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KINETICS OF AUTOXIDATION OF ATACTIC POLYPROPYLENE IN THE PRESENCE OF COBALT SALTS BY INFRARED SPECTROSCOPY

by

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Synopsis

The autoxidation of a film of atactic polypropylene (APP) in the presence of cobalt salts was studied quantitatively by means of infrared spectroscopy. Reactions were traced as a function of temperature, oxygen concentration and time. Temperatures varied from 100° to 130°C and oxygen concentrations from 5 to 100% by volume. A general reaction scheme previously reported by the authors for the uncatalyzed autoxidation of atactic polypropylene was modified to account for the cobalt acetylacetonate-catalyzed autoxidation of APP in the bulk phase.

INTRODUCTION

Mathematical expressions derived from a general kinetic scheme have been satisfactorily applied to the uncatalyzed autoxidation of polyolefins such as, polypropylene (1-3) and polybutene (1,4,5) in the bulk phase. This scheme was recently modified by Bawn and Chaudhri (6) to account for the kinetics of manganese salts-catalyzed autoxidation of atactic polypropylene (APP) in solution. Other workers (1,7-10) have also investigated the metal catalyzed autoxidation of polyolefins, but in a relatively qualitative manner. The purpose of this paper is to extend the modified general scheme, in a quantitative manner, to the cobalt (III) acetylacetonate-catalyzed autoxidation of APP in the bulk phase.

EXPERIMENTAL

A. Starting Materials

1. Atactic polypropylene (APP)

An uninhibited sample of APP, obtained from Avisun Corporation, was refluxed with diethyl ether for two hours and insoluble residue (presumably an isotactic fraction) was removed by filtration through glass wool. The resulting filtrate was slowly added to methanol to precipitate the APP. The precipitate was repeatedly washed with methanol and dried at room temperature under vacuum. The dried APP was redissolved in diethyl ether, reprecipitated and re-washed with methanol. This procedure was repeated once more. The dried APP was finally purified by passing its ether solution through a column of aluminum oxide. The APP was precipitated from the resulting eluent and dried under vacuum at 40°C for two hours.

The yield, based on the original weight of APP, was about 60 wt.-%. An infrared spectrum of the dried APP was similar to that reported by Luongo (11). From this spectrum it was ascertained, using the bands at 974 and 995 cm^{-1} (11), that the sample was close to 100% atactic. Upon ignition, the APP sample gave an ash content of 0.008%, and by the use of a membrane osmometer a number average molecular weight of 30,000 was obtained.

2. Metal salt catalyst

Cobalt (III) and cobalt (II) acetylacetonates (2,4-pentanediones) were obtained from J. T. Baker Chemical Co. (highest purity grade) and were used without further purification; mp [Co(III) salt], 210 - 213°C.

B. Apparatus

Infrared spectra were obtained from a Perkin-Elmer recording spectrophotometer, Model 21. Attached to this instrument was an oxidation cell which was essentially similar to that described previously (1). Briefly, the cell consists of a brass cylindrical body into which are introduced a standard salt plate, an aluminum spacer, a salt plate holder, a second salt plate containing the film specimen, and a threaded lock ring, respectively. The body of the cell is equipped with a temperature-controlling thermistor, reaction temperature-indicating thermistor, and numerous turns of heating wire. A 1/4 in. metallic orifice perpendicular to the main body of the cell is used to admit gas, e.g., O_2 and O_2—N_2 , and a second smaller opening at the opposite end permits the escape of the gas. The temperature controller, Thermonitor Model ST (E. H. Sargent & Co.) had a temperature range up to 150°C with a nominal temperature variation of ± 0.05°C. The cell chamber temperature was measured with an iron-constantan thermocouple connected to a Millivolt Potentiometer (Leeds & Northrup). The Thermonitor temperature reading was calibrated against the potentiometer.

For the quantitative estimation of carbonyl content in the oxidized APP as ketones and aldehydes, in the form of hydrazones, a Beckman DU Spectrophotometer Model 2400 was used (3).

C. Procedure

Purified APP was dissolved in carbon tetrachloride and a portion of this solution was poured onto an optical sodium chloride disc attached to which was a Teflon gasket serving as a mold. Immediately following, a solution of either cobalt (III) or cobalt (II) acetylacetonate in carbon tetrachloride was added to the mold. Films of about 2 1/2 mils thickness were obtained by the slow evaporation of the solvent at room temperature and by drying under vacuum for ca. 30 minutes. The films on the sodium chloride discs were assembled in the oxidation cell which was then attached to the infrared spectrophotometer. Known amounts of purified oxygen and nitrogen mixtures (purified by means of sodium hydroxide and anhydrous calcium chloride) were passed into the oxidation cell at a constant rate of 30 ml/min after the desired reaction temperature had been reached. (Prior to reaching this temperature, the APP sample was heated under a blanket of nitrogen). The ratios (by volume) of oxygen to nitrogen mixtures used were: 5/95, 10/90, 25/75, 50/50, 75/25, and 100/0. The catalyst content in the film was varied from (0.3-82.0) x 10^{-7} mole/7.5 mg APP. Reaction temperatures ranged from 100° - 130°C. Infrared spectra of the carbonyl region were recorded as a function of reaction time, at a constant catalyst concentration, for different temperatures and O_2/N_2 ratios, cf. Figs. 1 and 2. Further, at a constant temperature of 110°C and at O_2/N_2 ratios of 100/0 and 50/50 carbonyl concentration was determined as a function of reaction time for various metal catalyst concentrations, cf. Fig. 3. Apparent weight losses of APP films during oxidation were found to be low (< 1%).

The character of the infrared carbonyl absorption band (5.4 - 6.1μ) was generally the same as that obtained for the uncatalyzed oxidation of APP (3). The amount of carbonyl (from aldehydes, acids, etc.) formed as a function of time was measured in terms of the total absorbance area (arbitrary units of cm^2) of the carbonyl band as described previously (3). Further, based upon work reported for the uncatalyzed oxidation of APP, the following should be valid for the metal salt-catalyzed oxidation of APP: (a) The Lambert-Beer law holds; (b) Diffusion control does not apply to the 2 1/2 mil thick APP film under the various experimental conditions employed; (c) No oxidation products containing ester moieties could be detected.

The amounts of various carbonyl-containing species were estimated by the same technique employed for the uncatalyzed oxidation of APP. In this manner, the following results were obtained under various experimental conditions: aldehydes and ketones ≈ 15 wt.-%, acids ≈ 85 wt.-% (by difference). (These values are similar to those found in the uncatalyzed APP oxidation (3)]. Thus, absorbance areas (5.4 - 6.1μ) are directly proportional to total carbonyl concentration. Under the experimental conditions employed, the maximum conversion (up to the maximum rate of carbonyl formation) was ca. 2 wt.-% as carbonyl.

The wt.-% of hydroperoxide (as peroxidic oxygen) was estimated as follows (12). Briefly, an APP sample was added to isopropanol followed by 1 ml. of saturated KI and 1 ml. of glacial acetic acid. The mixture was heated almost to boiling, kept at incipient boiling for ca. 5 min. and then titrated without cooling with standard sodium thiosulfate to the disappearance of the yellow color.

