

Estimation of Rate Constants During Polypropylene Autoxidation

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Synopsis

Recently, Chien and Boss calculated rate constants for the autoxidation of isotactic polypropylene based upon a postulated relatively simple scheme. Electron spin resonance, volumetric, and chemical techniques were employed. It behooved the authors of this paper to demonstrate that similar values of these rate constants could also be calculated from a more general scheme. From this general scheme, expressions were derived which involved the rate constants of interest and other constants which had been previously calculated from experimental data based upon the use of infrared absorption techniques. The values of our calculated rate constants at various temperatures agreed well with those reported by Chien and Boss where comparison was possible.

INTRODUCTION

Recently, we presented a general scheme for the thermal oxidation, in the absence of additives, of isotactic polypropylene (PP)¹⁻⁵ and atactic poly-1-butene (PB).^{5,6} The thermal oxidation kinetics of films of these polyolefins were studied by infrared spectroscopy, as a function of temperature and oxygen-to-nitrogen ratios, by observing rates of carbonyl and hydroperoxide formation. Activation energies were estimated for various steps in the scheme. We have found that the scheme and the mathematical expressions derived therefrom satisfactorily explain the experimental results obtained. Furthermore, results obtained for PP and PB by other investigators, i.e., rate of formation of volatile products,^{3,5,7,8} chemiluminescence,^{4,9,10} oxygen absorption,^{4,9,10} and changes in intrinsic viscosity as a function of time^{11,12} could also be accounted for by means of the scheme.

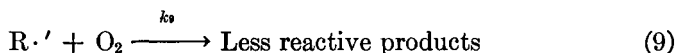
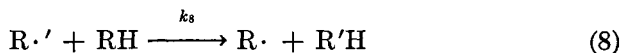
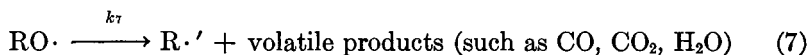
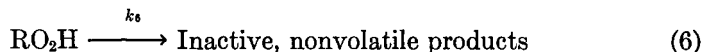
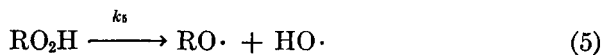
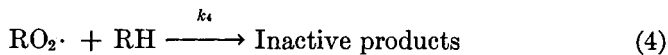
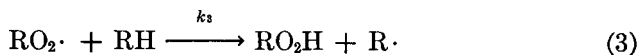
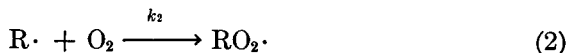
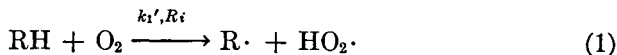
Recently, Chien and Boss¹³ investigated the kinetics of autoxidation of PP by means of electron spin resonance (ESR), volumetric, and chemical techniques. By employing a relatively simple scheme, they were able to estimate various rate constants for their proposed initiation, propagation, and termination steps. The values of the rate constant and activation energy for the initiation step were found to be the same as those for the decomposition of polypropylene hydroperoxide, thus identifying the latter as the principal initiation process. Furthermore, the values of the propagation and termination rate constants obtained compared favorably with

those obtained for initiated autoxidations of squalane and other related systems.

We would now like to demonstrate, by utilizing our more general polyolefin autoxidation scheme along with constants obtained therefrom during a study of rate of formation of carbonyl moieties by means of infrared absorption spectroscopy, that values of various rate constants can be estimated from the experimental data of Chien and Boss which compare favorably with reported values.

THEORY

For convenience, the general scheme for polyolefin autoxidation we previously presented^{1,3} is given in eqs. (1)–(9) in a slightly modified form.



We may write [neglecting the initiation step (1)] from this scheme

$$-d[\text{O}_2]/dt \equiv \rho = k_2[\text{R}\cdot][\text{O}_2] + k_9[\text{R}'\cdot][\text{O}_2] \quad (10)$$

Assuming steady-state conditions for the various radical species formed and for hydroperoxide,¹³ the expressions (11)–(13) may be readily obtained:

$$[\text{RO}_2\cdot] = k'[\text{RO}_2\text{H}]_s/k_3[\text{RH}] \quad (11)$$

$$[\text{R}'\cdot] = k_5[\text{RO}_2\text{H}]_s/k_8[\text{RH}] + k_9[\text{O}_2] \quad (12)$$

$$[\text{R}\cdot] = (k_3 + k_4)[\text{RH}][\text{RO}_2\cdot]/k_2[\text{O}_2] \quad (13)$$

where $k' = k_5 + k_6$, and $[\text{RO}_2\text{H}]_s$ denotes the steady-state concentration of hydroperoxide.

