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A New Kinetic Model for Polypropylene Thermal Oxidation at Moderate Temperatures

Stefan Verdu and Jacques Verdu*

ENSAM, 151 Bd de l'Hôpital, 75013 Paris, France

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ABSTRACT: This work deals with a mechanistic scheme for polymer oxidation, in which the unique source of radicals is the unimolecular decomposition of hydroperoxides. The corresponding kinetic scheme is resolved in the general case where no stationary state for radical concentration is postulated. The numerical results are in good agreement with experimental data such as, for instance (a) the existence of a close relationship between the duration of the "induction period" and the reciprocal of the POOH decomposition rate constant, (b) the fact that the induction time tends toward a finite value when the initial POOH concentration tends toward zero, and (c) the fact that the steady state rate is independent of the POOH decomposition rate constant and that the apparent activation energy of oxidation varies with the exposure time. The practical use of this model appears, however, almost impossible, owing to the difficulty of determining certain parameters. Fortunately, a peculiar solution of the kinetic scheme based on the hypothesis of the existence of a stationary state for radical concentration displays the double advantage of having an analytical form and keeping all the predictive qualities of the general model, despite the wrong character of the starting hypothesis. This somewhat paradoxical result can be attributed to the structure of the basic differential equations and to the chosen ranges of parameter values. Ways for experimental checking of the model are proposed.

Introduction

One half century is elapsed since the pionneering work of Bolland et al.[1] on the oxidation of hydrocarbon polymers; however, there is not yet consensus on a kinetic model or even an approach for kinetic modeling. Mechanistic complexity, as attested, for instance, by the high diversity of oxidation products[2,3] and/or spatial heterogeneity of the reaction[4−6] are often cited as the major difficulties in kinetic studies. These obstacles are, however, not insuperable: complex mechanistic schemes can be sometimes reduced to simpler ones by using the concept of "kinetically equivalent reaction", e.g., a hypothetical single reaction equivalent to a more or less important set of elementary steps. In the same way, a reaction can be heterogeneous at large scale—for instance at the morphological scale—but homogeneous at smaller scale. What is important here is the degree of polydispersity of the spatial distribution of oxidation rates in the domains where oxidation occurs.[7] This research area remains thus largely open. A given approach to the problem must be judged by its success in predicting the main features of oxidation kinetics, but in most of the cases we lack a precise description of these latter, in terms sufficiently general to be used as universal criteria of the validity of kinetic models. In the case of the thermal oxidation of unstabilized polypropylene (PP), the following characteristics could be taken as targets for the elaboration of kinetic models:

(a) The oxidation kinetic curves (in isothermal conditions) display a steady state preceded by a pseudo induction period during which oxidation is autoaccelerated. The duration of the "induction period" t_i can be arbitrarily defined[8] as the coordinate of the intercept of the steady state straight line with the time axis for oxygen absorption or carbonyl growth curves. In the case of chemiluminescence, it is convenient to take the integral curves: $\int_0^t i\,dt = f(t)$ to apply the same definition. Hydroperoxide (POOH) growth curves can be in principle used in the same way as chemiluminescence curves.

(b) The duration of the induction period t_i depends on the sample purity and preoxidation, but for reasonably clean samples, it tends to be independant of the sample origin and preparation mode.[9] In the 80−150 °C temperature interval, t_i seems to obey the Arrhenius law with an apparent activation energy E_i of 105 ± 15 kJ·mol^{-1}

$$E_i \sim 105 \pm 15\ \mathrm{kJ{\cdot}mol^{-1}}$$

(c) t_i is of the same order of magnitude as the POOH lifetime determined from independent experiments of decomposition in a neutral atmosphere.[3]

(d) The steady state rate obeys also the Arrhenius law, but with an activation energy lower than for t_i.[8] In other words, the overall apparent activation energy of oxidation decreases with the conversion ratio.