THEORY

The following represents a general scheme (2,3) that was modified to account for the experimental results obtained during the cobalt (III) acetylacetonate-catalyzed autoxidation of APP in the bulk phase.

$$\text{Initiation rate} \equiv \varphi = k_1[RH][O_2][Co(III)] \quad (1)$$

$$R\cdot + O_2 \xrightarrow{k_2} RO_2\cdot \quad (2)$$

$$RO_2\cdot + RH \xrightarrow{k_3} RO_2R + H\cdot \text{ (one R can be H)} \quad (3)$$

$$RO_2\cdot + RH \xrightarrow{k_4} \text{inactive products} \quad (4)$$

$$RO_2\cdot + Cat \xrightarrow{k_4'} \text{inactive products} \quad (4')$$

$$RO_2R(RO_2H) + Co(III) \xrightarrow{k_5} RO_2\cdot + Co(II) + R^+ \quad (5)$$

$$RO_2R(RO_2H) + Co(II) \xrightarrow{k_5'} RO\cdot + Co(III) + RO^- \tag{5'}$$

$$RO_2R(RO_2H) + Cat \xrightarrow{k_6} \text{inactive non-volatile products } (>C{=}O,\ -CHO,\ \text{etc.}) \tag{6}$$

$$RO_2R(RO_2H) \xrightarrow{k_{6a}} \text{inactive non-volatile products } (>C{=}O,\ -CHO,\ \text{etc.}) \tag{6a}$$

$$RO\cdot \xrightarrow{k_7} R\cdot' + \text{volatile products} \tag{7}$$

$$R\dot{'} + RH \xrightarrow{k_8} R'H + R\cdot \tag{8}$$

$$R\dot{'} + O_2 \xrightarrow{k_9} \text{less active products} \tag{9}$$

In Eq. (1), the initiation step is assumed to provide R· radicals. (The assumption of $RO_2\cdot$ radicals will not greatly affect the kinetic expressions derived subsequently). Betts and Uri (13) have postulated a similar initiation step to account for the autoxidation of several hydrocarbons in the presence of various cobalt complexes. Steps (2)-(4), (6a), and (7)-(9) have been previously reported for the uncatalyzed autoxidation of various polyolefins (1). Steps (4) and (4') have been included to account for the deactivation of $RO_2\cdot$ radicals by inherent impurities in the substrate, RH , and by the catalyst, Cat, respectively. No differentiation is made as to the oxidation state of the catalyst molecule which undergoes this deactivation reaction. Other workers (14) have also postulated a deactivation step such as (4') to account for the metal salt-catalyzed autoxidation of tetralin. Steps (5) and (5') have been frequently utilized for the metal catalyzed autoxidation of various hydrocarbons (1). Kamiya (15) has postulated a reaction similar to step (6) during the metal catalyzed autoxidation of tetralin.

It was experimentally observed, Fig. 4, that when the Co(II) salt was used as catalyst, a relatively long induction period obtained (ca. 50 min.) followed by a rapid increase in carbonyl rate formation to a maximum value (ρ_m) of 13 1/2 cm^2/min. Under identical conditions, the Co(III) salt showed virtually no induction period (ρ_m = 15 cm^2/min). Thus, the latter valence form is the more effective catalyst. Since the catalyst is added in the Co(III) form and any Co(II) produced during the oxidation would be converted into the higher valence state, we may write

$$k_5[\mathrm{Co(III)}] \equiv k_5[\mathrm{Cat}] = k_5'[\mathrm{Co(II)}] \qquad (10)$$

In obtaining Eq. (10), it has been assumed that steady-state conditions apply and that steps (4') and (6) are of relatively minor importance in comparison with steps (5) and (5') ($k_5 \gg k_6$). Further, Eq. (10) would be more valid at relatively low conversions. Also, from the scheme, assuming steady-state conditions for $[R\cdot]$, $[R\cdot']$, and $[RO_2\cdot]$,

$$[RO_2\cdot] = \frac{\varphi}{(k_3 + k_4)[RH] = k_4'[\mathrm{Cat}]} + \frac{k_5[\mathrm{Cat}][RO_2R](2k_8[RH] + k_9[O_2])}{(k_8[RH] + k_9[O_2])[(k_3 + k_4)[RH] + k_4'[\mathrm{Cat}]]} \qquad (11)$$

The rate of hydroperoxide formation may be written as,

$$d[RO_2R]/dt = k_3[RO_2\cdot][RH] - (2k_5 + k_6)[\mathrm{Cat}][RO_2R] - k_{6a}[RO_2R] \qquad (12)$$

Upon substituting Eq. (11) into (12) and integrating, there is obtained,

$$[RO_2R] = (B/A)(1 - e^{-At}) \qquad (13)$$

where,

$$A \equiv (2k_5 + k_6)[Cat] + k_{6a} - \frac{k_3k_5[Cat][RH]}{(k_3 + k_4)[RH] + k_4'[Cat]}\left(\frac{2k_8[RH] + k_9[O_2]}{k_8[RH] + k_9[O_2]}\right)$$

$$B \equiv k_3[RH]\varphi \Big/ (k_3 + k_4)[RH] + k_4'[Cat]$$

From Eq. (13), the maximum concentration of hydroperoxide, $[RO_2R]_m$, at time, t_m, may be written as,

$$[RO_2R]_m = \left[B/(k_{6a} + A_o[Cat])\right](1 - e^{-At_m}) \qquad (14)$$

where,

$$A_o \equiv (A - k_{6a})/[Cat].$$

Now, let the maximum rate of carbonyl formation, $(d[{>}C{=}O]/dt)_m$, be denoted by $\rho_{m,tot}$, where,

$$\rho_{m,tot} \equiv \rho_{m,M} + \rho_{m,o} \qquad (15)$$

and,

$$\rho_{m,M} \equiv k_6[Cat][RO_2R]_m ;$$

$$\rho_{m,o} \equiv k_{6a}[RO_2R]_m .$$

Combining Eqs. (14) and (15) and assuming $A_o/k_6 \gg 1$, we obtain,

$$(\rho_{m,tot} - \rho_{m,o}) \equiv \rho_{m,net} =$$

$$\frac{k_6 k_3 [RH] \varphi \left(1 - e^{-At_m}\right) \Big/ (k_3 + k_4)[RH] + k_4'[Cat]}{2k_5 + k_6 - \left(\dfrac{k_3 k_5 [RH]}{(k_3 + k_4)[RH] + k_4'[Cat]}\right)\left(\dfrac{2k_8[RH] + k_9[O_2]}{k_8[RH] + k_9[O_2]}\right)} \qquad (16)$$

In the derivation of Eq. (16), it was also assumed that the value of $[RO_2R]_m$ for the uncatalyzed oxidation is of the same order of magnitude as that for the metal catalyzed autoxidation under similar experimental conditions. This was experimentally verified. Thus, the following values of $[RO_2R]_m$ (as peroxidic oxygen) were obtained: at 120°C and an O_2/N_2 ratio of 100/0, the value of $[RO_2R]_m = 0.79$ wt.-% for the uncatalyzed oxidation while for the catalyzed oxidation $[RO_2R]_m = 0.75$ wt.-%; and 130°C and an O_2/N_2 ratio of 100/0, the value of $[RO_2R]_m = 0.91$ wt.-% for the uncatalyzed reaction while for the catalyzed oxidation $[RO_2R]_m = 0.85$ wt.-%. In both cases of catalyzed oxidation, $[Co(III)] = 3 \times 10^{-7}$ mole/7.5 mg. APP. Further, in the subsequent use of Eq. (16), it was assumed that $At_m \approx$ constant under the various experimental conditions employed. This was justified as follows. If we assume that $A \gg k_{6a}$ [cf. Eq. (14)] then at constant [Cat], At_m is directly proportional to $A_o t_m$, where $A_o = (2k_5 + k_6)\psi \approx 2k_5\psi$ [cf. Eq. (10)] and $\psi \equiv 1 - \beta(2K_3 + [O_2]/K_3 + [O_2])$ [see Eq. (17) for the definitions of K_3 and β]. At any particular temperature and various O_2/N_2 ratios, it was found that ψt_m (and hence At_m) was approximately constant. In order to correct for temperature effects, it was assumed that E_5 [activation energy corresponding to step (5) and k_5] was 24 kcal/mole (5). Thus, it was found that k_5 increased by a factor of 2.1 for every 10° increase in reaction temperature. Using this factor, values of K_3 and β, and using 110°C as a basis for comparison, it was found that an average value of $(A_o t_m)_{110^o}/(A_o t_m)_T = 1.0 \pm 0.15$ was obtained over a range of temperatures (T) of 100 - 130°C and for O_2/N_2 ratios of 5/95 - 100/0 at a value of $[\mathrm{Cat}] = 3 \times 10^{-7}$ mole/7.5 mg APP.

