alcohols, since these alcohols could presumably react with acid products to yield esters.

The amounts of carbonyl present as aldehydes and ketones ($\approx$ 15%), determined as hydrazones, were found to be similar to those estimated in the uncatalyzed and cobalt-catalyzed APP oxidations.[6,10] Further, it is tacitly assumed that the formation of carbonyl is the rate-controlling step. Thus, carbonyl absorbance areas are directly proportional to the total carbonyl concentration. The maximum conversion, under the exerimental conditions, was $\approx$ 2 wt-% as carbonyl.

RESULTS AND DISCUSSION

The presence of iron acetylacetonate in the film has an influence on the rate of carbonyl formation. Similarly to the cobalt-catalyzed oxidation of APP, the induction periods were short but the maximum steady rates were much lower under identical experimental conditions. Thus, at an oxygen-to-nitrogen ratio of 25:75, [Cat] = 3×10^{-7} mole/7.5 mg APP, and 120°C, the maximum rate, $\rho_{m,tot}$, was equal to 12.1 cm²/min for cobaltic and to 4.0 cm²/min for ferric acetylacetonate. Since the authors found that catalytic activity of salts of transition metals (logarithm of maximum carbonyl formation) increased approximately linearly with the increasing redox potential of these metals,[9] such behavior was anticipated.

It was experimentally observed (Fig. 4) that when the catalyst was added in the lower valency state, the maximum steady rate (ρ_m = 6.6 cm²/min) was reached only after a relatively long induction period (ca. 30 min). Under identical conditions, the ferric salt showed virtually no induction period (ρ_m = 6.8 cm²/min). A similar effect was observed with the cobaltous and cobaltic pair of catalysts.[6]

Maximum steady rates of carbonyl formation, $\rho_{m,tot}$, were determined from plots of carbonyl absorbance area versus time for various temperatures and concentrations of catalyst and oxygen (cf. Figs. 1 to 3). From these maximum rates were subtracted values of the maximum rates, $\rho_{m,0}$, reported previously for the uncatalyzed oxidation of APP, in order to obtain the maximum rate of the catalyzed reaction, $\rho_{m,net}$ (see Table I of ref. 10).

Using the modified oxidation scheme which has been put forward for the cobalt-catalyzed autoxidation of APP,[6] and taking into account all assumptions made in this connection, we may write

$$\rho_{m,net} = \rho_{m,tot} - \rho_{m,0}$$

$$= \frac{k_3 k_6 [RH] \varphi (1 - e^{-A t_m})/(k_3 + k_4)[RH] + k_4'[Cat]}{2k_5 + k_6 - (k_3 k_5 [RH]/(k_3 + k_4)[RH] + k_4'[Cat])} \quad (1)$$
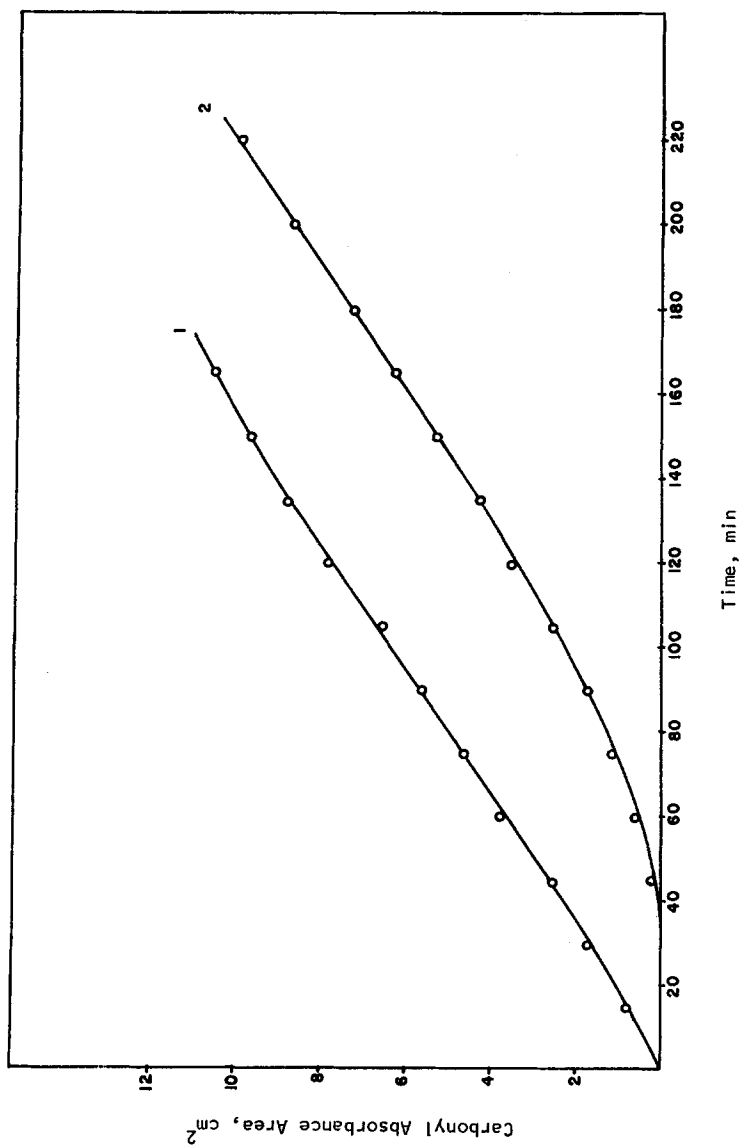$$(2k_8[RH] + k_9[O_2]/k_8[RH] + k_9[O_2])$$

