(4) J. A. Marinsky, *Coord. Chem. Rev.*, **19**, 125 (1976).
(5) G. Torrence, S. Amdur, and J. A. Marinsky, *J. Phys. Chem.*, **76**, 2144 (1971).
(6) M. M. Reddy and J. A. Marinsky, *J. Phys. Chem.*, **74**, 3889 (1970).
(7) R. G. Bates, "Determination of pH", Wiley, New York, 1964.
(8) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Butterworths, London, revised edition, 1965, p 519.
(9) H. Takesada, H. Yamazaki, and A. Wada, *Biopolymers*, **4**, 713 (1966).
(10) T. H. Butler, M.A. Thesis, State University of New York at Buffalo, 1969.

Polymer Reaction. 9. Effect of Polymer-Bound Chromium on Oxidative Pyrolysis of Poly(propylene)[1]

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ABSTRACT: Poly(propylene) has been reacted with chromyl chloride (Etard reaction) to covalently bind chromium to the polymer. The thermal pyrolysis and oxidative pyrolysis of poly(propylene) with and without chromium have been compared, using an interfaced pyrolysis GC peak identification system. Between 388 and 438 °C the thermal pyrolysis of the two materials in an inert atmosphere have comparable reaction rates, but chromium tends to lower the pyrolysis activation energy of poly(propylene) from 51 to 44 kcal mol^{-1} while increasing the temperature of the maximum pyrolysis endotherm by 15 °C. Chromium does not alter the amount of major pyrolysis products but tends to increase the formation of methane, isobutylene, and 2,4,6-trimethyl-1-heptane. The effect of chromium on oxidative pyrolysis is more substantive by comparison. Chromium suppresses the formation of all major products, though no new product was detected. It increases the activation energy of oxidative pyrolysis by 10 kcal mol^{-1} and promotes char formation. The behavior suggests possible catalysis by chromium in the termination processes. The combustion properties of poly(propylene) are significantly modified by the bound chromium. At only a 1.5% level of chromium the poly(propylene) has a limiting oxygen index of 26.4 and a self-ignition temperature of 400 °C in air as compared to 17.4 and 250 °C, respectively, for normal poly(propylene).

Polymer combustion is an extremely complicated chemical process. In the condensed phase there is thermal decomposition as well as oxidative degradation of the polymer; the latter process is diffusion limited. The rate of oxidative pyrolysis should thus be dependent upon sample thickness and oxygen pressure.[3,4] In the gas phase the flame is sustained by these volatile decomposition products; the combustion process itself involves degenerative chain branching oxidations. The heat liberated by combustion in turn provides the energy needed for the condensed phase reactions. There are, therefore, several approaches to flame retardation. A flame retardant may decompose into free-radical scavengers to interfere with chain reactions in the gas phase or release noncombustible gases to lower the oxygen concentration at the polymer surface. Some flame retardants form intumescent coatings which act as a thermal insulating barrier. Current flame retardants for polymers are limited to compounds of a few elements. Bromine- and chlorine-containing compounds, especially those in synergistic combination with antimony oxide, have been demonstrated to be effective radical scavengers in the gas phase.[5] Some phosphorus compounds decompose to form phosphate glasses to reduce polymer flammability.[6] Less effective and of uncertain function are nitrogen- and boron-containing flame retardants. Even the best flame retardant formulations are relatively inefficient, up to 40 wt % of chlorine and antimony compounds being necessary to obtain a nondripping flame-retarded poly(propylene). At such high levels, the flame retardants tend to alter and decrease the material's physical properties.

In the past, most studies tried to differentiate the gas phase from the condensed phase mode of retardancy activity by some macroscopic criteria. For instance, if there is volatilization of the retardant element from the substrate and its activity is insensitive to the polymer structure or the nature of the oxidant, then the flame retardant is said to act in the gas phase. If contrary behavior is observed or there is evidence of char formation, then the flame retardant is thought to act in the condensed phase.

The research in our laboratories has two objectives: to find new elements which are effective in the flame retardation of polymers at levels much lower than those currently employed and to develop methods for the determination of whether a flame retardant acts primarily in the condensed or the gas phase. A candidate is introduced directly into a hydrocarbon flame, such as a CH_4–O_2 flame, and the lowering of the flame temperature or flame velocity is measured to assess its efficacy in the supression of gas phase reactions. The candidate's activity in the condensed phase is determined through its effects on the thermal pyrolysis and oxidative pyrolysis of the polymeric substrate under flameless conditions. In this paper we report the effect of covalently bonded chromium on the condensed phase degradation of poly(propylene). The choice of chemical binding of chromium to the polymer over simple blending of a chromium complex with poly(propylene) was made to avoid volatilization, incompatibility, and other complications.

The rationale of this work is predicated on the hypothesis that if chromium plays a role in the inhibition of thermal pyrolysis of poly(propylene), then its presence

Table I
Sample Preparation

sample	wt of poly-(propylene), g	vol of CCl_4, mL	CrO_2Cl_2 in CCl_4		swelling time, h	reaction time, h	analysis wt %	
			mmol	mL			Cr	Cl
A	5.2	100	12.4	60	15	15	2.22	3.20
B	103	500	24.6	50	48	15	1.50	0.98
C	304	780	131	100	120	15	1.90	3.00

should affect either the rates or the products of the thermal pyrolysis in its absence.[7] Similarly, a comparison of the rates and product distributions in the oxidative pyrolysis of poly(propylene) with and without chromium could reveal its effect on such reactions.

Experimental Section

Sample Preparation. Poly(propylene) (Profax 6501 of Hercules, Inc.) was reacted with chromyl chloride from Aldrich. The Etard reaction[8,9] was performed on poly(propylene) swollen in CCl_4. Chromyl chloride was dissolved in CCl_4 in a glove bag filled with nitrogen and transferred into a dropping funnel. The funnel was then attached to the reaction flask containing the poly(propylene) and continuously purged with nitrogen. Following dropwise addition of the chromyl chloride solution at room temperature, the mixture was stirred for a prolonged period of time. The product was filtered, washed repeatedly with CCl_4, and vacuum dried at 80 °C for 40 h. The exact reaction conditions and anlysis of the products are given in Table I. The molar ratios of Cr to Cl in these samples range from 1:1 to 1:2.

Samples of lower chromium content were prepared for limiting oxygen index measurements in the following manner. Samples D and E were obtained by adding 4 and 9 parts by weight of virgin poly(propylene) to 1 part of sample B, respectively. They were compression molded at 230 °C and 10000 psi for 4 min in a 5 in. × 5 in. × 0.063 in. mold.

Pyrolysis in Inert Atmosphere. Thermogravimetric analysis, thermal pyrolysis, and on-line analysis of products by the interfaced pyrolysis GC peak identification system were performed according to previously given procedures.[7] Differential thermal analyses of sample C were made with a duPont 950 plug-in module at a nitrogen flow rate of 60 mL min^{-1} and a heating rate of 10 °C min^{-1}. The sample size in these studies was about 10 mg.

Pyrolysis in Oxygen Atmosphere. Oxidative pyrolysis in air and in oxygen, thermogravimetric analysis, and product analysis were performed as described earlier.[3] About 5 mg of sample A was used in each experiment at 264, 289, 313, and 338 °C. The self-ignition temperature was determined both with thermogravimetric and differential thermal analysis methods. Even though the results are not directly comparable to ASTM methods, the relative self-ignition temperature provides meaningful measures for the effect of chromium. The limiting oxygen index was measured according to the standard ASTM D 2863A, B procedure.

Results

Pyrolysis in Inert Atmosphere. Figure 1 shows the thermogravimetric curves in nitrogen for sample A and poly(propylene). The temperatures for 50% weight loss are about 400 and 385 °C, respectively, for sample A and poly(propylene). About 3% of sooty residue remained at 460 °C for sample A while poly(propylene) was completely pyrolyzed at 420 °C leaving no residue behind.