In a similar manner, it was found that $A_o[\mathrm{Cat}]t_m$ (and hence At_m) was constant at 110°C, and 100% oxygen for various values of [Cat]. Thus, the ratio $(t_m[\mathrm{Cat}]_s)/(t_m[\mathrm{Cat}])$ was found to be about 1.0 ± 0.14 over a range of values of [Cat] of $(0.3 - 82.0) \times 10^{-7}$ mole/7.5 mg APP relative to $[\mathrm{Cat}]_s = 3 \times 10^{-7}$ mole/7.5 mg APP.

Various simpler expressions may be derived from Eq. (16) depending upon experimental conditions employed.

Rate Dependence on Oxygen Concentration

When [RH], [Cat], and temperature are all constant

Under these conditions, Eq. (16) reduces to,

$$\rho_{m,\mathrm{net}} = \frac{\alpha\varphi}{1 - \beta\left(\frac{2K_3 + [O_2]}{K_3 + [O_2]}\right)} \tag{17}$$

where, $K_3 \equiv k_8[\mathrm{RH}]/k_9$;

$$\alpha \equiv \frac{k_3[\mathrm{RH}](1 - e^{-At_m})}{(k_3 + k_4)[\mathrm{RH}] + k_4'[\mathrm{Cat}]}\left(\frac{k_6}{2k_5 + k_6}\right) ;$$

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

(a) When oxygen concentration is relatively high, i.e., $(1 - \beta)[O_2] \gg (1 - 2\beta)K_3$

Under these conditions, Eq. (17) becomes,

$$\rho_{m,net} = \alpha_1 K_3 + \alpha_1 [O_2] \tag{18}$$

where,

$$\alpha_1 \equiv \alpha k_i [RH][Cat]/(1 - \beta).$$

(b) When oxygen concentration is relatively low, i.e., $(1 - \beta)[O_2] \ll (1 - 2\beta)K_3$

Under these conditions, Eq. (17) reduces to,

$$\rho_{m,net} = \frac{\alpha_1(1 - \beta)}{(1 - 2\beta)} [O_2]$$

$$= \alpha_2 [O_2]/(1 - 2\beta) \tag{19}$$

where, $\alpha_2 \equiv \alpha_1(1 - \beta)$

Rate Dependence on Catalyst Concentration

When [RH], $[O_2]$, and temperature are all constant

Under these conditions, Eq. (16) becomes,

$$\rho_{m,net} = C_1[Cat]/k_4'[Cat] + C_2[RH] \tag{20}$$

where,

$$C_1 \equiv k_3[RH]^2(1 - e^{-At_m})\left(\frac{k_6}{2k_5 + k_6}\right) k_i[O_2] \quad ;$$

$$C_2 \equiv (k_3 + k_4) - k_3\left(\frac{k_5}{2k_5 + k_6}\right)\left(\frac{2K_3 + [O_2]}{K_3 + [O_2]}\right).$$

(a) When catalyst concentration is relatively low, i.e., $k_4'[\mathrm{Cat}] \ll C_2[\mathrm{RH}]$.

Equation (20) now becomes,

$$\rho_{m,net} = (C_1/C_2[\mathrm{RH}])[\mathrm{Cat}] \tag{21}$$

(b) When catalyst concentration is relatively high, i.e., $k_4'[\mathrm{Cat}] \gg C_2[\mathrm{RH}]$.

Equation (20) now becomes,

$$\rho_{m,net} = C_1/k_4' = \text{constant} \tag{22}$$

RESULTS AND DISCUSSION

The rate of carbonyl formation was strongly influenced by the addition of cobalt acetylacetonate. Contrary to the uncatalyzed oxidation of APP (3), it was generally observed in the metal catalyzed oxidation of APP that the induction periods were of much shorter duration, when they existed, under similar experimental conditions. Thus, at an O_2/N_2 ratio of 10/90 and at 130°C, an induction time of ca./30 min obtained for the uncatalyzed oxidation (3) whereas, an induction time of ca. 5 min obtained for the catalyzed oxidation (3×10^{-7} mole Co(III)/7.5 mg). Maximum rates of formation of total carbonyl were determined from plots of carbonyl absorbance area versus time for various catalyst and oxygen concentrations and temperatures (cf. Figs. 1 -3). From these maximum rates were subtracted values of the maximum rates reported, in a previous paper, for the uncatalyzed oxidation of APP in order to obtain $\rho_{m,net}$ [see Table 1 of Ref. (3)].

Rate Depdendence on Catalyst Concentration

From Eq. (21), a plot of $\rho_{m,net}$ versus [Cat] should afford a linear relationship, at relatively low values of [Cat], whose kinetic dependency in respect to [Cat] should be of first order. Figure 5 shows a plot of log $\rho_{m,net}$ versus log[Co(III)]. When the relatively low values of [Co(III)] are only included in this plot, the kinetic order in respect to [Co(III)] was found to be 1.0 (cf. Fig. 5), as anticipated, over a range of [Cat] from $(3\text{-}45) \times 10^{-8}$ mole/7.5 mg sample (0.024-0.36 wt.-% as Co) and at 110°C and an O_2/N_2 ratio of 100/0. It may be interesting to note here that when log $\rho_{m,tot}$ was plotted against log[Co(III)], a kinetic order with respect to the latter of 0.6 was obtained. In this connection may be mentioned the work of Bawn and Chaudhri (6). These investigators observed that when the logarithm of the observed maximum rate of oxygen uptake was plotted against log[Mn(III)], a kinetic order of 0.6 was obtained with respect to the latter. However, we have estimated that a kinetic dependency close to unity can be obtained from the data of Bawn and Chaudhri when from the maximum rate of oxygen uptake for the metal catalyzed oxidation is subtracted the appropriate value of the maximum rate for the uncatalyzed reaction (16).

At relatively high values of [Cat], Eq. (22) should be applicable. From this expression, it can be seen that $\rho_{m,net}$ should be constant at high [Cat]. This can be observed from Fig. 5. Thus, at 110°C and an O_2/N_2 ratio of 100/0, the kinetic dependency of $\rho_{m,net}$ upon [Cat] was found to be -0.1 (cf. curve 1 of Fig. 5) for a range of [Cat] from $(0.9 - 8.2) \times 10^{-6}$ mole/7.5 mg APP sample. It is noted from Eqs. (20) and (22), that $\rho_{m,net}$ at high [Cat] should be directly proportional to oxygen concentration. This relationship was found to apply as shown in Fig. 5. Thus, when the autoxidation was carried out at an O_2/N_2 ratio of 50/50 under otherwise similar experimental conditions as for the 100% O_2 oxidation, $\rho_{m,net}$ (avg.) was reduced by a factor of 0.50, as anticipated (cf. curve 2 of Fig. 5). From curve 2, a kinetic dependency of -0.06 was observed with respect to [Cat].