Fig. 4. Carbonyl absorbance area vs. reaction time at 120°C and oxygen:nitrogen ratio of 50:50; [Cat] = 3×10^{-7} mole/7.5 mg APP: (1) Fe(III) acetylacetonate; (2) Fe(II) acetylacetonate.

where φ is the rate of initiation ($= k_i[\text{RH}][\text{O}_2][\text{Fe}^{3+}]$), A is the value of the denominator in the above expression, t_m is time to reach the maximum reaction rate, and k's are all rate constants and subscripts denote reaction steps in the catalyzed oxidation mechanism.[6] Various simpler expressions could be derived from eq. (1) depending upon experimental conditions.

Rate Dependence on Oxygen Concentration

For the conditions of constant [RH], [Cat], and temperature, eq. (1) yields

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

where α, β, and K_3 are constants (cf. ref. 6).

(i) When oxygen concentration is relatively high, i.e., $(1 - \beta)[\text{O}_2] \gg (1 - 2\beta)K_3$, eq. (2) becomes

$$\rho_{m,net} = \alpha_1 K_3 + \alpha_1[\text{O}_2] \tag{3}$$

where $\alpha_1 \equiv \dfrac{\alpha\, k_i[\text{RH}][\text{Cat}]}{1 - \beta}$.

(ii) When oxygen concentration is relatively low, i.e., $(1 - \beta)[\text{O}_2] \ll (1 - 2\beta)K_3$, eq. (2) reduces to

$$\rho_{m,net} = \frac{\alpha_2[\text{O}_2]}{1 - 2\beta} \tag{4}$$

where $\qquad\qquad \alpha_2 = \alpha_1 (1 - \beta)$.

Equation (2) then may be rewritten as

$$\rho_{m,net} = \frac{\alpha_2[\text{O}_2]\,(K_3 + [\text{O}_2])}{K_3(1 - 2\beta) + [\text{O}_2](1 - \beta)}. \tag{5}$$

The constants K_3, α_2, and β where estimated prior to correlating $\rho_{m,net}$ as a function of oxygen concentration. Since values of K_3 are approximately the same as K_3 values in the uncatalyzed oxidation of APP, the latter values were utilized.[10] From these values of K_3, values of α_2 and β were estimated in a similar manner as for the cobalt-catalyzed oxidation.[6] The maximum steady rate of carbonyl formation for the uncatalyzed oxidation may be expressed as

$$\rho_{m,0} = \frac{K_1[\text{O}_2]}{1 - K_2/K_3 + [\text{O}_2]} \tag{6}$$

where constants have been defined previously.[10] Dividing eq. (5) by eq. (6), the following is obtained:

$$R = \frac{\alpha_2\,(K_3 - K_2 + [\text{O}_2])}{K_1\,\{K_3\,(1 - 2\beta) + [\text{O}_2]\,(1 - \beta)\}} \tag{7}$$

where $R = \rho_{m,net}/\rho_{m,0}$.

This equation reduces for high oxygen concentrations to

$$R \approx \frac{\alpha_2}{K_1 (1 - \beta)} \tag{8}$$

while for low concentrations

$$R \approx \frac{\alpha_2 (K_3 - K_2)}{K_1 K_3 (1 - 2\beta)}. \tag{9}$$

Values of constants α_2 and β were estimated by means of eqs. (8) and (9) and previously reported values of K_1, K_2, and K_3 (cf. Table I). From the values of α_2 and β in Table I and from eq. (5) were calculated theoretical values of $\rho_{m,net}$ at various oxygen concentrations and reaction temperatures. Figure 5 shows calculated curves in plots of $\rho_{m,tot}$ (obtained from $\rho_{m,net}$) versus the concentration of oxygen. A good agreement was found between calculated and observed values. The maximum rate of carbonyl formation in the iron-catalyzed system, similarly to the uncatalyzed and cobalt-catalyzed oxidations, shows the linear relationships for high oxygen concentrations which agrees with the theoretical predictions.