Pyrolysis was carried out in an MP3 instrument[7] for various lengths of time, and the weight of the unpyrolyzed polymer was weighed with a microbalance. The results are shown in Figure 2. Figure 3 gave the first-order kinetic plots. It was shown earlier[7] that a simplified mechanism for poly(propylene) pyrolysis consists of random carbon–carbon bond scissions

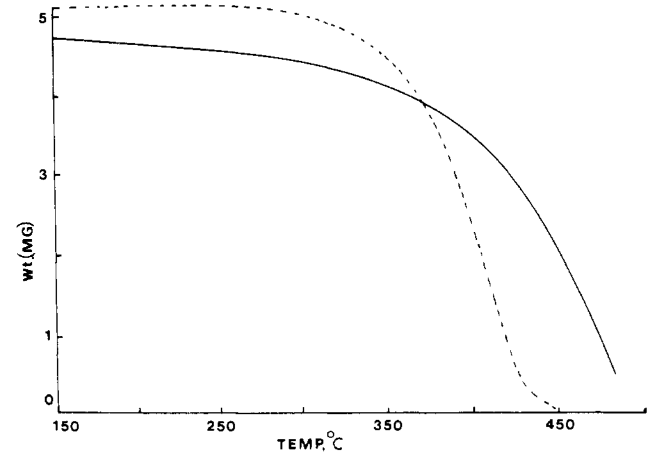
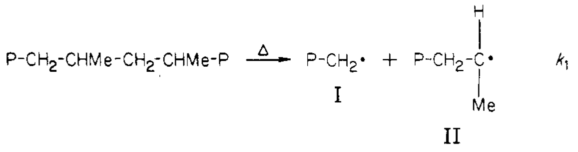


Figure 1. TGA thermograms of sample A (—) and of poly(propylene) (- - -) in nitrogen atmosphere.



$$\text{P-CH}_2\text{-CHMe-CH}_2\text{-CHMe-P} \xrightarrow{\Delta} \underset{\text{I}}{\text{P-CH}_2\cdot} + \underset{\text{II}}{\text{P-CH}_2\text{-}\overset{\text{H}}{\underset{\text{Me}}{\text{C}}}\cdot} \qquad k_1 \qquad (1)$$

followed by intramolecular hydrogen transfer reactions,

$$\text{I (II)} \rightarrow \text{I (II)} + \text{volatile products} \qquad k_2 \qquad (2)$$

and terminations by radical combination and/or disproportionation

$$2\text{I (II)} \rightarrow \text{nonvolatile products} \qquad k_3 \qquad (3)$$

The rate of pyrolysis is given by

$$\text{rate of pyrolysis} = k_2(k_1/k_3)^{1/2}[\text{PH}] \qquad (4)$$

where [PH] is the polymer concentration. The observed apparent rate constant may be associated with $k_2(k_1/k_3)^{1/2}$, and from the temperature dependence of the pyrolysis rate (Figure 4), $E_2 + {}^1/_2E_1 - {}^1/_2E_3$ can be calculated. These results are summarized in Table II.

The pyrolysis products of sample A are essentially the same as those found earlier for normal poly(propylene).[7] Table III compares the relative product distributions of the two substances obtained after 4 min of reaction at 438 °C. In this table, the relative weight percent of each product was normalized, using the method of Dietz,[10] by taking the total amount of volatiles up to C_{13} products to be unity. Figure 5 shows this normalized product distribution from the 438 °C pyrograms.

Oxidative Pyrolysis. Figure 6 compares the degradation of chromylated and normal poly(propylene) in air. It is apparent that the polymer degrades at much higher temperatures in the presence of chromium. In Figure 6b it is shown that in an atmosphere of oxygen, poly(propylene) self-ignites at ca. 260 °C in the absence of chromium but ignites at ca. 360 °C in the presence of chromium.

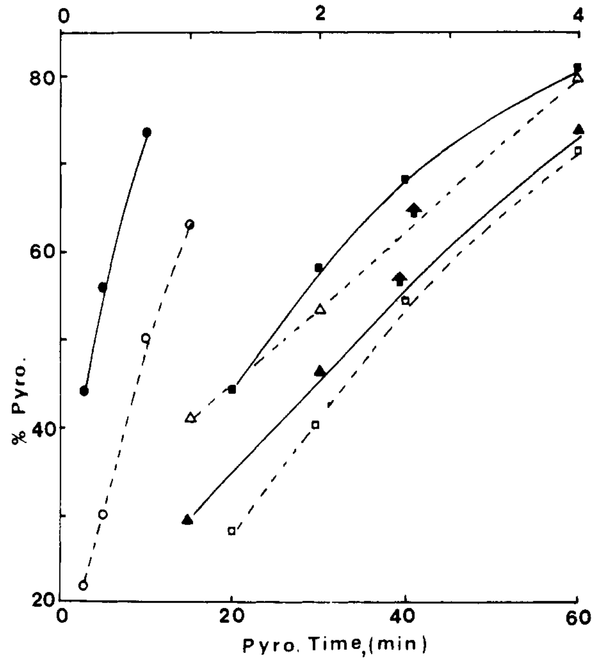


Figure 2. Rate of pyrolysis of sample A (—) and of poly(propylene) (- - -) in helium at: (□, ■) 388 °C, (○, ●) 414 °C, and (△, ▲) 438 °C. The upper abscissa is for the 438 °C experiments and the lower abscissa for the other two temperatures.

Table II
Kinetic Results of Pyrolysis of Sample A and Poly(propylene) in He

temp, °C	obsd rate constant, s^{-1}	
	sample A	poly(propylene)
388	4.4×10^{-4}	4.0×10^{-4}
414	2.2×10^{-3}	1.1×10^{-3}
438	4.5×10^{-3}	6.2×10^{-3}
activation energy, kcal mol^{-1}	44	51

In Figures 7 and 8 the weight loss of chromylated and normal poly(propylene) specimens as a function of temperature were compared. In air, ordinary poly(propylene) is stable up to about 222 °C whereas sample A exhibited about 7% weight loss. On the other hand, the temperatures for 50% weight loss are much higher for sample A, being about 425 and 325 °C, respectively, for sample A and poly(propylene).

Earlier,[3] we showed that the oxidative pyrolysis of poly(propylene) may be described by initiation involving homolysis of hydroperoxides

$$\mathrm{POOH} \rightarrow \mathrm{PO\cdot} + \mathrm{\cdot OH} \qquad k_4 \tag{5}$$

followed by the propagation reactions

$$\mathrm{PO\cdot} \rightarrow \mathrm{P\cdot} + \text{volatile products} \tag{6}$$

$$\mathrm{P\cdot} + \mathrm{O_2} \rightarrow \mathrm{PO_2\cdot} \tag{7}$$

$$\mathrm{PO_2\cdot} + \mathrm{PH} \rightarrow \mathrm{POOH} + \mathrm{P\cdot} \qquad k_5 \tag{8}$$

and bimolecular terminations

$$2\mathrm{PO_2\cdot} \rightarrow \text{nonvolatile products} \qquad k_6 \tag{9}$$

The rate of oxidative pyrolysis may be given as

$$\text{rate of oxidative pyrolysis} = k_5\left(\frac{k_4[\mathrm{POOH}]}{k_6}\right)^{1/2}[\mathrm{PH}] \tag{10}$$

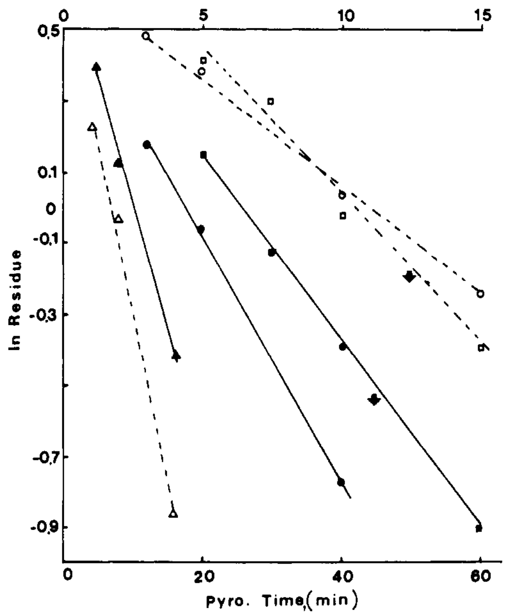


Figure 3. First-order kinetic plots for pyrolysis of sample A (—) and of poly(propylene) (- - -) in helium. Same legend as in Figure 3. The lower abscissa is for the 388 °C experiments and the upper abscissa for the other two temperatures.

