DEVELOPMENTS IN POLYMER STABILISATION—5

(The Developments Series)

GERALD SCOTT

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PREFACE

The purpose of the present series of publications is two-fold. In the first place it is intended to review progress in the development of practical stabilising systems for a wide range of polymers and applications. A complementary and ultimately more important objective is to accommodate these practical developments within the framework of antioxidant theory, since there can be little question that further major advances in the practice of stabilisation technology will only be possible on the basis of a firm mechanistic foundation.

A frequently observed phenomenon in the study of antioxidants in polymers is the existence of critical concentration limits within which they show predictable concentration dependent activity and outside of which they show discontinuity. A growing understanding of the factors determining antioxidant activity in polymers has made possible a kinetic approach to this problem and the important contribution made by Shlyapnikov and his co-workers in this area is reviewed by the author in Chapter 1. The micro-environment within the polymer, and in particular the solubility and rate of diffusion of oxygen, is shown to control the performance of antioxidants in polymer matrices by Denisov in Chapter 2. In particular the importance of alkyl radical trapping which results from limited oxygen diffusion is outlined. A specific and currently very important example of antioxidant action, alkyl radical trapping by nitroxyl radicals, is critically discussed by Shlyapintokh and Ivanov in Chapter 3 on the basis of their own and other published work.

In recent years, the potential importance of polymers with limited but reproducible lifetime has been recognised and has been the object of research in both academic and industrial laboratories. An important

industrial outcome of this research, the commercial development of controlled-life protective films and fibres for agricultural use, is described by Gilead and Scott in Chapter 4.

The performance of polymers in the fire environment remains a major cause of social and hence scientific concern. Considerable progress has been made towards empirical solutions to this problem and this has been reviewed in the technological literature. However, the scientific understanding of the mechanistic basis of the activity of flame retardants is still fairly rudimentary. The current position is critically reviewed by Hirschler in Chapter 5 and in Chapter 6 Tkac describes a novel and potentially very important experimental approach to the ESR study of the chemical processes involved in the function of flame retardants.

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Chapter 1

CRITICAL ANTIOXIDANT CONCENTRATION PHENOMENA AND THEIR APPLICATION

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SUMMARY

The theory of critical antioxidant concentrations is considered on the basis of branched chain reactions. This phenomenon, which is reflected in a sharp change in the oxidation rate, results from a change in the polymer oxidation mechanism.

Out of all critical concentrations the most important is the lower one, namely the minimal antioxidant concentration needed to retard the oxidation reaction. The lower critical concentration value may be used as a quantitative measure of antioxidant effectivity.

1. INTRODUCTION

Critical phenomena which are characterised by substantial changes in reaction kinetics with slight changes in reaction conditions are specific to branched chain reactions.[1] Critical antioxidant concentrations are among these phenomena and the theory of critical concentrations is basic to the physico-chemical theory of polymer stabilisation.

Mathematical calculations and expressions involved in this theory, though not difficult, are very cumbersome and can be omitted when only applications of the theory are of interest.

2. SIMPLIFIED THEORY OF CHAIN BRANCHING REACTIONS AND THEIR CONSEQUENCES

The oxidation of polymers involves a complex chain reaction. Chain branching in this reaction is the result of certain consecutive reactions, and added inhibitors not only terminate chains but at the same time take part in side reactions. It is therefore more convenient to discuss the theory first for a model chain reaction and, only after this simplified treatment, to take into account the complicating factors experienced in practical systems.

Consider the chain reaction

$$X + A \longrightarrow B + X \tag{1}$$

where A is initial compound, B the reaction product, and X, a reactive intermediate, the active centre. The active centre concentration [X] will change during the reaction time according to

$$\frac{d[X]}{dt} = W_0 - W_t = W_0 - k_t[X] \tag{2}$$

where W_0 is the rate of the active centre formation, and $W_t = k_t[X]$ is the rate of their termination.