TABLE I
Values of α_2 and β under Various Experimental Conditions[a]

Reaction temp., °C	K_1, (cm²/min) × 10⁴	K_2	K_3	α_2, (cm²/min) × 10⁴	β
110	2.15	27.0	34.9	1.46	.468
120	5.50	35.2	44.0	2.06	.477
130	9.20	48.6	57.6	2.81	.487

[a] Constants K_1 and α_2 are expressed in arbitrary units depending upon the scale used in obtaining carbonyl absorbance areas.

Rate Dependence on Catalyst Concentration

Rewriting eq. (1) for constant values of oxygen and APP concentrations and temperature,

$$\rho_{m,net} = \frac{C_1 [Cat]}{k_4' [Cat] + C_2 [RH]} \tag{10}$$

where constants C_1 and C_2 have been defined earlier.[6]

Two cases may be considered:

(i) At relatively low values of the catalyst concentration, $k_4' [Cat] \ll C_2 [RH]$, eq. (10) becomes

$$\rho_{m,net} = \frac{C_1 [Cat]}{C_2 [RH]}. \tag{11}$$
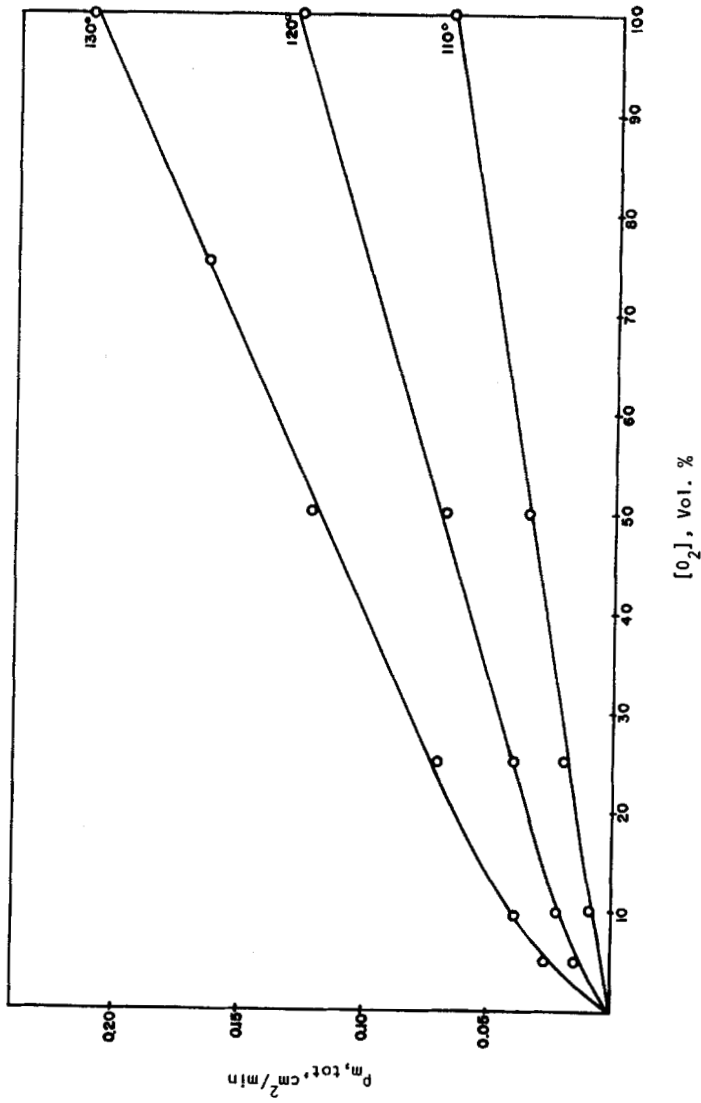
Fig. 5. Effect of oxygen concentration on the maximum rate for various temperatures; [Fe(III)] = 3×10^{-7} mole/7.5 mg APP.
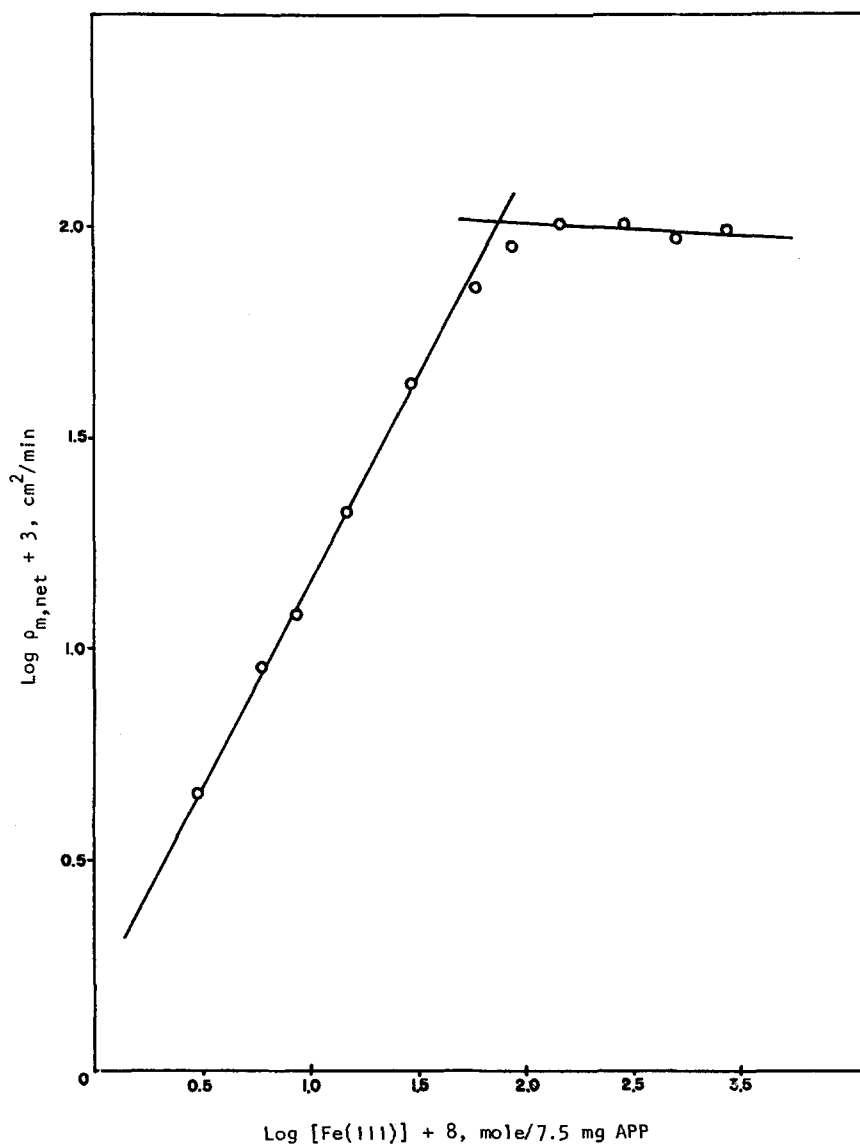
Fig. 6. Relationship between maximum rate and concentration of ferric acetylacetonate at 110°C in pure oxygen.