(e) The steady state rate is independent of the initiation rate constant k_1. As a matter of fact, the introduction in the polymer of variable amounts of transition metals capable of catalyzing the POOH decomposition modifies the induction time but does not affect the steady state rate.[8]

Surprisingly, it has been recently shown that all these features are well predicted by a simple mechanistic scheme in which unimolecular decomposition of hydroperoxides is the unique source of radicals:[9]

$$\text{(I)}\quad \mathrm{POOH} \rightarrow \alpha\mathrm{P}^{\bullet} \qquad (k_1)$$

$$\text{(II)}\quad \mathrm{P}^{\bullet} + \mathrm{O_2} \rightarrow \mathrm{PO_2}^{\bullet} \qquad (k_2)$$

$$\text{(III)}\quad \mathrm{PO}^{\bullet} + \mathrm{PH} \rightarrow \mathrm{PO_2H} + \mathrm{P}^{\bullet} \qquad (k_3)$$

$$\text{(VI)}\quad \mathrm{PO_2}^{\bullet} + \mathrm{PO_2}^{\bullet} \rightarrow \text{inact prod} + \mathrm{O_2} \qquad (k_6)$$

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* To whom correspondance should be addressed. Tel.: (33) 01 44 24 63 72. Fax: (33) 01 44 24 63 82. E-mail: LTVP@ensam.paris.fr.

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N.B.: Only the case where O_2 is in excess, e.g., where reactions from radicals $P^{\bullet}$ other than oxygen addition (II) can be neglected, is considered here.

Using the assumption of stationary state for the radical concentration, and considering only the case of low initial POOH concentrations, one obtains the following expression for the oxidation rate:

$$r = r_{\infty}\left(1 - \exp - \frac{k_i t}{2}\right)^2$$

where r_{∞} is independant of k_i and is essentially linked to $(k_3{}^2k_6{}^{-1})$.

Chemiluminescence intensity and hydroperoxide concentration vary proportionally to r, whereas carbonyl concentration varies as $\int_0^t r\,\mathrm{d}t$.

This model, which was previously used by Karpukhin and Slobodetskaya to describe the PP photooxidation,[10] displays remarkable predictive properties[9,11] despite the fact that it is based on a wrong assumption. As a matter of fact, the whole radical concentration cannot be considered constant in such a branched chain process.

The aim of this article is to propose a resolution of the kinetic scheme corresponding to the above chain mechanism without any hypothesis of stationary state for radical concentration. Incidentally, we will try to explain why good results can be obtained from the wrong hypothesis relative to the existence of such a stationary state.

Results

The above mechanistic scheme leads to the following set of differential equations:

$$\frac{\mathrm{d}[P^{\bullet}]}{\mathrm{d}t} = \alpha k_1[\mathrm{POOH}] - k_2[P^{\bullet}](O_2) + k_3[PO_2^{\bullet}][\mathrm{PH}] \quad (1)$$

$$\frac{\mathrm{d}[PO^{\bullet}_2]}{\mathrm{d}t} = k_2[P^{\bullet}](O_2) - k_3[PO_2^{\bullet}][\mathrm{PH}] - k_6[PO_2^{\bullet}]^2 \quad (2)$$

$$\frac{\mathrm{d}[\mathrm{POOH}]}{\mathrm{d}t} = k_3[PO_2^{\bullet}](\mathrm{PH}) - k_1[\mathrm{POOH}] \quad (3)$$

N.B.: k_6 includes the factor 2 linked to the fact that two $PO_2^{\bullet}$ radicals disappear per termination event. The system reaches a steady state when the POOH decomposition equilibrates its formation. One may consider a stationary state for radical concentrations; all the above rates tend toward zero, so that one obtains the following values of steady state concentrations:

$$[P^{\bullet}]_{\infty} = \frac{\alpha k_3{}^2(\mathrm{PH})^2(\alpha + 1)}{k_6k_2[O_2]} \qquad [PO_2^{\bullet}]_{\infty} = \frac{\alpha k_3(\mathrm{PH})}{k_6}$$

$$[PO_2H]_{\infty} = \frac{\alpha k_3{}^2(\mathrm{PH})^2}{k_1k_6}$$

It can be recalled that the terminations involving radicals $P^{\bullet}$ were neglected:

(IV) $P^{\bullet} + P^{\bullet} \rightarrow$ inact prod (k_4)

(V) $P^{\bullet} + PO_2^{\bullet} \rightarrow$ inact prod (k_5)

This is possible if, schematically

$$k_4[P^{\bullet}]^2 << k_6[PO_2]^2 \quad (4)$$

provided that k_5 is intermediary between k_4 and k_6.