The active centre concentration is very small. The upper limit of [X] can be found assuming that $d[X]/dt = 0$. In this case

$$[X] = \frac{W_0}{k_t}[A] \tag{3}$$

and the upper limit of the reaction rate is

$$-\frac{d[A]}{dt} = k_p[X][A] = k_p\frac{W_0}{k_t} \tag{4}$$

where k_p is the rate constant of chain propagation (reaction 1). A short time after the start of the reaction, the real rate virtually attains this upper limit; the rate of the reaction becomes stationary.

If the active centre is terminated in the reaction with an inhibitor (IH), i.e. $k_t = k_i[IH]$, the stationary rate of the reaction will smoothly diminish with increase of inhibitor concentration.

For branched chain reactions however, the law will be different. If processes occur which result in the formation of f active centres per initial active centre in unit time, eqn. 2 describing the active centre concentration changes to eqn. 5:

$$\frac{d[X]}{dt} = W_0 + f[X] - k_t[X] \tag{5}$$

If the rate of active centre termination is higher than that of chain branching (i.e. $k_t > f$), the stationary concentration of X (determined by $d[X]/dt = 0$), will be

$$[X] = \frac{W_0}{k_t - f} \tag{6}$$

or for $k_t = k_i[IH]$

$$[X] = \frac{W_0}{k_i[IH] - f} \tag{7}$$

It is obvious that expressions 6 and 7 are valid only when $f < k_i[IH]$. If $f > k_i[IH]$, eqn. 5 has no stationary solution. Denoting $f - k_t = \Psi$, we obtain the differential equation

$$\frac{d[X]}{dt} = W_0 + \Psi[X] \tag{8}$$

where $\Psi > 0$. The solution to this equation, provided $[X] = 0$ when $t = 0$, is

$$[X] = \frac{W_0}{\Psi}(e^{\Psi t} - 1) \tag{9}$$

This shows that when $\Psi > 0$, i.e. $f > k_i[IH]$, the active centre concentration, and consequently the reaction rate, will rise until the reactant consumption or some other factor will limit it. Such a reaction, the rate of which is an explicit function of time, is non-stationary.

Thus, when $f < k_i[IH]$ the active centre concentration is limited, and when $f > k_i[IH]$ it is unlimited. The intermediate case is $f = k_i[IH]$ and corresponds to the critical reaction conditions. The inhibitor concentration for which this condition is true is called the critical concentration and for the model chain reaction considered, it is equal to

$$[IH]_{cr} = \frac{f}{k_i} \tag{10}$$

In the course of the chain reaction the inhibitor is consumed. The system of differential equations describing the reaction in relation to inhibitor consumption is[2]

$$\frac{d[X]}{dt} = W_0 + f[X] - k_i[IH][X]$$

$$-\frac{d[IH]}{dt} = k_i[IH][X] \tag{11}$$

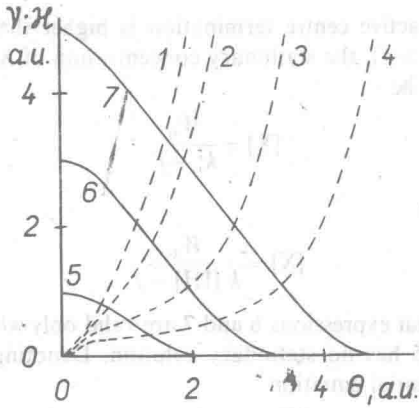

FIG. 1. Concentrations of active centres, ν (curves 1–4) and of inhibitor, $\mathscr{H}$ (curves 5–7) as a function of time, θ, in arbitrary units chosen to make the critical inhibitor concentration unity, in the course of branched chain reaction described by system 11. $W_0 = f = k_i = 1$; initial inhibitor concentrations: 0 (1), 1 (2, 5), 3 (3, 6) and 5 (4, 7).