(ii)   At relatively high catalyst concentrations, when k_4' [Cat] $\gg C_2$ [RH], eq. (10) reduces to

$$\rho_{m,net} = \frac{C_1}{k_4} = \text{const.} \tag{12}$$

Equations (11) and (12) suggest that at very low concentrations of the catalyst the order with respect to [Cat] will be one, which eventually tends
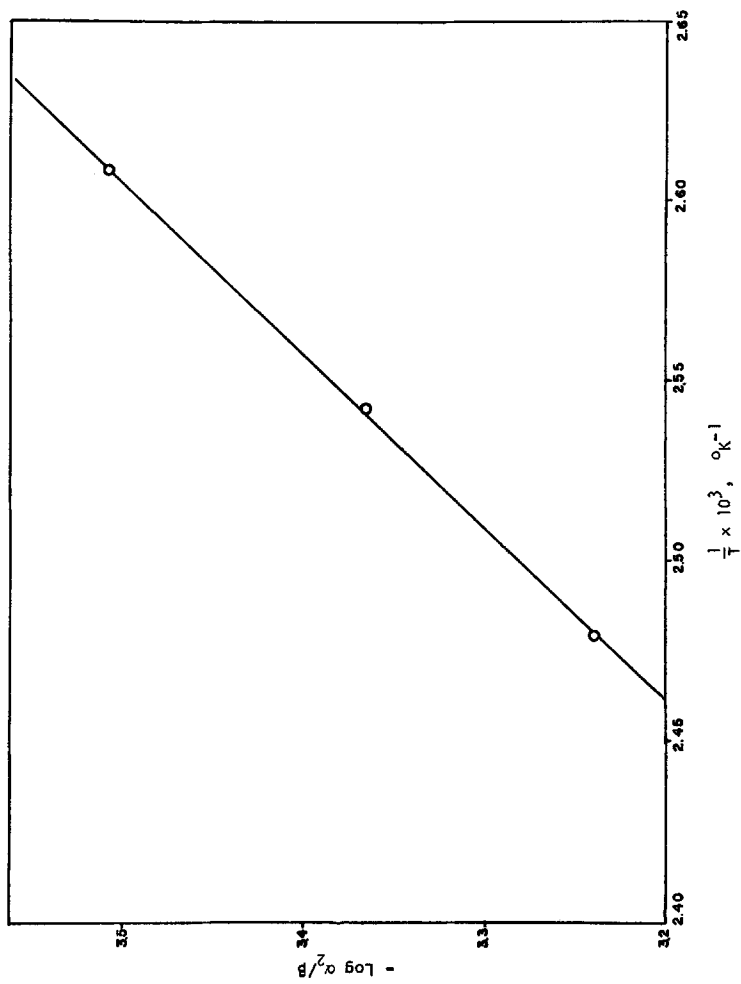
Fig. 7. Plot of log (α_2/β) vs. reciprocal temperature, $1/T$.