Applied to steady state, this inequality becomes

$$\frac{k_2[O_2]}{(\alpha + 1)k_1} >> \left(\frac{k_4}{k_6}\right)^{1/2} \quad (5)$$

At temperatures close to 100 °C, where $k_1 \sim 10^{-3}–10^{-4}$ s^{-1}, $k_2[O_2]$ is of the order of $10^3–10^4$ s^{-1}, and $\alpha \sim 2$, it is easy to see that the above assumption is effectively valid, except in the cases where an enormous difference would exist between termination rates of $P^{\bullet}$ and $PO_2^{\bullet}$ radicals, which seems unlikely.[12]

To solve the above system of differential equations, it is convenient to use reduced variables such as

$$x = \frac{[PO_2^{\bullet}]}{[PO_2^{\bullet}]_{\infty}} \qquad y = \frac{[\mathrm{POOH}]}{[\mathrm{POOH}]_{\infty}} \qquad z = \frac{[P^{\bullet}]}{[P^{\bullet}]_{\infty}}$$

Then, the system becomes

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_3[\mathrm{PH}][(\alpha + 1)z - x - \alpha x^2] \quad (6)$$

$$\frac{\mathrm{d}y}{\mathrm{d}t} = k_1(x - y) \quad (7)$$

$$\frac{\mathrm{d}z}{\mathrm{d}t} = \frac{k_2[O_i]}{\alpha + 1}[\alpha y + x - (\alpha + 1)\,z] \quad (8)$$

In the case of PP it can be reasonably assumed that $\alpha = 2$ since the radical yield of POOH decomposition cannot be limited by cage disproportionation in the case of tertiary hydroperoxides.

For $t = 0$: $x = 0$; $z = 0$; $y = y_0$.

For $t \rightarrow \infty$: $x \rightarrow 1$; $z \rightarrow 1$ $y \rightarrow 1$.

$$y_0 = \frac{[\mathrm{POOH}]_0}{[\mathrm{POOH}]_{\infty}}$$

where $[\mathrm{POOH}]_0$ is the initial hydroperoxide concentration if POOHs are effectively initially present or the hypothetical POOH concentration kinetically equivalent to the radical producing impurities initially present in the polymer.[9]

Products resulting from initiation events are formed at a rate r_i such as

$$r_i = \varphi k_1[\mathrm{POOH}] \quad (9)$$

where φ is the yield of the product under consideration.

Thus

$$r_i = \varphi k_1[\mathrm{POOH}]_{\infty}y \quad (10)$$

so that the concentration C_i of the products of initiation events is given by

$$C_i = \varphi k_1[\mathrm{POOH}]_{\infty}\int_0^t y\,\mathrm{d}t \quad (11)$$

In the same way, the concentration C_T of products of termination events is given by

$$C_i = \varphi k_6[\,PO_2^{\bullet}\,]_{\infty}^2\int_0^t x^2\,\mathrm{d}t \quad (12)$$

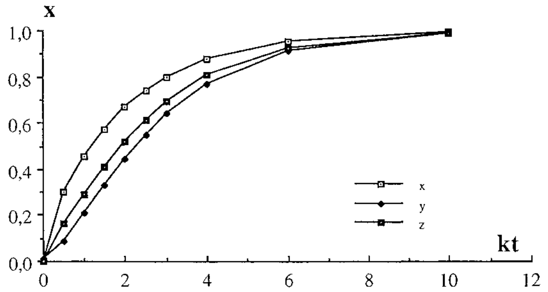

Figure 1. Example of computed time variations of peroxy radical (x), alkyl radical (z), and hydroperoxide (y) reduced concentrations for $y_0 = 10^{-2}$; $k_1 = 10^{-3}$ s^{-1}, $k_3(\mathrm{PH}) = 10$ s^{-1}, and $k_2[02]/(\alpha + 1) = 1000$ s^{-1}.

The oxygen absorption rate r is given by

$$r = -\,k_2[\mathrm{P}^\bullet][\mathrm{O}_2] + \frac{1}{2}k_6[\mathrm{PO}_2^{\bullet}]^2 = -\frac{\alpha k_3^{\,2}(\mathrm{PH})^2}{k_6}\left[(\alpha + 1)z - \frac{1}{2}\alpha x^2\right] \quad (13)$$

e.g.

$$R = \frac{r}{r_\infty} = (\alpha + 1)z - \frac{1}{2}\,\alpha x^2$$

and

$$C_{\mathrm{O}_2} = -\,\frac{\alpha k_3^{\,2}(\mathrm{PH})^2}{k_6}\int_0^t\left[(\alpha + 1)z - \frac{1}{2}\,\alpha x^2\right]\mathrm{d}t \quad (14)$$

where the minus sign indicates consumption.