Rate Dependence on Oxygen Concentration

Equation (17) may be rewritten as,

$$\rho_{m,net} = \frac{\alpha_2[O_2]\ (K_3 + [O_2])}{K_3(1 - 2\beta) + [O_2](1 - \beta)} \tag{17a}$$

Prior to correlating $\rho_{m,net}$ as a function of oxygen concentration, it is necessary to estimate the constants K_3, α_2, and β in Eq. (17a). It should be possible from Eq. (18) to estimate K_3 for high values of $[O_2]$ by plotting $\rho_{m,net}$ versus $[O_2]$, Fig. 6. These values of K_3 should be identical with corresponding K_3-values previously reported for the uncatalyzed oxidation of APP (3) under similar experimental conditions. In the following are listed K_3-values (cf. Table 1) for the catalyzed and uncatalyzed oxidations and various reaction temperatures respectively: 39, 35, 110°C; 42, 44, 120°C; and 50, 58, 130°C. Although the agreement appears to be satisfactory, we prefer to utilize K_3-values from the uncatalyzed oxidation since the experimental error is less for this oxidation [cf. Table 1 of Ref. (3)]. (This would be anticipated because of the much slower rates of carbonyl formation encountered in the uncatalyzed reaction). From such values of K_3, values of α_2 and β can be estimated as follows. For the uncatalyzed oxidation of APP, it has been reported (3) that the maximum rate of carbonyl formation may be expressed as,

$$\rho_{m,o} = \frac{K_1[O_2]}{1 - \dfrac{K_2}{K_3 + [O_2]}} \tag{23}$$

where, the parameters K_1 and K_2 have been previously defined in Eqs. (7a) and (7b) of Ref. (3). [Also see Ref. (1)]. When Eq. (17a) is divided by

Eq. (23), the following is obtained,

$$\frac{\rho_{m,net}}{\rho_{m,o}} \equiv R = \frac{\alpha_2(K_3 - K_2 + [O_2])}{K_1\left\{K_3(1 - 2\beta) + [O_2](1 - \beta)\right\}} \tag{24}$$

From Eq. (24), at high values of $[O_2]$,

$$R \approx \alpha_2/K_1(1 - \beta) \tag{25}$$

while at low values of $[O_2]$,

$$R \approx \alpha_2(K_3 - K_2)/K_1K_3(1 - 2\beta) \tag{26}$$

From Eqs. (25) and (26), it should be possible to estimate values of α_2 and β utilizing previously reported (3) values of K_1 and K_2 (and K_3), cf. Table 1. In this manner were estimated values of α_2 and β which are listed in Table 1 for various experimental conditions. Values of R at high $[O_2]$ were calculated at $[O_2]$ = 100% whereas values at low $[O_2]$ were estimated at $[O_2]$ = 3% by means of interpolation. From the values of α_2 and β in Table 1 and from Eq. (17a) were calculated theoretical values of $\rho_{m,net}$ at various values of $[O_2]$ and reaction temperatures.

Table 1. Values of α_2 and β under various experimental conditions

Reaction temp., °C	$^*K_1 \times 10^4$, cm^2/min	K_2	K_3	$^*\alpha_2 \times 10^4$, cm^2/min	β
100	1.26	17.0	25.7	6.65	0.471
110	2.15	27.0	34.9	8.78	0.476
120	5.50	35.2	44.0	11.42	0.481
130	9.20	48.6	57.6	14.10	0.486

* Arbitrary units depending upon the scale utilized in obtaining carbonyl absorbance areas.

In Fig. 6 are shown calculated curves in plots of $\rho_{m,tot}$ (obtained from $\rho_{m,net}$) versus $[O_2]$. The agreement between calculated and observed values appears to be satisfactory. (Values at 100°C were obtained from extrapolated values of K_1, K_2, K_3, and $\rho_{m,o}$).

Utilizing the definitions of α_2 and β [cf. Eqs. (17) and (19)], an Arrhenius plot of $\log(\alpha_2/\beta)$ versus reciprocal temperature, 1/T, should afford an activation energy, E, which is equal to $E_i + E_6 - E_5$. Figure 7 shows such a plot. From this figure, E = 7 kcal/mole. For the uncatalyzed reaction E = 17 kcal/mole (this E also involves the initiation step as well as steps (5) and (6) for the uncatalyzed reaction). In this connection, a lower E-values may be anticipated for the catalyzed reaction since E_i for the catalyzed oxidation should be of lower magnitude than the corresponding value for the initiation step of the uncatalyzed oxidation and if it is assumed that $E_6 - E_5$, which involves steps (5) and (6) for both catalyzed and uncatalyzed reactions, is of a similar order of magnitude for catalyzed as well as uncatalyzed oxidations. Finally, it may be mentioned that a value of E = 13 kcal/mole was obtained during the uncatalyzed autoxidation of isotactic polybutene-1 (5). In this oxidation, a relatively large amount of metallic ash was observed (ca. 0.17%).

REFERENCES

1. L. Reich and S. S. Stivala, "Autoxidation of Hydrocarbons and Polyolefins," M. Dekker, Inc., New York, 1969.
2. S. S. Stivala, L. Reich, and P. G. Kelleher, Makromol. Chem., 59, 28 (1963).
3. B. R. Jadrnicek, S. S. Stivala, and L. Reich, J. Appl. Polymer Sci., in press.
4. S. S. Stivala, E. B. Kaplan, and L. Reich, J. Appl. Polymer Sci., 9, 3557 (1965).

5. S. S. Stivala, G. Yo, and L. Reich, *J. Appl. Polymer Sci.*, **13**, 1283 (1969).

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

7. S. A. Chaudhri, *Polymer*, **9**, 604 (1968).

8. Y. Kamiya, *J. Polymer Sci.*, **B4**, 999 (1966).

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

10. L. L. Yasina, V. B. Miller, and Y. A. Shlyapnikov, *Izv. Akad. Nauk, S.S.S.R.*, **11**, 2635 (1968).

11. J. P. Luongo, *J. Appl. Polymer Sci.*, **3**, 302 (1960).

12. B. R. Jadrnicek, Ph.D. Thesis, Institute of Macromolecular Chemistry, Prague, 1967.

13. A. T. Betts and N. Uri, *Makromol. Chem.*, **95**, 22 (1966).

14. Y. Kamiya and K. U. Ingold, *Can. J. Chem.*, **42**, 1027 (1964).

15. Y. Kamiya, *Bull. Chem. Soc., Japan*, **38**, 2156 (1965).

16. C. E. H. Bawn and S. A. Chaudhri, *Polymer*, **9**, 123 (1968).

Captions

FIG. 1 - Carbonyl absorbance area versus reaction time at 120°C and $[Co(III)] = 3 \times 10^{-7}$ mole/7.5 mg of APP, for various ratios of oxygen : nitrogen; 1 - 5/95; 2 - 10/90; 3 - 25/75; 4 - 50/50; 5 - 100/0.

FIG. 2 - Carbonyl absorbance area versus reaction time at oxygen: nitrogen of 10/90 for various temperatures, $[Co(III)] = 3 \times 10^{-7}$ mole/7.5 mg of APP.