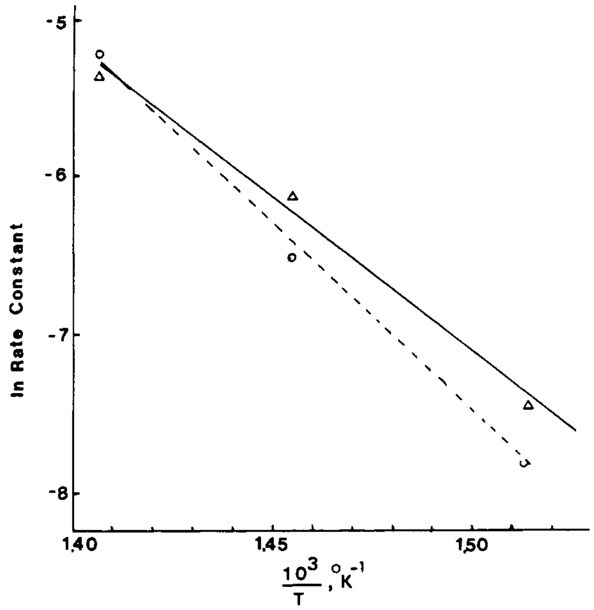


Figure 4. Arrhenius plots for pyrolysis of sample A (—) and poly(propylene) (- - -) in helium.

Table III
Pyrolysis Product Distributions of Sample A and Poly(propylene) at 438 °C

	relative wt %	
	sample A	poly-(propylene)
methane	0.38	0.1
ethane	0.80	1.0
propylene	12.0	10.0
isobutylene	6.1	2.5
2-pentene	12.0	14.0
2-methyl-1-pentene	7.0	9.4
3-methyl-3,5-hexadiene	3.3	1.6
2,4-dimethyl-1-heptene	36.0	40.0
2,4,6-trimethyl-1-heptene	5.8	2.1
2,4,6-trimethyl-1-nonene	1.6	1.5
2,4,6-trimethyl-1-nonene	7.1	9.7
$C_{13}H_{24}$	1.0	1.8
unidentified	5.7	6.7

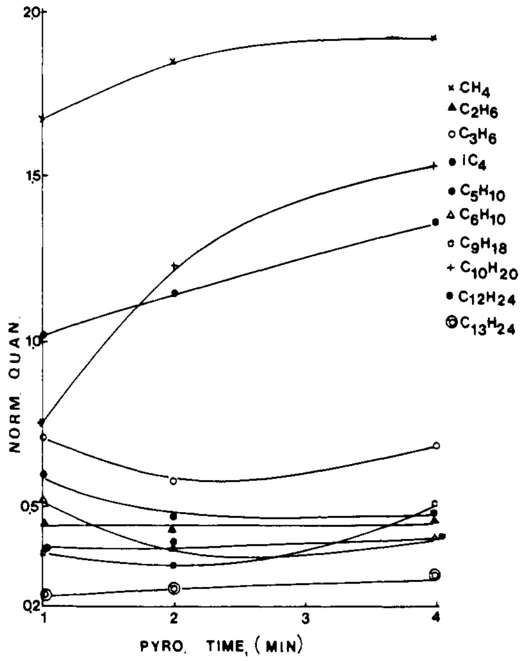


Figure 5. Comparisons of relative distributions of products of pyrolysis of sample A and of poly(propylene) at 438 °C as a function of the time of pyrolysis.

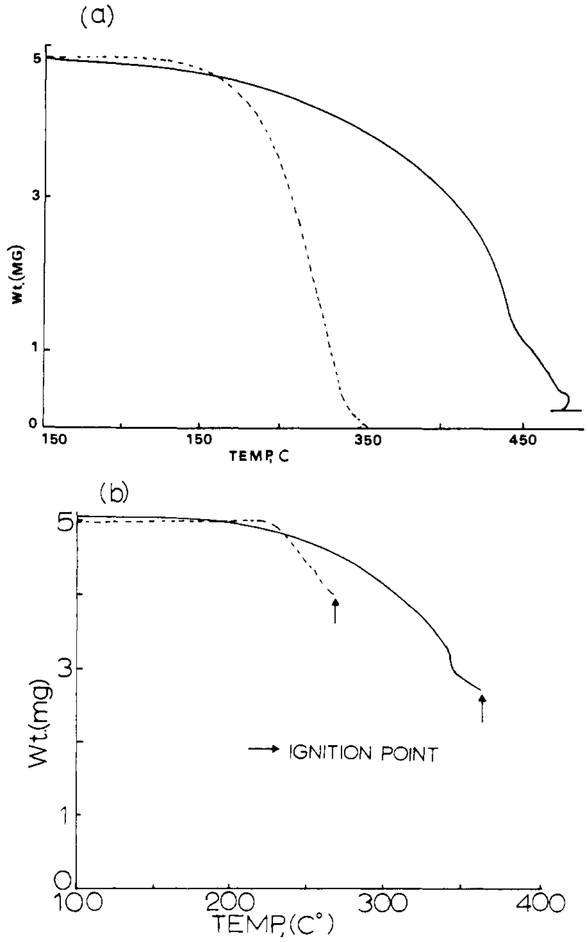


Figure 6. TGA thermograms of sample A (—) and of poly(propylene) (- - -) (a) in air and (b) in pure oxygen.

In the above equations, P·, PO·, and PO_2· are the alkyl, alkoxyl, and peroxyl radicals of poly(propylene). The apparent rate constants and activation energies obtained from Figures 9 and 10 for the oxidative pyrolysis of poly(propylene) in air and in oxygen with and without chromium are compared in Table IV.

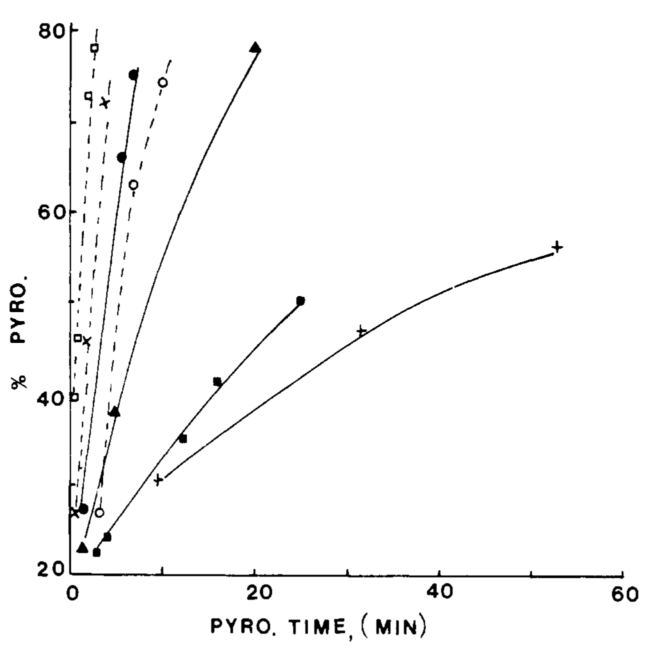


Figure 7. Rate of oxidative pyrolysis of sample A (—) and of poly(propylene) (- - -) in air: (○) 240 °C; (+, ×) 264 °C; (□, ■) 289 °C; (▲) 313 °C; and (●) 338 °C.