For given values of y_0, k_1, $k_3[\mathrm{PH}]$, and $k_2[\mathrm{O}_2]$, the system of differential equations (6)−(8) has been resolved by using the Runge−Kutta method and always taking $\alpha = 2$. The quantities

$$Y = \int_0^t y\,\mathrm{d}t \qquad X = \int_0^t x^2\,\mathrm{d}t \qquad Z = \int_0^t\left[(\alpha + 1)z - \frac{1}{2}\,\alpha x^2\right]\mathrm{d}t$$

have been computed, and the corresponding induction times have been determined.

An example of the time variations of x, y, and z is given in Figure 1. Some typical values of induction times multiplied by the corresponding value of k_1 are given in Table 1. These results call for the following comments:

The kinetic curves display the expected shape.

In the domain under investigation corresponding typically to $y_0 \le 10^{-1}$, $k_1 \le 10^{-2}$ s^{-1}, $k_3[\mathrm{PH}] \ge 10k_1$, and $k_2[\mathrm{O}_2] \ge 10k_3[\mathrm{PH}]$, the induction times are such as

$$\frac{2}{k_1} \le t_{\mathrm{i}}(C_{\mathrm{i}} \text{ or } C_{\mathrm{T}}) \le \frac{4}{k_1} \qquad \frac{1}{k_1} \le t_{\mathrm{i}}(\mathrm{O}_2) \le \frac{3}{k_1}$$

The duration of the autoaccelerated period of oxidation is thus always of the order of the characteristic time of POOH decomposition (k_1^{-1}).

It is practically impossible to distinguish between X and Y, e.g. between C_{i} and C_{T}, in the entire domain of variation of the parameters under consideration.

In contrast, it is easy to distinguish between C_{i} (or C_{T}) and [O$_2$] kinetic curves since their induction times differ always by $1/2k_1^{-1}$. In other words

$$k_1[t_{\mathrm{i}}(C_{\mathrm{i}}) - t_{\mathrm{i}}(\mathrm{O}_2)] = \frac{1}{2} \quad (15)$$

Table 1. Product (Initiation Rate Constant "Induction Time") for Products Originating from Initiation (C_i) and Termination (C_T), and for Oxygen Absorption ([O$_2$]), for Various Values of the Rate Constants[a]

					$k_1 - t_{\mathrm{i}}$		
run	y_0	k_1 (s^{-1})	k_3(PH) (s^{-1})	$k_2(\mathrm{O}_2)/(\alpha + 1)$ (s^{-1})	C_{i}	C_{T}	[O$_2$]
A	10^{-5}	10^{-3}	5×10^{-2}	2.5	2.97	2.96	2.60
B	10^{-4}	10^{-3}	5×10^{-2}	2.5	2.79	2.78	2.41
C	10^{-3}	10^{-3}	5×10^{-2}	2.5	2.60	2.59	2.21
D	10^{-2}	10^{-3}	5×10^{-2}	2.5	2.37	2.36	1.97
E	10^{-1}	10^{-3}	5×10^{-2}	2.5	1.89	1.88	1.52
F	10^{-5}	10^{-3}	10^{-1}	10	2.77	2.77	2.40
G	10^{-4}	10^{-3}	10^{-1}	10	2.64	2.64	2.26
H	10^{-3}	10^{-3}	10^{-1}	10	2.50	2.50	2.12
I	10^{-3}	10^{-3}	10^{-1}	10	2.51	2.51	2.12
J	10^{-3}	10^{-3}	10^{-2}	10^{-1}	3.16	3.13	2.77
K	10^{-2}	5×10^{-6}	5×10^{-4}	5×10^{-2}	4.64	4.63	3.86
L	10^{-2}	10^{-4}	10^{-2}	1.00	2.32	2.32	1.93
M	10^{-2}	10^{-3}	10^{-1}	10	2.32	2.32	1.93
N	10^{-2}	10^{-2}	1	100	2.32	2.32	1.93
O	10^{-2}	10^{-3}	10^{-1}	1.0	2.32	2.32	1.93
P	10^{-2}	10^{-3}	1	10	2.27	2.27	1.89
Q	10^{-2}	10^{-3}	10^{-2}	10	2.71	2.66	2.28
R	10^{-2}	10^{-3}	10	10^{3}	2.27	2.27	1.88

[a] These results were obtained from a numerical resolution of the kinetic scheme without hypothesis of stationary state.