FIG. 3 - Carbonyl absorbance area versus reaction time at 110°C; pure oxygen; for various concentrations of Co(III) acetylacetonate (per 7.5 mg of APP) 1 - $.3 \times 10^{-7}$ mole; 2 - $.9 \times 10^{-7}$ mole; 3 - 1.5×10^{-7}; 4 - 3×10^{-7} mole; 5 - 9×10^{-7} mole.

FIG. 4 - Carbonyl absorbance area versus reaction time at 110°C and oxygen: nitrogen of 50/50. 1 - $[Co(III)] = 3 \times 10^{-7}$ mole/7.5 mg of APP; 2 - $[Co(II)] = 3 \times 10^{-7}$ mole/7.5 mg of APP

FIG. 5 - Relationship between the maximum rate and the concentration of Co(III) acetylacetonate at 110°C and oxygen:nitrogen of 100/0 (1) and 50/50 (2).

FIG. 6 - Effect of oxygen concentration on the maximum rate at various temperatures; $[Co(III)] = 3 \times 10^{-7}$ mole/7.5 mg of APP.

FIG. 7 - Plot of $\log(\alpha_2/\beta)$ versus reciprocal temperature, 1/T.

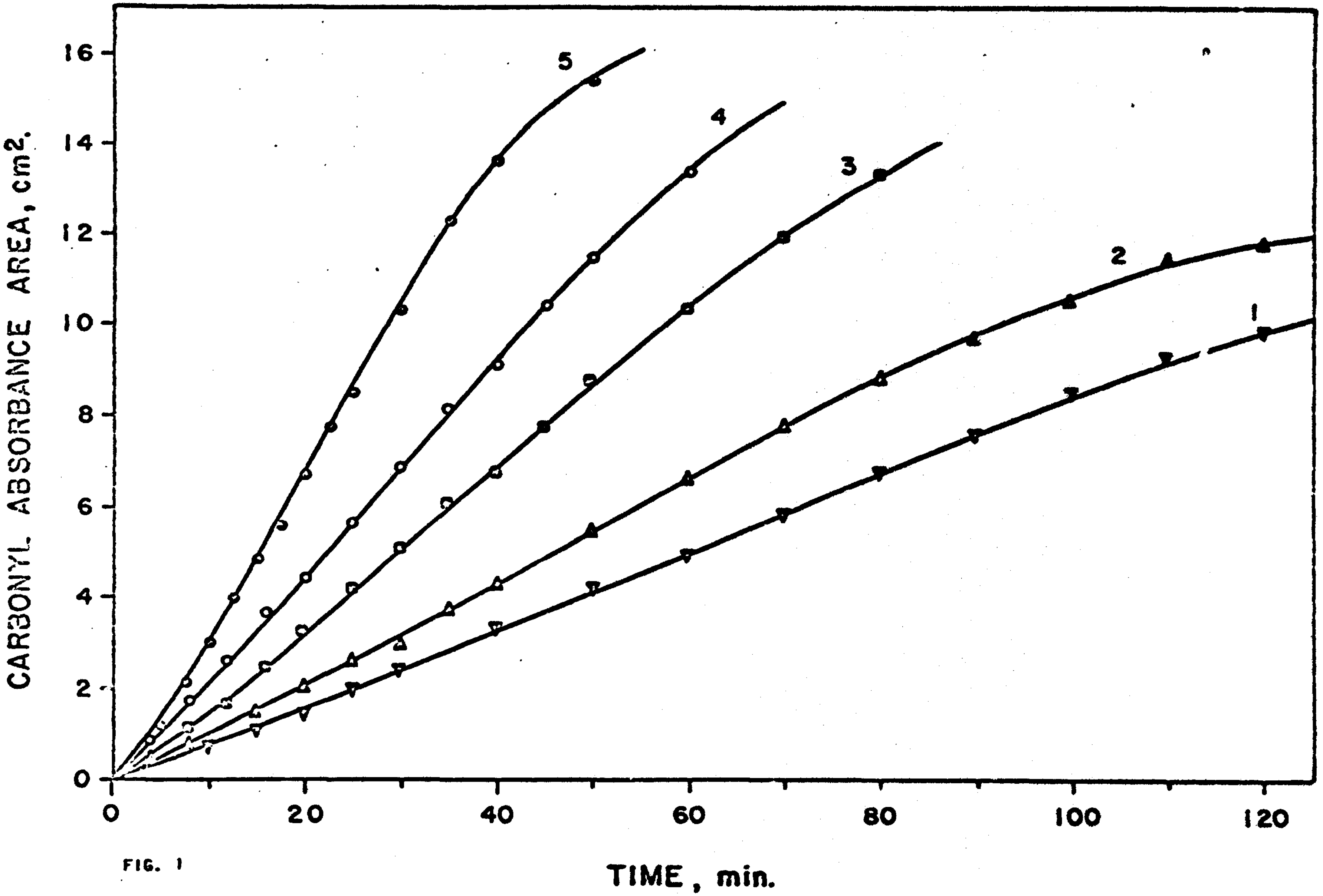
CARBONYL ABSORBANCE AREA, cm^2.
0
2
4
6
8
10
12
14
16
0
20
40
60
80
100
120
TIME, min.
1
2
3
4
5

FIG. 1

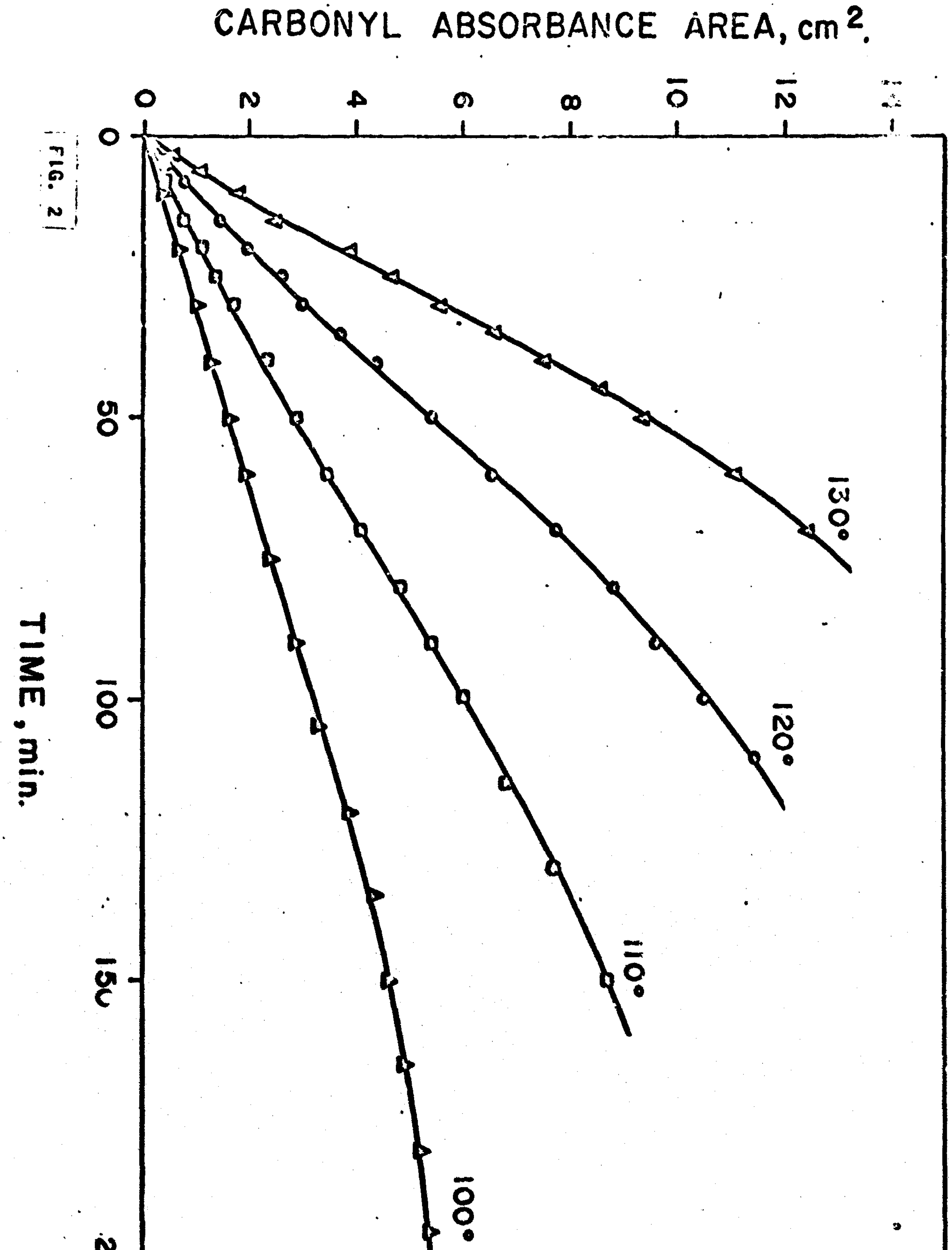
CARBONYL ABSORBANCE AREA, cm^2.
0
2
4
6
8
10
12
14
TIME, min.
0
50
100
150
200
130°
120°
110°
100°