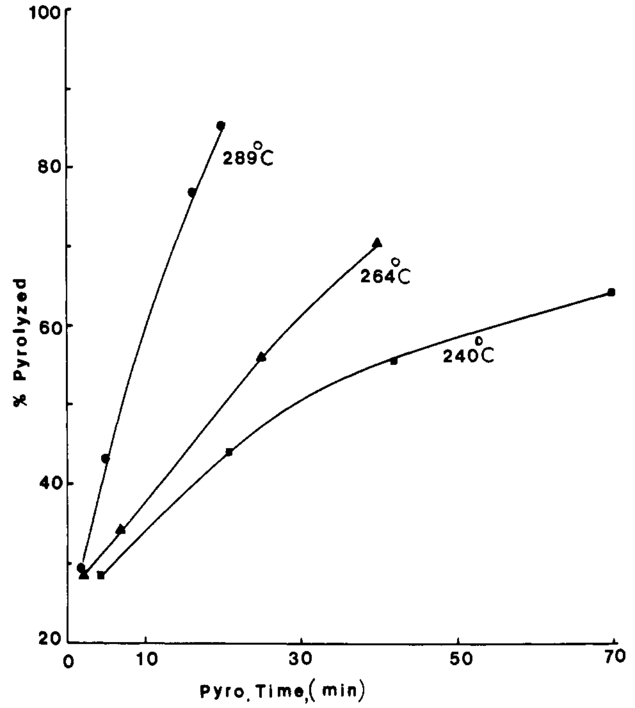


Figure 8. Rate of oxidative pyrolysis of sample A in pure oxygen.

The major products from the oxidative pyrolysis of chromylated and normal poly(propylenes) are both acetaldehyde, acetone, butan-1-al, and an unsaturated C_6 ketone. If we take the amount of a given product obtained from normal poly(propylene) as the reference, then the normalized quantity for the same product from the chromylated polymer will be smaller or greater than unity, depending upon whether chromium inhibits or promotes its formation. Figure 11 showed that chromium suppresses the formation of the four major products at all temperatures.

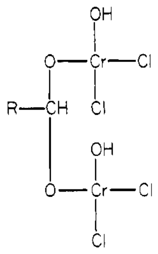
Table IV
Kinetic Results of Oxidative Pyrolysis of Sample A and Poly(propylene)

	apparent rate constants, s^{-1}		
temp, °C	poly-(propylene) (air)	sample A (air)	sample A (O_2)
240	2.5×10^{-3}	1.8×10^{-4}	1.5×10^{-4}
264	5.4×10^{-3}	3.4×10^{-4}	3.9×10^{-4}
289	9.2×10^{-3}	1.2×10^{-3}	1.4×10^{-3}
313		3.2×10^{-3}	
338			
activation energy, kcal $mole^{-1}$	16	26	26

Combustion Properties. Figure 12 gives the DTA curves of ordinary and chromium-containing poly(propylene) obtained in air at a flow rate of 60 mL min^{-1}, showing ignition exotherms at 250 and 400 °C, respectively. The limiting oxygen index was determined for samples B, D, E, and poly(propylene); the values are 26.4, 18.3, 17.7, and 17.4, respectively. Therefore, the limiting oxygen index is significantly raised by chromium; the concentration dependence is shown in Figure 13. Table V gives the analysis of char after the burning of sample B.

Discussion of Results

Etard Reaction. The oxidations of hydrocarbons by hexavalent chromium compounds (chromic oxide, chromic acid, chromyl chloride) are referred to as the Etard reaction.[8] These reagents are effective under different experimental conditions.[16-20] The reaction of chromyl chloride with toluene has been most extensively investigated. A product containing 2 mol of Cr per mol of toluene was obtained. Three structures have been proposed:[8,21]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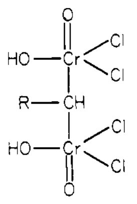
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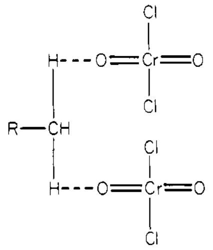
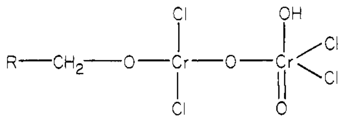

V

In structure III, the two chromium atoms are in a tetravalent state whereas they are hexavalent in IV and V. Necsoiu et al.[22] found that the chromyl chloride adduct of toluene has one-half of the electron paramagnetic resonance intensity of $[Cr(III)(NH_3)_5Cl]Cl_2$ which was used as the standard. The authors concluded that half of the chromium in the former is tetravalent and the remainder hexavalent and proposed a structure for the adduct as


VI

However, Wiberg and Eisenthal[19] pointed out that Necsoiu et al.[20] failed to correct for the fact that Cr(III) and Cr(IV) have different spin angular momenta of $^3/_2$ and 1, respectively. Taking that into consideration, the electron paramagnetic resonance results become consistent with structure III. Furthermore, the less ambiguous magnetic susceptibility measurements on the chromyl chloride–toluene complex gave a value of 3.16 μ_B for one chromium atom[23] in support of structure III.

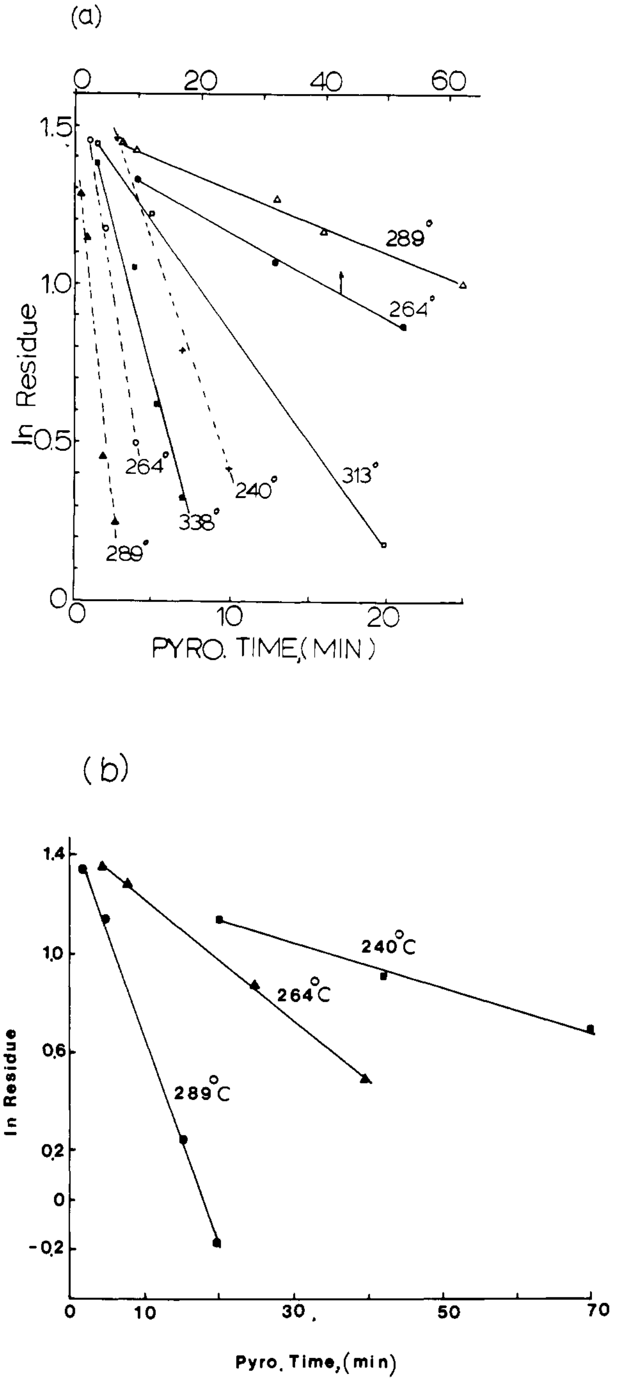


Figure 9. First-order kinetic plots of oxidative pyrolysis of sample A (—) and of poly(propylene) (- - -) (a) in air and (b) in pure oxygen.