Discussion

The fact that, systematically, POOH decomposition seems to govern the whole oxidation kinetics results from two important characteristics of the system of differential equations (6)−(8):

(1) Since x, y, and z are continuously increasing functions of time, e.g., their derivatives are always positive, it comes

$$x > y > x^2$$

and

$$x + \alpha x^2 < (\alpha + 1)z < x + \alpha y$$

The characteristic times of x, y, and z variations must therefore be of the same order of magnitude.

(2) The system contains three "time constants": $\tau_1 = k_1^{-1}$, $\tau_2 = (\alpha + 1)(k_2[\mathrm{O}_2])^{-1}$, and $\tau_3 = (k_3[\mathrm{PH}])^{-1}$. In the conditions under study, $\tau_1 >> \tau_2$ or τ_3.

In these conditions, it is not surprising to find characteristic times for x, y, and z—and any other variable linked to the oxidation conversion during its autoaccelerated period—of the order of k_1^{-1}. Schematically, POOH decomposition governs kinetically the whole oxidation process because it is the slowest step. Indeed, these observations are only valid in the conditions under study (low to moderate temperatures, excess of oxygen). We see, for instance, that τ_2 varies hyperbolically with [O$_2$] so that there are situations, in the diffusion-controlled regime, where $\tau_2 > \tau_1$. In the same way, the activation energy is higher for k_1 than for k_3 so that there is a temperature limit above which $\tau_3 > \tau_1$. Then, the kinetic behavior can qualitatively differ from the above depicted one.

The fact that the curves $X = f(t)$ and $Y = f'(t)$ differ by less than 1% during the whole induction period (except perhaps at very short times where all the variables are below the sensitivity limit of common measurement methods) indicates that it is impossible to decide (from kinetic arguments) if a given species originates from the initiation or from the termination reaction. This is a well-known property of stationary state kinetic regimes, but what is new is that it can be extended to the nonstationary state regime, during which oxidation is autoaccelerated. There is apparently no way to identify the origin of chemiluminescence only from kinetic analysis.

The fact that the induction times of initiation/termination products, for instance, carbonyl groups, and oxygen absorption (or any other quantity linked to this latter, such as mass gain) differ by $^1/_2k_1^{-1}$ is interesting because it provides an opportunity for experimental checking (see below).

Usually, in classical kinetic modeling, it is assumed (for PP at moderate temperature) that the kinetic chain length λ is high so that O_2 regeneration by the termination can be neglected. The concept of kinetic chain length is, however, questionable in the case under study, since λ varies continuously with time as long as oxidation is autoaccelerated. In steady state, it can be written

$$\lambda_\infty = \frac{\text{propagation rate}}{\text{initiation rate}} = \frac{k_3[\mathrm{PH}][\mathrm{PO_2}^\bullet]}{\alpha k_1[\mathrm{POOH}]_\infty} = \frac{1}{\alpha}$$

Thus, $\lambda_\infty = 1/2$ in the case of PP.

We see that initiation, and thus termination, is far from a rare event in this case, the incidence of termination in kinetics of O_2 absorption explains the difference between the induction times of oxygen absorption and carbonyl or hydroperoxide buildup.

Let us now consider the case of the previously proposed model[9,10] based on the wrong assumption of a stationary state for radical concentration. It was shown that, for low initial POOH concentrations such as $y_0 << 1$

$$[\mathrm{PO_2H}] = [\mathrm{PO_2H}]_\infty\left[1 - \exp\left(-\frac{k_1 t}{2}\right)\right]^2$$

and

$$[\mathrm{PO_2}^\bullet] = [\mathrm{PO_2}^\bullet]_\infty\left[1 - \exp\left(-\frac{k_1 t}{2}\right)\right]$$

where $[\mathrm{PO_2}^\bullet]_\infty$ and $[\mathrm{PO_2H}]_\infty$ take the previously reported values.