The solution to system 11 obtained by numerical integration in coordinates $\nu = [X]/W_0\tau_0$, $\mathscr{H} = [IH]/W_0\tau_0$, and $\theta = t/\tau_0$ for the various initial concentrations of the inhibitor is shown in Fig. 1 as a system of curves describing ν and $\mathscr{H}$ as functions of time in arbitrary units, θ, the coordinates being arbitrarily chosen to make the critical inhibitor concentration unity.

As can be seen from Fig. 1, if $\mathscr{H} = 1$ (which means that $[IH]_0 = [IH]_{cr}$), the inhibitor only slightly affects the shape of the curve $\nu(\theta)$, but if $\mathscr{H} > 1$ (i.e. $[IH]_0 > [IH]_{cr}$), the fast rise of the active centre concentration (i.e. ν) is markedly delayed. The length of this delay time is a function of the initial inhibitor concentration.

The induction period of an auto-accelerated reaction is taken to be the time needed for the active centre concentration to attain a certain sufficiently high value (for example $\nu = 5$). The dependence of such an induction period calculated from data in Fig. 1 on the initial inhibitor concentration is shown in Fig. 2.

There is an explicit bend on the plot $\tau(\mathscr{H}_0)$ at point $\mathscr{H} = 1$, or $[IH]_0 = [IH]_{cr}$. Below this value the induction period only slightly depends on the initial inhibitor concentration, but above it the induction period rises rapidly with concentration. The value of critical inhibitor concentration corresponding to this bend, which is sometimes very sharp, can be readily measured. The simplicity of the experimental evaluation of the critical

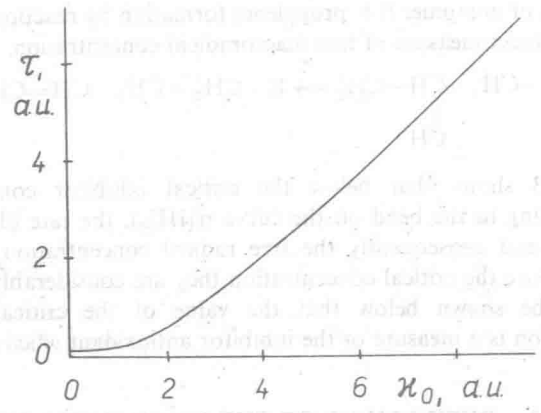

FIG. 2. Induction period, τ, as a function of initial inhibitor concentration, $\mathcal{H}$ (all in arbitrary units).

inhibitor concentration makes it an important tool in the investigation of the mechanisms of action of various types of antioxidants.

Figure 3 shows the experimental dependence of the induction period of isotactic polypropylene oxidation on the initial concentration of an inhibitor, phenyl-β-naphthylamine, at 200 °C and oxygen pressure P_{O_2} = 300 torr. There is a marked bend on the plot $\tau([IH]_0)$, corresponding to the critical concentration which is close to 0·025 mol kg^{-1}.[3]

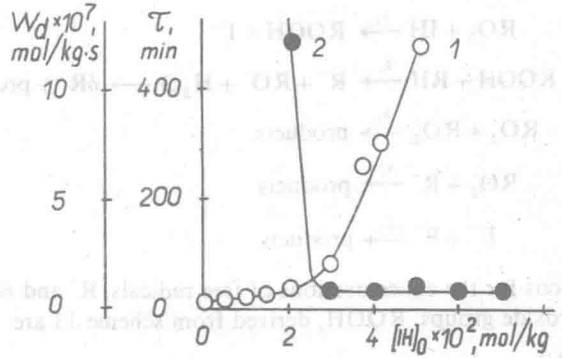

FIG. 3. Induction period of polypropylene oxidation (1) and initial rate of monomer formation in the course of oxidation (2) as functions of initial inhibitor concentration at 200 °C. Oxygen pressure 300 Torr; inhibitor phenyl-β-naphthylamine.