It can be shown from eqs. (10)–(13) that

$$\rho_s = [\text{RO}_2\text{H}] \left((k_3 + k_4) k'/k_3 + k_5[\text{O}_2]/k_3 + [\text{O}_2] \right) \quad (14)$$

where ρ_s denotes the oxidation rate during steady-state concentration of

hydroperoxide and $K_3 = k_8[\text{RH}]/k_9$. Moreover, it can be readily shown that

$$k_3k_6/k_4 = k'K_2/K_3 \quad (15)$$

where, $K_2 = k_3k_5k_8[\text{RH}]/k_9k_4k'$.

Substituting eq. (15) into eq. (14), we finally obtain

$$\frac{\rho_S}{[\text{RO}_2\text{H}]_S} = k_5 \left(\frac{K_3}{K_2} \left(1 + \frac{k_3}{k_4} \right) + \frac{[\text{O}_2]}{K_3 + [\text{O}_2]} \right) \quad (16)$$

In a similar manner, the following expressions may also be derived:

$$\frac{\rho_S}{[\text{RO}_2\cdot][\text{RH}]} = k_3 \left(\frac{k_4}{k_3} \right) \left[1 + \left(1 + \frac{K_2}{K_3} \frac{[\text{O}_2]}{(K_3 + [\text{O}_2])} \right) \right] \quad (17)$$

$$\frac{\rho_S}{[\text{RO}_2\cdot]^2} = \frac{k_3 k_4 [\text{RH}]^2}{k_5 [\text{RO}_2\text{H}]_S} \frac{K_2}{K_3} \left(1 + \frac{k_4}{k_3} \left(1 + \frac{K_2}{K_3} \frac{[\text{O}_2]}{(K_3 + [\text{O}_2])} \right) \right) \quad (18)$$

In eqs. (16)–(18), our symbols k_5 and k_3 are designated as k_i and k_p , respectively, by Chien and Boss.¹³ Since values of K_2 and K_3 have been calculated for PP at various temperatures³ and since experimental values of ρ_S , $[\text{RO}_2\cdot]$, and $[\text{RO}_2\text{H}]_S$ are listed by Chien and Boss¹³ at various temperatures for the oxidation of PP in pure oxygen, it should be possible to calculate values of k_5 and k_3 as shown in the following section.

RESULTS AND DISCUSSION

Estimation of k_5

From eq. (16), it can be seen that prior to the evaluation of k_5 the ratio, k_4/k_3 , must be estimated. It is evident from eq. (15) that the value of k_4/k_3 can be obtained since values of k' are known and those of k_5 have already been reported.¹³ (The values of k_5 from eq. (16) should agree well with the reported values.) However, since the values of k' have been presented more extensively for PB⁶ at various temperatures than for PP, values of k_4/k_3 were estimated for PB (assuming that the value of k_5 at the same temperature was valid both for PP and PB) and these values were assumed to apply to PP. In this manner, $(k_4/k_3)_{\text{av}} = 1.38 \pm 0.12$ for the temperatures, 130, 120, and 110°C.

Values of k_5 have been calculated at various temperatures from eq. (16) and are listed in Table I.

TABLE I
Calculation of Values of k_5 at Various Temperatures from eq. (16)

Temperature, °C	K_2	K_3	$(\rho_S/[\text{RO}_2\text{H}]_S)_{\text{av}}$ $\times 10^4, \text{sec}^{-1}$	$k_5 \times 10^4, \text{sec}^{-1}$	
				Eq. (16)	Chien and Boss ¹³
120	56	69	13.6	5	6.8 ± 0.8
130	70	81	33.0	13	16.5 ± 1.7
140	95	100	64.0	28	32 ± 2

It can be seen from Table I that values of k_3 calculated from eq. (16) are in reasonably good agreement with values reported by Chien and Boss.¹³

Estimation of k_3

By using the above value of $(k_4/k_3)_{av.}$ for PP and employing eq. (17), values of k_3 were calculated at various temperatures for PP and are listed in Table II along with values reported by Chien and Boss. (These authors have indicated that for isotactic polypropylene, 50% crystallinity, [RH] should be 11 mole/l).