The selectivity of chromyl compound oxidations of hydrocarbons differs quite widely depending on the particular compound and the reaction conditions.[18,24-26] In the oxidation of aliphatic hydrocarbons, the relative rates of reaction with chromyl chloride[26] at primary, secondary, and tertiary positions are 1:110:7000. Combining this selectivity with the susceptibility results, the structure for chromylated poly(propylene) is likely to be

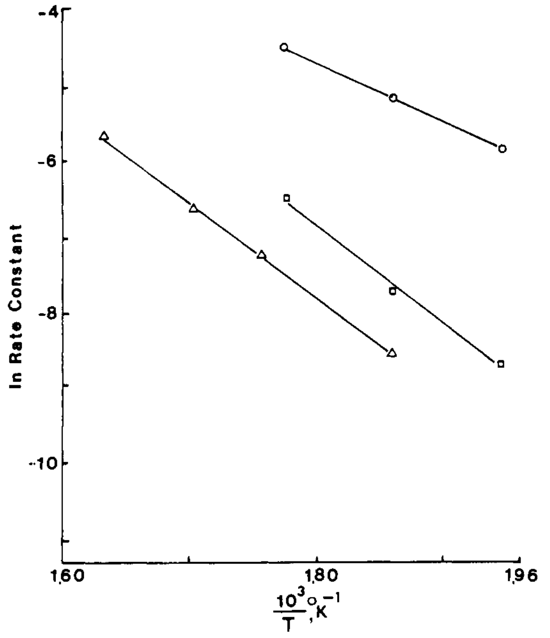
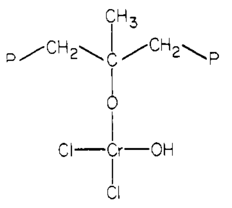


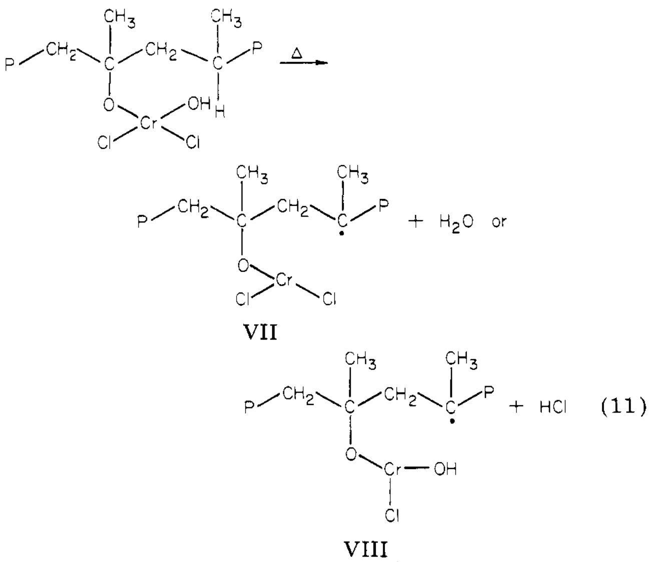
Figure 10. Arrhenius plots for oxidative pyrolysis: (○) poly(propylene) in air; (△) sample A in air; and (□) sample A in pure oxygen.



VI

The analyses of samples A and C (Table I) are in agreement with those of this structure. Sample B was found to contain smaller amounts of chlorine; this may be attributed to inadverant partial hydrolysis of the specimens.

Thermal Pyrolysis. The influence of chromium on the thermal pyrolysis appears to be a minor one. One of the main discernible effects seems to be a lowering of the apparent activation energy from 51 to 44 kcal mol^{-1} in the presence of chromium. The major contribution to this quantity comes from the activation energy for initiation which ranges from 77 to 84 kcal mol^{-1}.[27] This can be reduced if a redox reaction of lower activation energy contributes significantly toward initiation. A possible process which may occur at these temperatures may be



VII

VIII

(11)

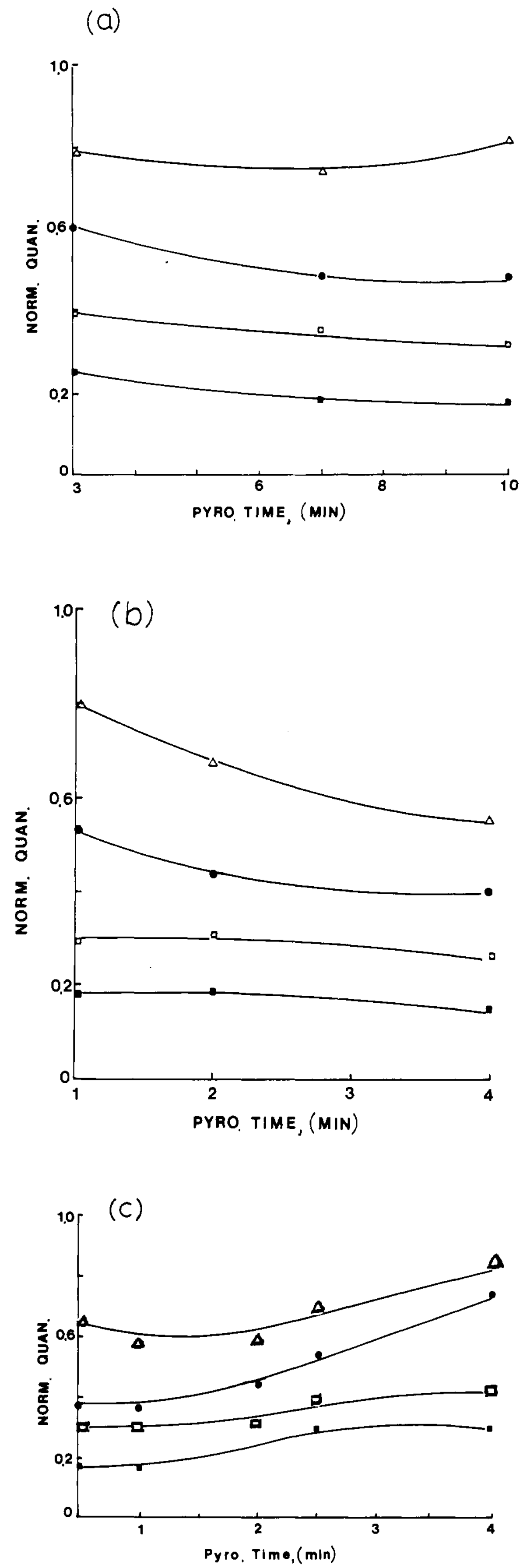


Figure 11. Yields of major oxidative pyrolysis products from chromylated poly(propylene) referenced to those from ordinary poly(propylene) as a function of the time of reaction: (a) 240 °C; (b) 264 °C; and (c) 289 °C. The products are: (●) acetaldehyde; (△) acetone; (□) butan-1-al; and (■) unsaturated C_6 ketones.