FIG. 2

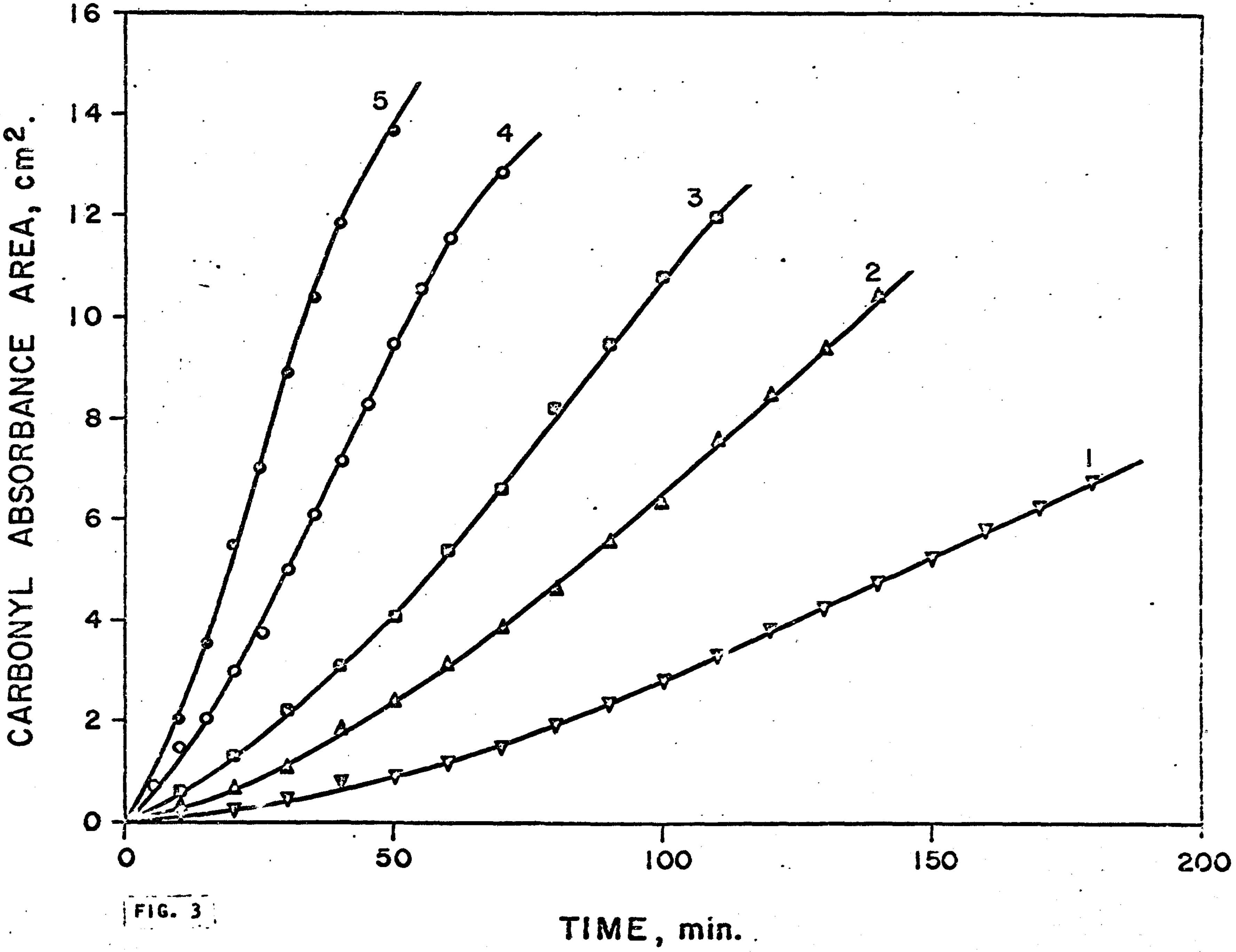
CARBONYL ABSORBANCE AREA, cm^2.
0
2
4
6
8
10
12
14
16
TIME, min.
0
50
100
150
200
1
2
3
4
5