The rate of monomer (i.e. propylene) formation by reaction 12 can be used as a direct measure of free macroradical concentration.

$$R{-}CH_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_2^{\cdot} \longrightarrow R{-}CH_2^{\cdot} + CH_3{-}CH{=}CH_2 \qquad (12)$$

Figure 3 shows that below the critical inhibitor concentration, corresponding to the bend on the curve $\tau([IH]_0)$, the rate of propylene formation and consequently the free radical concentration, are high, whereas above the critical concentration they are considerably lower.

It will be shown below that the value of the critical inhibitor concentration is a measure of the inhibitor antioxidant efficiency.

3. REFINEMENT OF THE MECHANISM OF POLYOLEFIN INHIBITED OXIDATION

The chain reaction of hydrocarbon oxidation in the presence of an inhibitor is described by the following scheme.[4-6]

$$\begin{aligned}
&0. && RH + O_2 \xrightarrow{k_0} \cdots \longrightarrow R^{\cdot} + \text{products} \\
&0'. && IH + O_2 \xrightarrow{k_0'} \cdots \longrightarrow R^{\cdot} + \text{products} \\
&1. && R^{\cdot} + O_2 \xrightarrow{k_1} RO_2^{\cdot} \\
&2. && RO_2^{\cdot} + RH \xrightarrow{k_2} ROOH + R^{\cdot} \\
&3. && RO_2^{\cdot} + IH \xrightarrow{k_3} ROOH + I^{\cdot} \qquad (13) \\
&4. && ROOH + RH \xrightarrow{k_4} R^{\cdot} + RO^{\cdot} + H_2O \longrightarrow \delta R^{\cdot} + \text{products} \\
&5. && RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_5} \text{products} \\
&6. && RO_2^{\cdot} + R^{\cdot} \xrightarrow{k_6} \text{products} \\
&7. && R^{\cdot} + R^{\cdot} \xrightarrow{k_7} \text{products}
\end{aligned}$$

Equations for the concentrations of free radicals, $R^{\cdot}$ and $RO_2^{\cdot}$, and of hydroperoxide groups, ROOH, derived from scheme 13 are

$$\frac{d[R^{\cdot}]}{dt} = \alpha k_0[RH][O_2] + \alpha' k_0'[IH][O_2] + \delta k_4[ROOH][RH] - k_1[R^{\cdot}][O_2] + k_2[RH][RO_2^{\cdot}] - k_6[R^{\cdot}][RO_2^{\cdot}] - 2k_7[R^{\cdot}]^2 \qquad (14)$$

$$\frac{d[RO_2^{\cdot}]}{dt} = k_1[R^{\cdot}][O_2] - k_2[RO_2^{\cdot}][RH] - k_3[RO_2^{\cdot}][IH] - 2k_5[RO_2^{\cdot}]^2 - k_6[R^{\cdot}][O_2] \quad (15)$$

$$\frac{d[ROOH]}{dt} = k_2[RO_2^{\cdot}][RH] + k_3[RO_2^{\cdot}][IH] - k_4[ROOH][RH] \quad (16)$$

Equations 14 and 15 are very cumbersome, but the terms involved in them depend upon the reaction conditions and in specific cases some of these can be neglected.

Consider the case when the inhibitor concentration is high enough, so that the chain termination processes in the absence of the inhibitor (steps 5–7 in scheme 13) can be neglected; i.e.

$$k_3[RO_2^{\cdot}][IH] \gg 2(k_5[RO_2^{\cdot}]^2 + k_6[R^{\cdot}][RO_2^{\cdot}] + k_7[R^{\cdot}]^2) \quad (17)$$

Summing eqns. 14 and 15 and excluding from the resulting expression the terms related to radical recombination, we obtain eqn. 18:

$$\frac{d([R^{\cdot}] + [RO_2^{\cdot}])}{dt} = \alpha k_0[RH][O_2] + \alpha' k_0'[IH][O_2] + \delta k_4[ROOH][RH] - k_3[RO_2^{\cdot}][IH] \quad (18)$$