The concentration of initiation or termination products is given by

$$C = \phi k_1 \int_0^t [\mathrm{POOH}]\,\mathrm{d}t = \phi[\mathrm{POOH}]_\infty\left[k_1 t - 3 + 4\exp\left(-\frac{k_1 t}{2}\right) - \exp(-k_1 t)\right]$$

The induction time is thus for these products (such as carbonyls), and for hydroperoxides or chemiluminescence, whatever its origin:

$$t_\mathrm{i}(C) = \frac{3}{k_1}$$

The oxygen absorption rate can be written

$$\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = -k_2[\mathrm{O_2}](\mathrm{P}^\bullet) + \frac{1}{2}k_6[\mathrm{PO_2}^\bullet]^2 = -\frac{\mathrm{d}[\mathrm{PO_2}^\bullet]}{\mathrm{d}t} - k_3[\mathrm{PH}][\mathrm{PO_2}^\bullet] - \frac{1}{2}k_6[\mathrm{PO_2}^\bullet]^2$$

$$\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = \frac{\alpha k_3[\mathrm{PH}]k_1}{2k_6}\exp\left(-\frac{k_1 t}{2}\right) - \frac{\alpha k_3^{\,2}(\mathrm{PH})^2}{k_6}\left[1 - \exp\left(-\frac{k_1 t}{k_6}\right)\right] - \frac{1}{2}\frac{\alpha^2 k_3^{\,2}(\mathrm{PH})^2}{k_6}\left[1 - \exp\left(-\frac{k_1 t}{2}\right)\right]^2$$

$$\frac{k_1}{2k_3[\mathrm{PH}]} << 1$$

Taking $\alpha = 2$, one obtains

$$\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = \frac{2k_3^{\,2}[\mathrm{PH}]^2}{k_6}\left[2 - \frac{6}{k_1}\exp\left(-\frac{k_1 t}{2}\right) + \frac{1}{k_1}\exp(-k_1 t)\right]$$

and

$$C_{\mathrm{O_2}} = -\frac{2k_3^{\,2}(\mathrm{PH})^2}{k_6 k_1}\left[2k_1 t - 5 + 6\exp\left(-\frac{k_1 t}{2}\right) - \exp(-k_1 t)\right]$$

The induction time is thus $t_\mathrm{i}(\mathrm{O_2}) = {}^5/_2k_1$.

We see, therefore, that this model does not differ qualitatively or quantitatively (within a reasonable incertitude range) from the preceding numerical model. Both models have in common the steady state values and the fact that the $\mathrm{PO_2}^\bullet$ concentration increases as the square root of the POOH concentration. These features presumably play a key role in the whole oxidation kinetics. Both models differ, however, by the behavior of $\mathrm{P}^\bullet$ radicals: In the analytical model, the initial value of their concentration $[\mathrm{P}^\bullet]_0$ is very high (equal to the asymptotic $\mathrm{PO_2}^\bullet$ concentration according to the hypothesis of stationary state). $[\mathrm{P}^\bullet]$ decreases continuously and tends toward zero. In the numerical model, $[\mathrm{P}^\bullet]$ varies more logically in the same way as $[\mathrm{PO_2}^\bullet]$, as shown in the example of Figure 1 and checked for all the cases listed in Table 1. $[\mathrm{P}^\bullet]$ increases from zero to a low asymptotic value about 10^4 times lower than $[\mathrm{PO_2}^\bullet]_\infty$. Both models are thus expected to differ essentially during the initial period, but this difference would be difficult to put in evidence since during this period oxidation products are in very low, practically undetectable concentrations, and after the end of the induction period, the models under study are characterized by their low sensitivity to initial conditions.

An interesting practical consequence of this result is that although it is based on a wrong hypothesis, the “stationary state” model can be used in oxidation kinetic studies where its analytical form would considerably simplify the investigations.

How, in practice, should one use these kinetic models? From the experimental point of view, the best way consists of using oxygen absorption data, since any other approach needs the knowledge of a supplementary parameter ϕ linked to the yield of the corresponding species in initiation and/or termination processes.

The steady state rate of oxygen absorption is $\alpha k_3^2[PH]^2/k_6$ independent of the approach chosen for the resolution of the kinetic scheme. Its activation energy is $E_\infty = 2E_3 - E_6$. In the case of PP: $[PH] = 20$ mol·L^{-1} (in the amorphous phase), and $\alpha = 2$. Values of $k_3k_6^{-1/2}$, which could be called the "intrinsec oxidizability of the polymer", have often been reported in the literature.[13,14]

If data relative to initiation or termination products are available together with oxygen absorption ones, they give access to the corresponding yield:

$$\phi = \frac{r_\infty(C_i \text{ or } C_T)}{r_\infty(O_2)}$$

The eventual temperature variations of ϕ can give interesting information on the mechanisms, for instance in the case of methyl ketones in PP, on the competition between hydrogen abstraction and β scission from alkoxy radicals.