TABLE II
Calculation of Values of k_3 at Various Temperatures from Eq. (17)

Temperature, °C	K_2	K_3	$(\rho_S/[RO_2\cdot] \times [RH])_{av.}$ 1/mole-sec	$k_3 \times 10^4$, 1/mole-sec	
				Eq. (17)	Chien and Boss ¹³
120	56	69	6.6	2.2	3.3 ± 0.1
130	70	81	8.4	2.8	4.2 ± 0.5
140	95	100	9.2	3.1	4.6 ± 0.5

From Table II it can be observed that the agreement between calculated and reported values of k_3 is reasonably good.

Estimation of $\rho_S/[RO_2\cdot]^2$

The termination rate constant k_t mentioned by Chien and Boss cannot be compared with any of the rate constants listed in the more general scheme we previously employed. Nevertheless, from eq. (18) and the ratio, $k_4/k_3 = 1.38$, the following expression may be readily obtained,

$$\frac{\rho_S}{[RO_2\cdot]^2} = \frac{1.82 k_3^2 [RH]^2 K_2}{k_5 [RO_2H]_S K_3} \left(1.74 + \frac{K_2 [O_2]}{K_3 (K_3 + [O_2])} \right) \quad (18a)$$

According to the relatively simple scheme of Chien and Boss, the termination rate constant could be determined from the experimentally obtained ratio, $\rho_S/[RO_2\cdot]^2$. We will reverse the procedure and show that the experimental ratio, $\rho_S/[RO_2\cdot]^2$, can be estimated from eq. (18a). Values of this ratio were calculated and are listed in Table III along with reported experimental values of this ratio.¹³

TABLE III
Calculations of $\rho_S/[RO_2\cdot]^2$ at Various Temperatures and for Pure Oxygen from Eq. (18)

Temperature, °C	$\rho_S/[RO_2\cdot]^2 \times 10^{-6}$ 1/mole-sec	
	Eq. (18)	Chien and Boss ¹³
120	12.5	9.0
130	12.0	9.0
140	8.6	6.6

From Table III, it can be seen that the calculated and experimentally obtained values for $\rho_8/[RO_2\cdot]^2$ agree reasonably well. It may also be mentioned here that obviously because of the good agreement between values of k_3 and k_5 obtained in this work with reported values at various temperatures, calculated activation energies will also compare favorably with reported values for the various steps represented by k_3 and k_5 .

Returning to our general scheme it may be apropos at this time to clarify some of the steps in the scheme. Although reaction (1) is not explicitly involved in the kinetic expressions in this paper, it was, however, used in kinetic expressions derived in our earlier papers.¹⁻⁶ Step (1), nevertheless, was included to maintain the general nature of the scheme, as was step (8). Reaction (9) is a termination step where the relatively small R' fragment forms the corresponding peroxy radical which in turn undergoes rapid termination by recombination. We have excluded a termination step by recombination of large free-radical fragments, e.g., $RO_2\cdot$, since this would require polymer-polymer type interaction which should be exceedingly slow due to the high bulk viscosity of the reaction medium. Step (4) is included in the scheme since small amounts of impurities in polymers [RH] are inherently present due to difficulties in purification. These impurities, which are proportional to [RH], may combine with $RO_2\cdot$ radicals inactivating them. A case in point is the inactivation of $RO_2\cdot$ radicals by metallic impurities (Cat), e.g., $RO_2\cdot + Cat \rightarrow RO_2\cdot Cat$. Such reactions have been reported in recent literature.¹⁴

In conclusion, we can state that the rate constants calculated by Chien and Boss from their postulated relatively simple scheme lend support not only to their simple scheme but also to the more general scheme we advocated. It would be interesting if Chien and Boss could demonstrate that their scheme could also be applied quantitatively (as we have demonstrated that our scheme can be applied quantitatively) to carbonyl and hydroperoxide formation, to rate of formation of volatile products, to chemiluminescence, and to changes in molecular weight as a function of time during the autoxidation of polyolefins such as PP or PB.

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