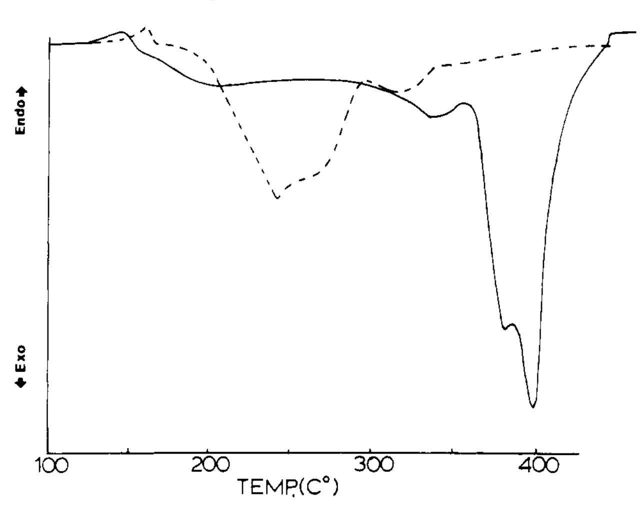


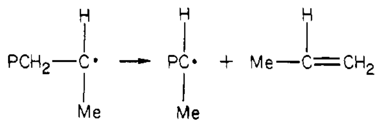
Figure 12. DTA thermograms of sample C (—) and poly(propylene) (- - -) in air.

Table V
Elemental Analysis of Combustion Char of Sample B[a]

elements	wt %	elements	wt %
Cr	0.9	C	80.51
Cl	0.17	H	9.52

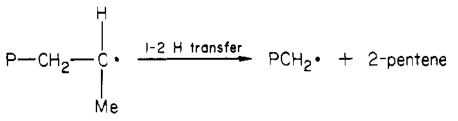
[a] The gross carbon hydrogen composition for the char is $C_1H_{1.4}$.

The three main products of thermal pyrolysis of poly(propylene) are propylene, 2-pentene, and 2,4-dimethyl-1-heptene. They are probably produced from the secondary radical II via two propagation reactions, unzipping, i.e.,

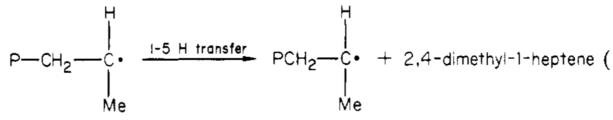
 (12)

$$\mathrm{PCH_2{-}\overset{H}{\underset{Me}{C}}\cdot \longrightarrow P\overset{H}{\underset{Me}{C}}\cdot + Me{-}\overset{H}{C}{=}CH_2} \quad (12)$$

and intramolecular hydrogen transfers

 (13)

$$\mathrm{P{-}CH_2{-}\overset{H}{\underset{Me}{C}}\cdot \xrightarrow{\text{1-2 H transfer}} PCH_2\cdot + \text{2-pentene}} \quad (13)$$

 (14)

$$\mathrm{P{-}CH_2{-}\overset{H}{\underset{Me}{C}}\cdot \xrightarrow{\text{1-5 H transfer}} PCH_2{-}\overset{H}{\underset{Me}{C}}\cdot + \text{2,4-dimethyl-1-heptene}} \quad (14)$$

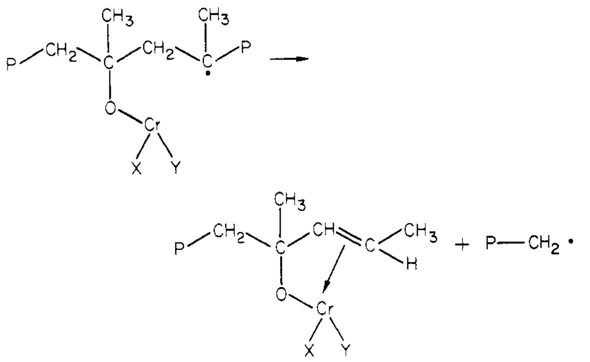
and termination by radical combination and/or disproportionation. Figure 5 showed that the relative amount of these three products remained relatively constant with the time of pyrolysis in the absence or presence of chromium, and they are produced in lesser amounts with chromium present.

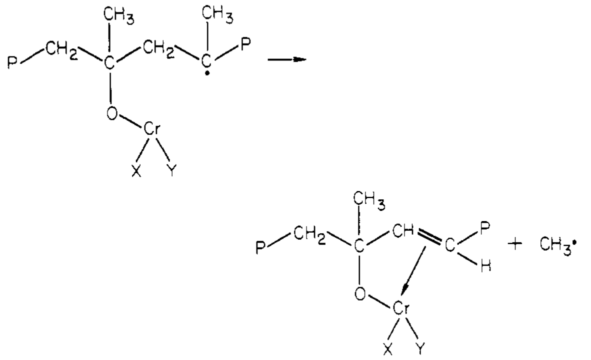
On the other hand, three minor products, methane, isobutylene, and 2,4,6-trimethyl-1-heptene, increase in yields with increasing time of pyrolysis for sample A in quantities exceeding that obtained from normal poly(propylene). Methane is most likely derived from methyl radicals. For the other two products, it has been postulated that they are formed from the primary alkyl radical, I[7] via

$$\mathrm{PCH_2\cdot \xrightarrow{\text{1-2 H transfer}} II + \text{isobutylene}} \quad (15)$$

$$\mathrm{PCH_2\cdot \xrightarrow{\text{1-5 H transfer}} II + \text{2,4,6-trimethyl-1-heptene}} \quad (16)$$

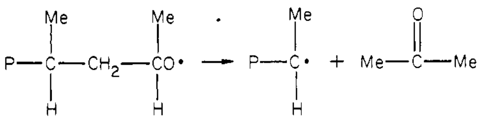
It is possible that product stabilization by chromium may lead to the formation of methyl and primary alkyl radicals.

 (17)

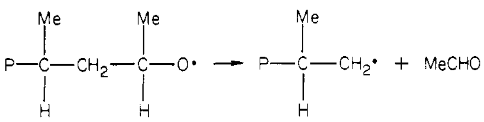
 (18)

Finally, 2% chromium lowers the melting transition of poly(propylene) by 13 °C but raises the maximum of the pyrolysis endotherm by 15 °C.

Oxidative Pyrolysis. The effect of chromium on the oxidative pyrolysis of poly(propylene) is most interesting and has several facets to it. First, the major products are the same with or without chromium. They are all suppressed by the presence of chromium, but not to the same extent (Figure 11). Earlier we offered mechanisms for the oxidative pyrolysis of poly(propylene).[3] Acetaldehyde and acetone are thought to be produced from secondary alkoxyl radicals,

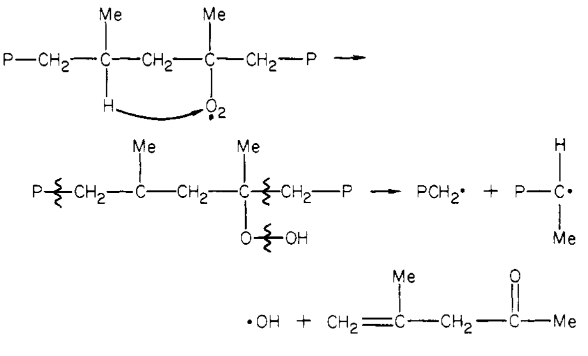
 (19)

$$\mathrm{P{-}\overset{Me}{\underset{H}{C}}{-}CH_2{-}\overset{Me}{\underset{H}{C}}O\cdot \longrightarrow P{-}\overset{Me}{\underset{H}{C}}\cdot + Me{-}\overset{O}{\overset{\|}{C}}{-}Me} \quad (19)$$

 (20)

$$\mathrm{P{-}\overset{Me}{\underset{H}{C}}{-}CH_2{-}\overset{Me}{\underset{H}{C}}{-}O\cdot \longrightarrow P{-}\overset{Me}{\underset{H}{C}}{-}CH_2\cdot + MeCHO} \quad (20)$$

The other major products, butyraldehyde and unsaturated C_6 ketone, are postulated to be derived from peroxyl radicals,