It is convenient to use the method of Bodenstein for the system of differential eqns. 16 and 18, i.e. to assume that $d([R^{\cdot}] + [RO_2^{\cdot}])/dt = 0$ and at the same time that $d[ROOH]/dt = 0$. This converts the differential equations into algebraic ones.[7] The latter can be easily solved to obtain the expressions for $[RO_2^{\cdot}]$ and [ROOH]. This method of solving differential equations can be used when the concentrations of reaction intermediates (i.e. of free radicals and hydroperoxide groups) are so low that their rates of change compared to those of the reacting species can be neglected.

Obtaining in this way the value of [ROOH] and substituting it into eqn. 18 we find that

$$\alpha k_0[RH][O_2] + \alpha' k_0'[IH][O_2] = k_3[RO_2^{\cdot}][IH] - \delta(k_2[RH] + k_3[IH])[RO_2^{\cdot}] \quad (19)$$

whence

$$[RO_2^{\cdot}] = \frac{\alpha k_0[RH][O_2] + \alpha' k_0'[IH][O_2]}{k_3[IH] - \delta(k_2[RH] + k_3[IH])} \quad (20)$$

A stationary concentration of $RO_2^{\cdot}$, determined from eqn. 20, exists only in the case when the denominator in expression 20 is higher than zero. The critical inhibitor concentration, that is the concentration corresponding to

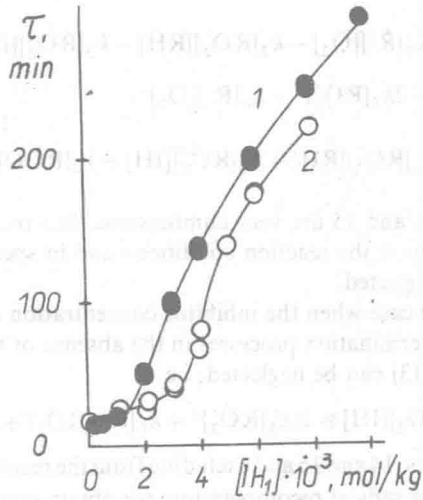

FIG. 4. Induction period of polypropylene oxidation in the absence (1) and in the presence (2) of 2,4,6-tri-*tert*-butylphenol, 0·01 mol kg^{-1} as a function of concentration of 2,2'-methylenebis(4-methyl-6-*tert*-butylphenol) at 200 °C. Oxygen pressure 300 Torr.

the boundary between the stationary and non-stationary solutions, can be found from the condition

$$k_3[\mathrm{IH}]_{cr} - \delta(k_2[\mathrm{RH}] + k_3[\mathrm{IH}]_{cr}) = 0 \qquad (21)$$

It follows from eqn. 21 that

$$[\mathrm{IH}]_{cr} = \frac{\delta k_2[\mathrm{RH}]}{(1-\delta)k_3} \qquad (22)$$

It was found in an investigation of the oxidation of isotactic polypropylene in the presence of mixtures of two inhibitors, that in some cases the partial critical concentration of one inhibitor $\mathrm{IH_A}$ increased when another inhibitor $\mathrm{IH_B}$ was added to the polymer (Fig. 4).[8,9] Consider the theory of these experiments.

The rate of chain termination produced by a mixture of two inhibitors A and B will be the sum of the rates of termination induced by each inhibitor separately, i.e. $k_t = k_{3A}[\mathrm{IH_A}] + k_{3B}[\mathrm{IH_B}]$. Substituting the latter into eqn. 22 for $k_3[\mathrm{IH}]_{cr}$ we find the expression for the critical concentration of one inhibitor in the presence of another

$$[\mathrm{IH}_1]_{cr} = \frac{\delta k_2[\mathrm{RH}]}{(1-\delta)k_{31}} - \frac{k_{3B}}{k_{3A}}[\mathrm{IH}_2] \qquad (23)$$