to zero at high catalyst concentrations. Figure 6 shows a plot of the maximum rate $\rho_{m,net}$ versus the concentration of ferric acetylacetonate. The experimental results show that over the concentration range of 0.3 to 6.0×10^{-7} mole (in pure oxygen at 110°C), the kinetic order with respect to [Fe(III)] is 0.97, as anticipated. The order continues to decrease over the concentration range 0.6 to 1.5×10^{-6} mole iron, after which the rate becomes independent of the catalyst concentration, as is commonly observed with the metal-catalyzed oxidations of aromatic hydrocarbons.[1] This can be seen from Figure 6. The kinetic dependency of the maximum rate $\rho_{m,net}$ upon the catalyst concentration was found to be approximately zero for the range of [Fe(III)] from 1.5 to 9.0×10^{-6} mole/7.5 mg APP. Similar relationships were observed for the oxidation of APP catalyzed by cobaltic acetylacetonate. However, the catalyst concentration at which the maximum rate starts to level off was somewhat lower, 5.1×10^{-7} mole, as compared with 7.6×10^{-7} mole for Fe(III) acetylacetonate (using extrapolation).

An Arrhenius plot of log (α_2/β) versus reciprocal temperature, $1/T$ (cf. Fig. 7), yields an activation energy $E = 10$ kcal/mole, which equals $E_i + E_6 - E_5$. (The subscripts denote corresponding reaction steps in the oxidation mechanism.[6]) For the uncatalyzed reaction, $E = 17$ kcal/mole. The lower value of the activation energy for the catalyzed reaction is, of course, anticipated, since activation energy of initiation, E_i, should be lower than that for the uncatalyzed oxidation. The value of $E = 7$ kcal/mole was obtained during the cobalt salt-catalyzed oxidation of APP.[6] The higher value of E for iron salt-catalyzed reaction is expected, as iron acetylacetonate showed a lower catalytic activity in earlier studies.[9]

References

1. L. Reich and S. S. Stivala, *Autoxidation of Hydrocarbons and Polyolefins*, M. Dekker, New York, 1969.

2. Z. Osawa, T. Shibamiya, and K. Matsuzaki, *Kogyo Kagaku Zasshi*, 71, 552 (1968).

3. C. E. H. Bawn and S. A. Chaudhri, *Polymer*, 9, 81 (1968).

4. L. H. Lee, C. L. Stacy, and R. G. Engel, *J. Appl. Polym. Sci.*, 10, 1699 (1966).

5. L. L. Yasina, V. B. Miller, and Yu A. Shlyapnikov, *Izv. AN SSSR, Ser. Khim.*, 11, 2635 (1968).

6. S. S. Stivala, B. R. Jadrnicek, and L. Reich, *Macromolecules*, 4, 61 (1971).

7. L. Reich, B. R. Jadrnicek, and S. S. Stivala, *Polym. Eng. Sci.*, in press.

8. B. R. Jadrnicek, S. S. Stivala, and L. Reich, *J. Appl. Polym. Sci.*, in press.

9. L. Reich, B. R. Jadrnicek, and S. S. Stivala, *J. Polym. Sci.*, 9, 231 (1971).

10. B. R. Jadrnicek, S. S. Stivala, and L. Reich, *J. Appl. Polym. Sci.*, 14, 2537 (1970).