FIG. 3

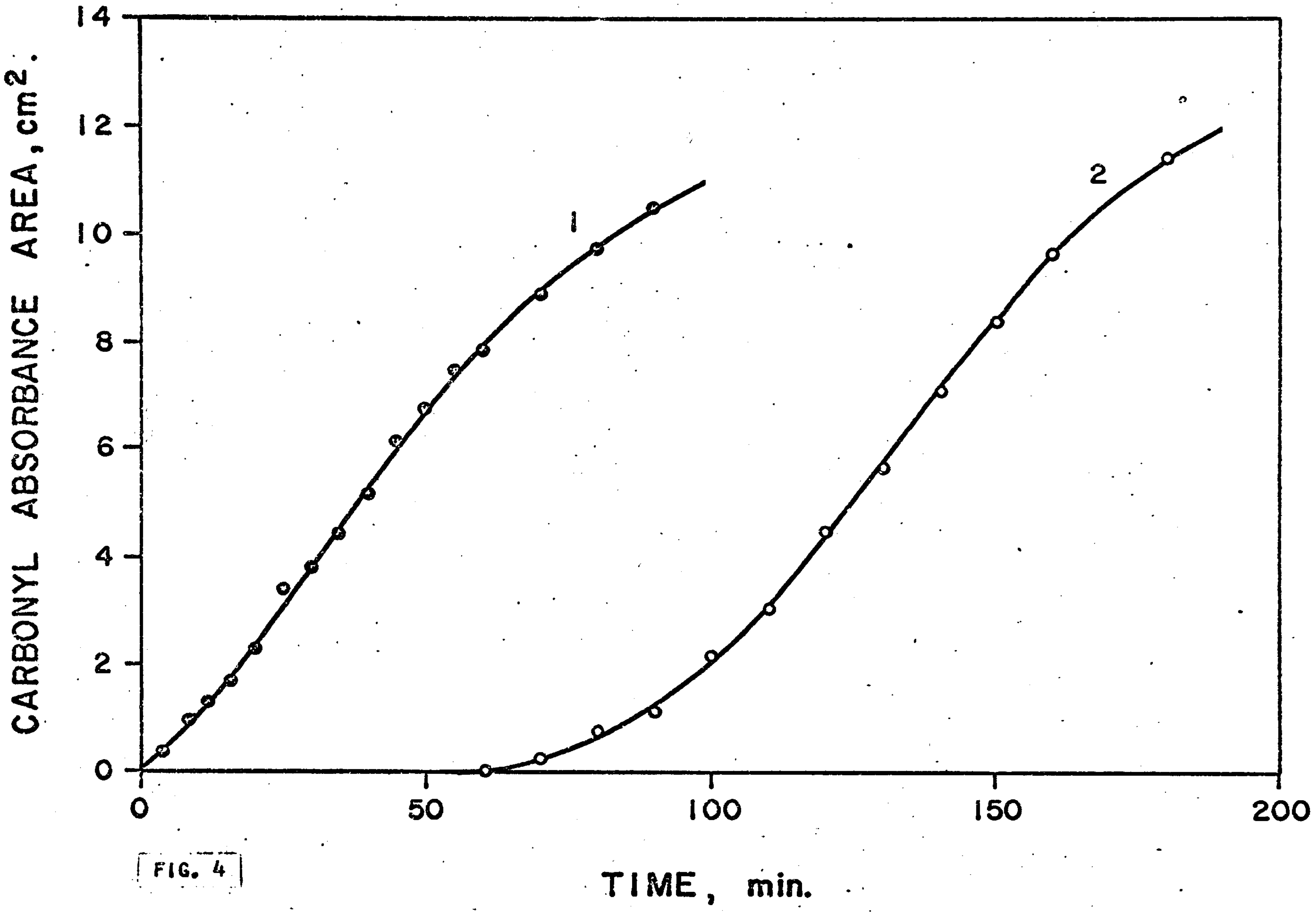
CARBONYL ABSORBANCE AREA, cm².
0
2
4
6
8
10
12
14
1
2
0
50
100
150
200
TIME, min.

FIG. 4

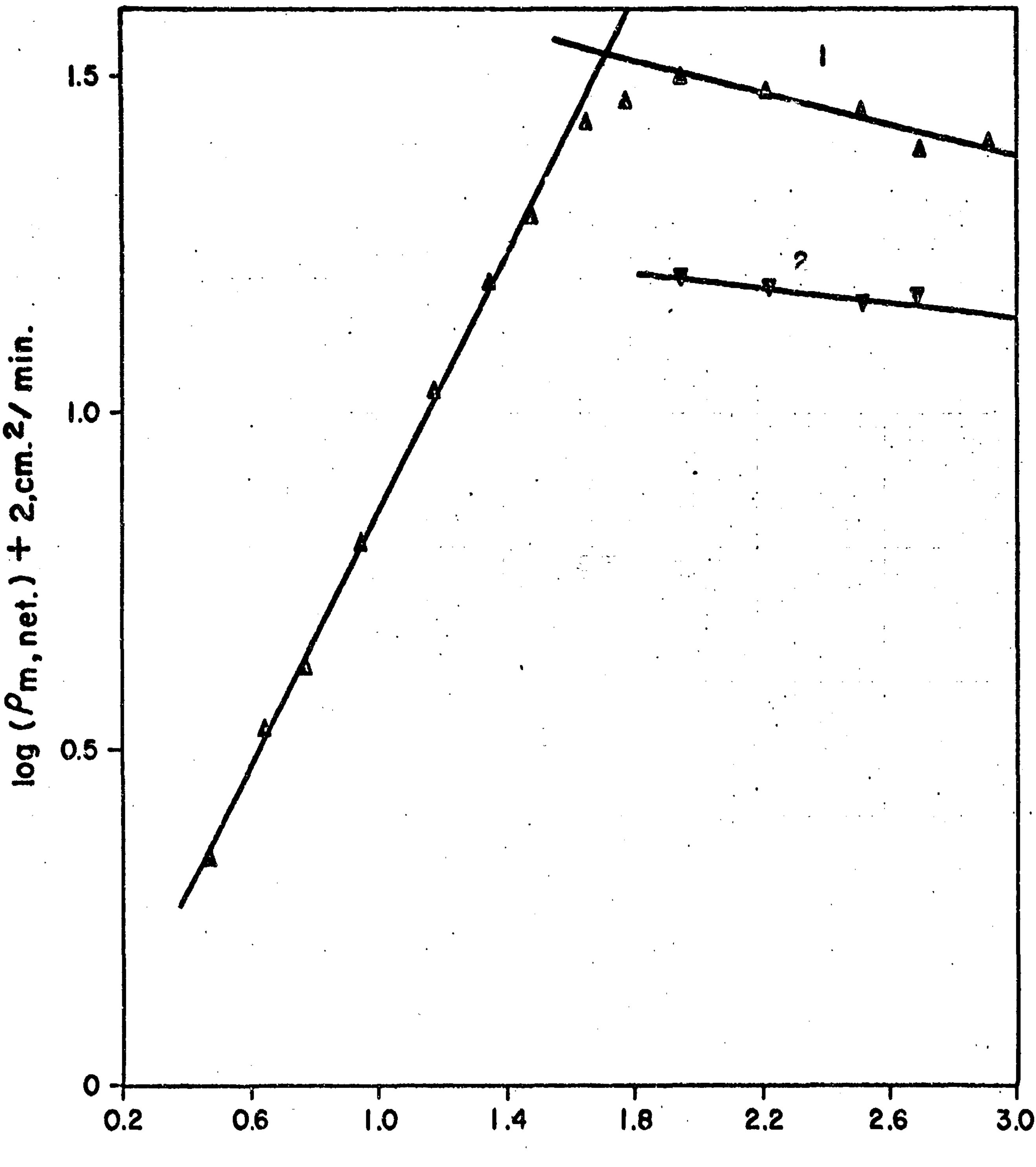
log ($\rho_{m,net.}$) + 2,cm.^{2}/ min.
1.5
1.0
0.5
0
0.2
0.6
1.0
1.4
1.8
2.2
2.6
3.0
1
2
log Co[(III)] + 8, mole / 7.5 mg.