The induction time gives access to k_1 since

$$k_1 = \frac{5}{2}/t_i(O_2) = 3/t_i(C_i)$$

This equality is exact in the case of the "analytical model" (stationary state), but only approximative in the case of the "numerical model" (no stationary state).

In the case of the analytical model, the knowledge of the steady state rate and of the induction time at a few temperatures gives all the elements necessary to generate any kinetic curve in the domain of validity of the starting hypotheses. If the sample is significantly preoxidized (y_0 is measurable), the influence of y_0 can be easily taken into account in the equations.[9]

In the case of the numerical model, however, the knowledge of the above kinetic parameters, derivable from experimental curves in classical experiments (oxygen absorption, mass increase, carbonyl or hydroxyl growth, hydroperoxide buildup, chemiluminescence, thermal analysis, etc., ...) is not sufficient.

k_1 can be approximatively determined from the induction time, but $k_3[PH]$ (or k_6) and $k_2[O_2]$ have to be determined in independent ways.

In principle, their determination directly from the kinetic model is possible using a trial and error procedure, but in fact, beyond certain threshold values, the sensitivity of the whole kinetics to variations of $k_3[PH]$ or $k_2[O_2]$ is too low to permit their precise determination.

We are thus in the presence of two approaches: Both are identical at the steady state level but differ slightly in the modeling of the autoaccelerated period of oxidation. The "right" approach starts from physically sound hypotheses and is in principle capable of predicting accurately all the aspects of oxidation kinetics, but certain parameters needed for the resolution of kinetic equations are practically inaccessible. The "wrong" approach starts from a physically questionable hypothesis, but it gives predictions practically undistinguishable from right ones. Thus the use of the wrong approach can be recommended in practice; the right approach serves practically only as its justification.

How does one check this kinetic model?

The characteristics enumerated in the introduction can be used as criteria of validity:

(a) The model is capable of generating kinetic curves having the desired shape, from the variation of only two parameters: k_1 and $\alpha k_3^2(PH)^2/k_6$.

(b) The model predicts that the duration of the induction period depends essentially on the initiation rate constant k_1. Its apparent activation energy can vary significantly from author to author. The highest values, as, for instance, the one determined from chemiluminescence experiments (149 kJ·mol^{-1}) by Celina and George[6] are close to the expected value from model compound data. Lower values could be attributed to the presence of catalytic impurities in variable concentrations. For most of the industrial specimens, they range between 90 and 120 kJ·mol^{-1}. Globally, these dates are not inconsistent with the hypothesis of unimolecular POOH decomposition.

(c) The model predicts that for low initial [POOH] concentration, the induction time tends to become independent of this concentration; see for instance results of runs A to E in Table 1. This is confirmed by the analytical model which shows, moreover, that this is a specific property of the unimolecular POOH decomposition.[9]

(d) The model predicts that the steady state rates are independent of the rate constant of POOH decomposition, which can be effectively observed in results where variable amounts of catalytic impurities have been intentionaly,[8] or not,[15] incorporated to the samples.

(e) The model predicts that whole oxidation is a non-Arrhenian process: its apparent activation energy deceases with time until it reaches an asymptotic value $E_\infty = 2E_3 - E_6$.

(f) The model predicts that there is a systematic difference between the induction times of oxygen absorption $t_i(O_2)$ and carbonyl chemiluminescence or any other initiation/termination product:

$$t_i(C_i) - t_i(O_2) = \frac{k_i^{-1}}{2}$$

Achimsky et al. have recently shown that $t_i(O_2)$ as estimated from gravimetric measurements is effectively lower than t_i(carbonyl).[11]

Conclusions

It appears that the proposed kinetic schemes based on a very simple chain mechanism, where the unique radical source is the POOH unimolecular decomposition and where termination is bimolecular, are able to predict the main features of PP thermal oxidation kinetics in the 80−150 °C temperature range.

The general solution is numerical. It is very difficult to use in practice because certain parameters are almost inaccessible. Fortunately, a peculiar analytical solution, although based on a wrong hypothesis, displays the same predictive qualities as the general solution and is very easy to use in practice since it involves only two parameters graphically determinable from the oxidation kinetic curves.

References and Notes

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