 (21)

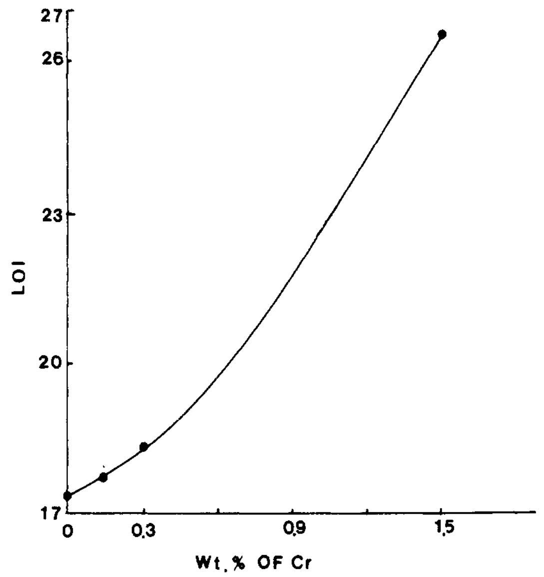
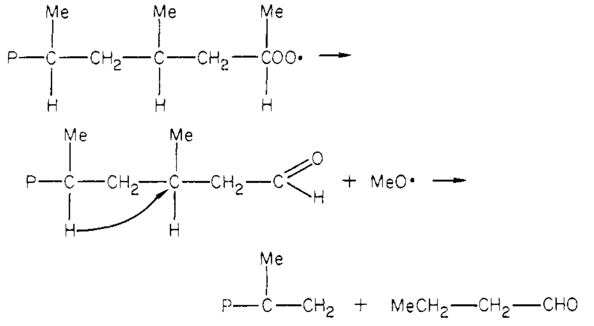


Figure 13. Variation of the limiting oxygen index of poly(propylene) with chromium contents.



(22)

At 1.5% chromium, the yields of acetone and acetaldehyde are about half of that from oxidative pyrolysis of normal poly(propylene); the yields of butanal and C_6 ketone are reduced by about three-fourths. Second, chromium apparently promotes char formation. The fact that oxidative pyrolysis of chromylated poly(propylene) leaves a char whereas normal poly(propylene) does not is not unexpected. Chromium oxide is one of the most effective dehydrogenation catalysts at low temperature,[15] which is in fact the reason for our selecting chromium for this study.

There is some prior knowledge about the possible effects of chromium on hydrocarbon oxidations. At low temperatures of less than 150 °C, there have been many investigations on the deleterious effects of a small amount of transition metals on polymer autoxidation. A review of the subject is available.[28] For instance, chromium stearate accelerates the autoxidation of poly(propylene) both in bulk[24] and in solution,[30] the acceleration being greater for the bulk polymer. This action is undoubtedly the catalytic decomposition of poly(propylene) hydroperoxide by the chromium ion, such as

$$\mathrm{POOH} + \mathrm{Cr(III)} \rightarrow \mathrm{PO\cdot} + \mathrm{OH^-} + \mathrm{Cr(IV)} \qquad (23)$$

$$\mathrm{POOH} + \mathrm{Cr(IV)} \rightarrow \mathrm{POO\cdot} + \mathrm{H^+} + \mathrm{Cr(III)} \qquad (24)$$

On the other hand, if the chromium is in the form of thiocarbamate, then it possesses slight inhibitive effects on the autoxidation of poly(propylene).[31] The mechanism of this reaction has been elucidated[32] for the more effective thiocarbamates of nickel and zinc. Based on the plausible structure for the chromylated poly(propylene), the metal ion would be expected to accelerate rather than inhibit the autoxidation of poly(propylene).

Experimentally, at temperatures between 240 and 340 °C, the chromium ion significantly retards the oxidative pyrolysis of poly(propylene), increases the overall activation energy, yet does not change the nature of the products. This suggests that chromium probably does not alter the propagation reactions but may be interfering either with the initiation or the termination reaction or both.

Let us consider the possible influence of chromium on the termination reaction. Betts and Uri[33] have demonstrated that under certain conditions transition metal ions such as cobalt can inhibit instead of accelerating autoxidation. This occurs when hydroperoxide is either absent or present only in minute amounts; reactions 23 and 24 may become unimportant. Based on the dependence of the effect on the metal ion concentration, the authors postulated a bridged complex of two metal ions with two peroxyl radicals leading to termination. At the temperature of our experiments, the steady state hydroperoxide concentration can be shown to be very low,[3] favoring the inhibitory action of chromium on oxidative degradation. This possibility appears to be supported by the large suppression by chromium of butyraldehyde and an unsaturated C_6 ketone, two products which are thought to be derived from the peroxyl radicals.

A simplified reaction sequence for the oxidative pyrolysis of chromylated poly(propylene) at very low hydroperoxide concentration may be represented by reactions 5–9 with an added termination process catalyzed by Cr.

$$2\mathrm{PO_2\cdot} + 2\mathrm{Cr} \rightarrow \text{nonvolatile products} + 2\mathrm{Cr} \qquad k_7 \qquad (25)$$

Or if a bridged complex of two chromium atoms is unfeasible, termination may be possible through

$$2\mathrm{PO_2\cdot} + \mathrm{Cr} \rightarrow \text{nonvolatile products} + \mathrm{Cr} \qquad k_7' \qquad (26)$$

This reaction may indeed occur via two fundamental steps

$$\mathrm{PO_2\cdot} + \mathrm{Cr} \rightarrow \mathrm{Cr(PO_2\cdot)}$$

$$\mathrm{Cr(PO_2\cdot)} + \mathrm{PO_2} \rightarrow \mathrm{Cr} + \text{products} \qquad (27)$$

The rate of oxidative pyrolysis becomes

$$\text{rate} = k_5\left[\frac{k_4[\mathrm{POOH}]_s}{k_6 + k_7[\mathrm{Cr}]^2}\right]^{1/2}[\mathrm{PH}] \qquad (28)$$

or

$$\text{rate} = k_5\left[\frac{k_4[\mathrm{POOH}]_s}{k_6 + k_7'[\mathrm{Cr}]}\right]^{1/2}[\mathrm{PH}] \qquad (29)$$

depending upon whether the reaction involving chromium is either by eq 25 or eq 26. If these processes are much faster than the normal termination reaction 9, then the overall activation energy for oxidative pyrolysis retarded by chromium is $E_5 + {}^1/_2E_4 - {}^1/_2E_7$. The activation energies E_5 and E_4 have been determined[34] to be 12.1 and 25 kcal mol^{-1}, respectively. Since the observed overall activation energy is 26 kcal mol^{-1}, it may be concluded that E_7 or E_7' is very small.

In addition to the above possible effect of chromium on the termination process, the chromium ion may also modify the initiation process by reducing the radical yield. For example, the simple homolysis of poly(propylene) hydroperoxide in the absence of chromium

$$\mathrm{POOH} \rightarrow \mathrm{PO\cdot} + \mathrm{\cdot OH} \qquad (30)$$

may be replaced by a nonradical process in its presence, i.e.

$$\mathrm{Cr} + \mathrm{POOH} \rightarrow \mathrm{CrO} + \mathrm{POH} \qquad (31)$$

In eq 25–29 and 31 the oxidation state of chromium is unspecified. More than one oxidation state may be effective and further research is needed regarding this point. Another possibility is suggested by Burchill's[35] observation that in nonpolar medium the following equilibrium for hydroperoxides can take place

$$2\mathrm{POOH} + \mathrm{Cu(II)\ hexanoate} \rightleftharpoons \mathrm{Cu(OOP)_2} + 2(\mathrm{hexanoic\ acid}) \quad (32)$$

If this reaction also occurs for chromium and the complex dissociates to nonradical products, then initiation may be retarded.