FIG. 5

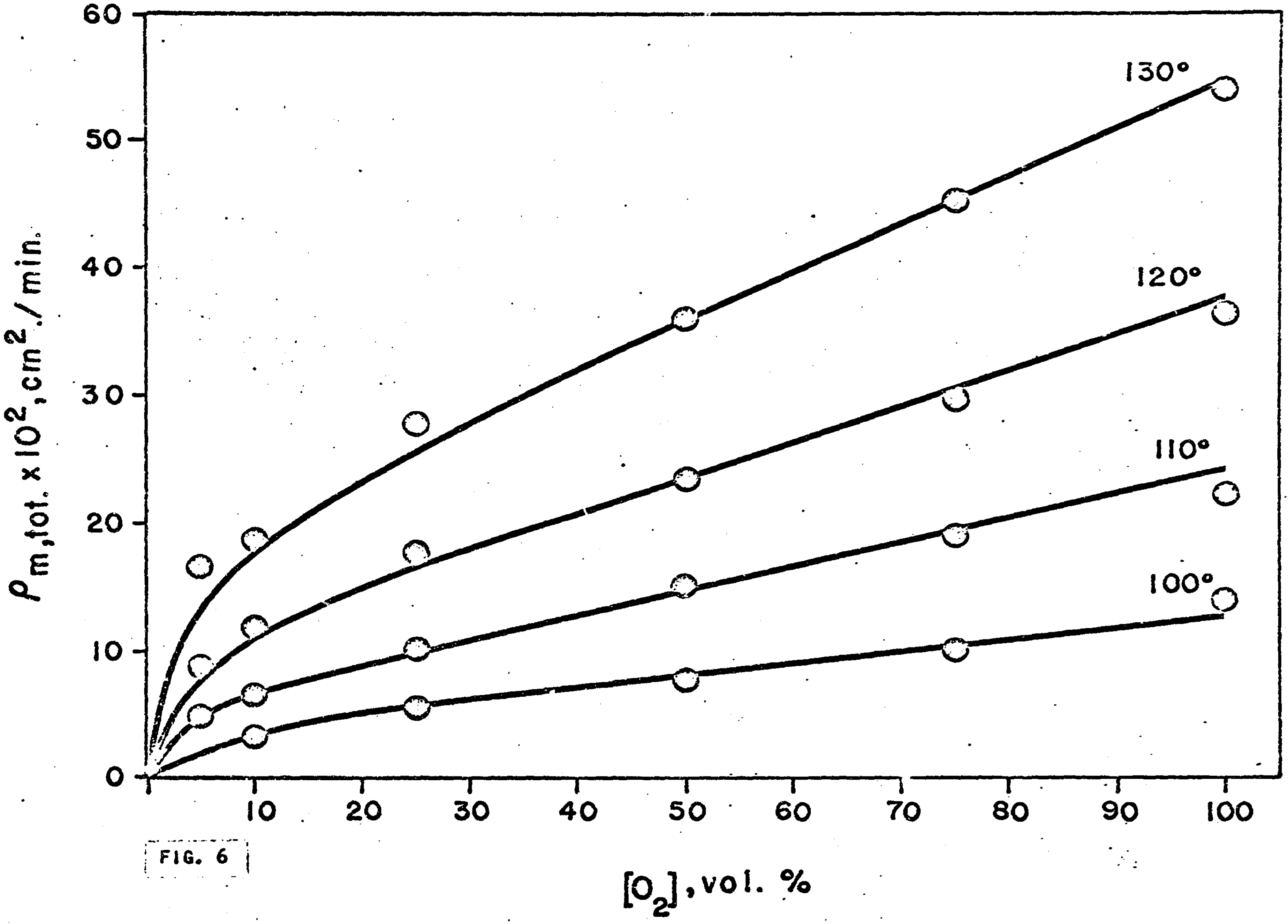
60
50
40
30
20
10
0
10
20
30
40
50
60
70
80
90
100
$\rho_{m,tot.} \times 10^2$, cm^2./min.
[O$_2$], vol. %
130°
120°
110°
100°

FIG. 6

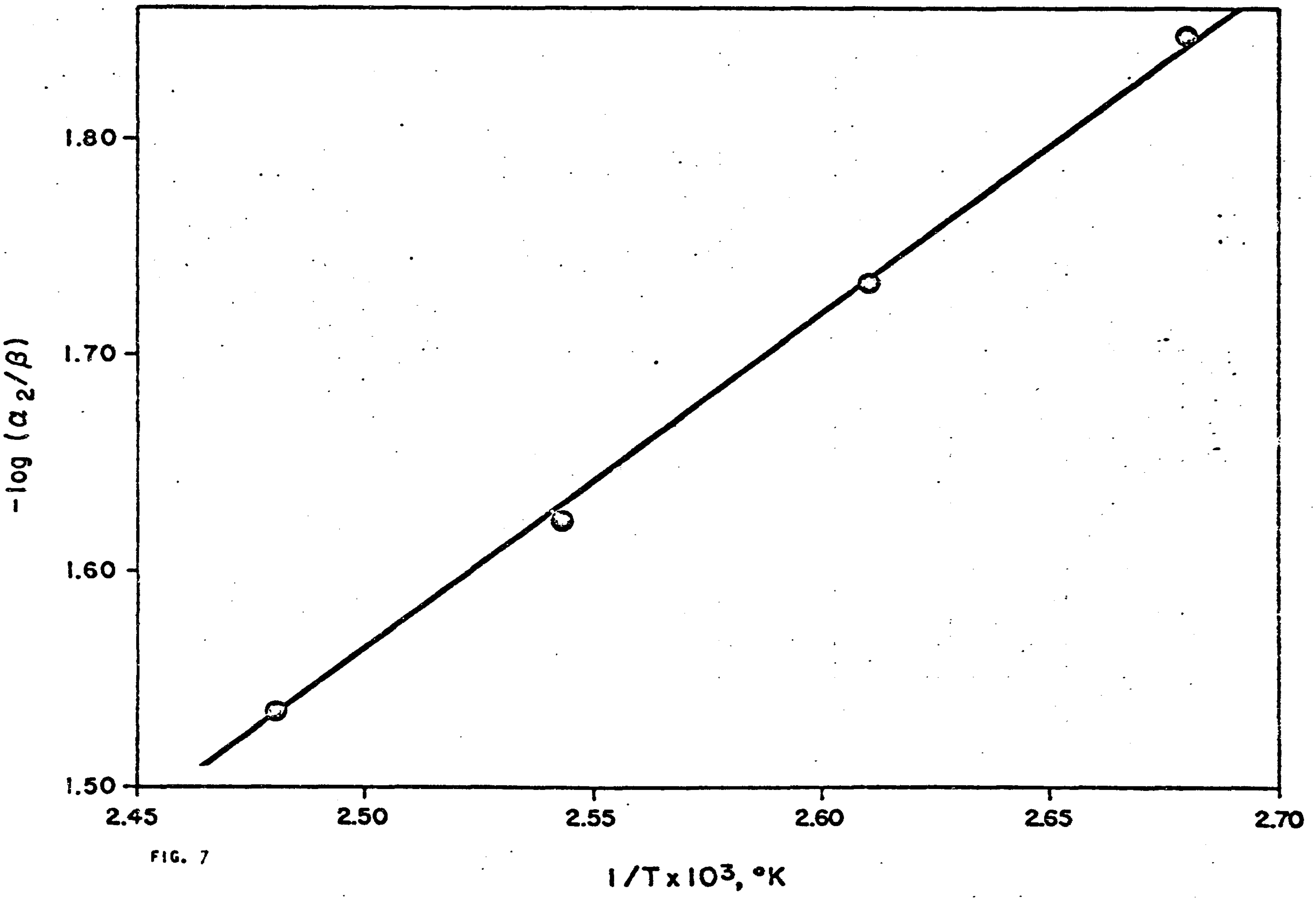

FIG. 7

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13. ABSTRACT

The autoxidation of a film of atactic polypropylene (APP) in the presence of cobalt salts was studied quantitatively by means of infrared spectroscopy. Reactions were traced as a function of temperature, oxygen concentration and time. Temperatures varied from 100° to 130°C and oxygen concentrations from 5 to 100% by volume. A general reaction scheme previously reported by the authors for the uncatalyzed autoxidation of atactic polypropylene was modified to account for the cobalt acetylacetonate-catalyzed autoxidation of APP in the bulk phase.