Combustion of Poly(propylene). Figure 13 shows that poly(propylene) becomes self-extinguishing with about 1% of covalently bonded chromium (the limiting oxygen index = 23); the self-ignition temperature is raised from 240 to 400 °C. Even though the sample also contains about 0.6% chlorine, its presence is not believed to make any significant contribution to the flame retardancy. It takes about 40% of chlorine to impart self-extinguishing properties to poly(propylene).[13,14] This result illustrates the amazing effectiveness of chromium in imparting flame retardancy to poly(propylene).

Poly(propylene), even in the most flame-retarded formulations, does not leave an organic char upon combustion. In the presence of chromium a significant amount of char formation was observed. This may be attributed to the dehydrogenation catalytic activity of some chromium compounds.

$$\mathrm{CrO} + -\mathrm{CH_2{-}CH_2}- \rightarrow \mathrm{Cr} + -\mathrm{CH{=}CH}- + \mathrm{H_2O} \quad (33)$$

$$\mathrm{Cr} \xrightarrow{[\mathrm{O}]} \mathrm{CrO} \quad (34)$$

Table V shows that the char contains 0.9% Cr and 0.17% Cl. If Cr and Cl were not consumed or volatilized, the char would have 3 and 0.9% of these two elements, respectively, since the char represents 5% of the original specimen. Therefore, a portion of the chromium and chlorine is lost during combustion. Consequently, chromium may be contributing toward flame retardancy in the gas phase in the limiting oxygen index experiments. Whereas in this paper we have stressed the condensed phase action of chromium, we must point out that it can definitely act in the gas phase as well. Bulewicz and Padley[36] have suggested that at the very high temperatures of a $H_2 + O_2$ flame, inhibition by chromium can occur via

$$\mathrm{Cr} + \cdot\mathrm{OH} \rightleftharpoons \mathrm{CrO} + \mathrm{H}\cdot \quad (35)$$

$$\mathrm{CrO} + \cdot\mathrm{OH} \rightleftharpoons \mathrm{CrO_2} + \mathrm{H}\cdot \quad (36)$$

$$\mathrm{Cr_2O_3(s)} + \mathrm{H}\cdot + \mathrm{H}\cdot\ (\mathrm{or}\ \cdot\mathrm{OH}) \rightarrow \mathrm{Cr_2O_3(s)} + \mathrm{H_2}\ (\mathrm{or}\ \mathrm{H_2O}) \quad (37)$$

Hastie[37] has reported the relative effectiveness of different inhibitors for an *n*-hexane–air flame and has found chromyl chloride to be one of the most effective ones.

Conclusion

The present work establishes that covalently bonded chromium can slightly alter the thermal pyrolysis and significantly retard the oxidative pyrolysis of poly(propylene). The latter activity is thought to be derived from an acceleration of the chain termination reaction, providing a nonradical pathway for the destruction of the reactive hydroperoxide intermediate and promoting char formation. The remarkable efficacy of chromium in imparting flame retardancy to poly(propylene) prompted an intensive investigation of other metallic elements as inhibitors for polymer combustion in our laboratories. Since the Etard reaction is limited to chromyl compound, a more general procedure for the chemical incorporation of any metal ion into a common polymer substrate has been developed, and the activities of flame retardancy of elements other than chromium has been studied.[38]

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References and Notes

(1) This work was supported in part by Grant No. G7-9010 from the Center for Fire Research of the National Bureau of Standards.
(2) Raychem. Corp., Menlo Park, CA 94025.
(3) Part 8: J. C. W. Chien and J. K. Y. Kiang, *Makromol. Chem.*, in press.
(4) C. R. Boss and J. C. W. Chien, *J. Polym. Sci., Part A-1*, **4**, 1543 (1966).
(5) J. W. Hastie, *Combust. Flame*, **21**, 49 (1973).
(6) A. E. Sherr, H. G. Gillham, and H. G. Klein, *Adv. Chem. Ser.*, **No. 85**, 307 (1968).
(7) Part 7: J. K. Y. Kiang, P. C. Uden, and J. C. W. Chien, *Polym. Degrd. Stability*, in press.
(8) A. Etard, *Ann. Chim. Phys.*, **22**, 218 (1881).
(9) P. C. Makhija and R. A. Stairs, *Can. J. Chem.*, **46**, 1255 (1968).
(10) W. A. Dietz, *J. Gas Chromator.*, 68 (1967).
(11) J. C. W. Chien and C. R. Boss, *J. Polym. Sci., Part A-1*, **5**, 3091 (1967).
(12) J. C. W. Chien and H. Jabloner, *J. Polym. Sci., Part A-1*, **6**, 393 (1968).
(13) J. W. Lyons, *J. Fire Flammability*, **1**, 302 (1970).
(14) J. W. Lyons, "The Chemistry and Uses of Fire Retardants", Wiley-Interscience, New York, 1970, pp 20–24.
(15) R. N. Shreve, "The Chemical Process Industries", McGraw-Hill, New York, 1956, p 844.
(16) W. F. Sager and A. Bradley, *J. Am. Chem. Soc.*, **78**, 1187 (1956).
(17) W. F. Sager, *J. Am. Chem. Soc.*, **78**, 4970 (1956).
(18) G. Foster and W. J. Hickinbottom, *J. Chem. Soc.*, 680 (1960).
(19) K. B. Wiberg and R. Eisenthal, *Tetrahedron*, **20**, 1151 (1964).
(20) B. E. Burgert, *J. Polym. Sci., Part C*, **24**, 233 (1968).
(21) G. Rohde, *Samml. Chem. Chem.-Tech. Vortage*, **6**, 241 (1901).
(22) I. Necsoiu, A. T. Balatan, I. Pascaru, E. Sliam, M. Elian, and C. D. Nenitzesai, *Tetrahedron*, **19**, (1963).
(23) O. H. Wheeler, *Can. J. Chem.*, **36**, 667 (1958); **38**, 2137 (1960).
(24) F. Mares and J. Rocek, *Collect. Czech. Chem. Commun.*, **26**, 2370 (1961).
(25) G. A. Russell, C. DeBoer, and K. M. Desmond, *J. Am. Chem. Soc.*, **85**, 365 (1963).
(26) F. Mares, J. Rocek, and J. Sicher, *Collect. Czech. Chem. Commun.*, **26**, 2370 (1961).
(27) J. W. Benson, "The Foundations of Chemical Kinetics", McGraw-Hill, New York, 1960, p 670.
(28) W. L. Hawkins, "Polymer Stabilization", Interscience, New York, 1972.
(29) Z. Osawa, T. Shibamiyam, and K. Matsuzaki, *Kogyo Kagaku Zasshi*, **71**, 552 (1968).
(30) Z. Osawa and T. Saito, *Adv. Chem. Ser.*, **No. 169**, 159 (1978).
(31) Z. Osawa, T. Ishizuka, Y. Ogiwara, H. Suzuki, and H. Ishikawa, *J. Appl. Polym. Sci.*, **16**, 955 (1972).
(32) J. C. W. Chien and C. R. Boss, *J. Polym. Sci., Part A-1*, **10**, 1579 (1972).
(33) A. T. Betts and N. Uri, *Makromol. Chem.*, **95**, 22 (1966).
(34) J. C. W. Chien and D. S. T. Wang, *Macromolecules*, **8**, 920 (1975).
(35) P. J. Burchill, *Aust. J. Chem.*, **25**, 1653 (1972).
(36) E. M. Bulewicz and P. J. Padley, *Proc. R. Soc. London, Ser. A*, **323**, 377 (1971).
(37) J. W. Hastie, *J. Res. Natl. Bur. Stand., Sect. A*, **77**, 733 (1973).
(38) Part 12: J. C. W. Chien and J. K. Y. Kiang, *Polym. Degrad. Stability*, accepted for publication.