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D. G. KNORRE, Z. K. MAIZUS, and Corresponding Member of the Academy of Sciences of the USSR N. M. EMANUEL

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Abstract

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D. G. KNORRE, Z. K. MAIZUS, and Corresponding Member of the Academy of Sciences of the USSR N. M. EMANUEL

ON THE RATE OF DEGENERATE CHAIN BRANCHING

IN THE OXIDATION OF *n*-DECANE

According to current concepts, the inhibiting action of inhibitors on chain reactions is due to chain termination during the interaction of the free radicals that carry the chain process with inhibitor molecules. As a result of this interaction the inhibitor is consumed and ultimately disappears from the system. The disappearance of the inhibitor from the system leads to a sharp acceleration of the chain process, i.e., the reaction then leaves the induction period. The rate of consumption of the inhibitor and, consequently, the duration of the induction period are determined by the concentration of radicals in the system.

If the reaction takes place in the liquid phase, where in the absence of inhibitor quadratic chain termination predominates, then the concentration of radicals in the presence of inhibitor I is determined by the equation

$$\frac{d[\mathrm{R}]}{dt} = w_0 - ak_i[\mathrm{R}][\mathrm{I}] - k[\mathrm{R}]^2,$$

where w_0 is the rate of generation of free radicals, k_i is the rate constant for the interaction of radicals with inhibitor molecules, k is the rate constant for radical recombination, and a is a stoichiometric coefficient that takes into account how many free radicals are destroyed by one inhibitor molecule.

Assuming the radical concentration to be stationary, we obtain for the rate of inhibitor consumption the expression

$$-\frac{d[\mathrm{I}]}{dt} = \frac{k_i[\mathrm{I}]}{2k}\left(\sqrt{a^2k_i^2[\mathrm{I}]^2 + 4kw_0} - ak_i[\mathrm{I}]\right). \qquad (1)$$

At sufficiently high inhibitor concentrations, when $a^2k_i^2[\mathrm{I}]^2 \gg 4kw_0$, we find:

Fig. 1

Figure 1: Fig. 1

$$-\frac{d[\mathrm{I}]}{dt} = \frac{w_0}{a}. \tag{2}$$

Thus, the consumption of the inhibitor at sufficiently high concentrations proves to be a zero-order reaction with respect to the inhibitor concentration.

It is often assumed that relation (2) holds up to complete consumption of the inhibitor. Proceeding from the fact that upon consumption of the inhibitor the system leaves the induction period, i.e., that at $[\mathrm{I}] = 0$, $t = t_i$, where t_i is the duration of the induction period, by integrating (2) we obtain the relation

$$[\mathrm{I}]_0 - \frac{w_0}{a} t_i = 0 \quad \text{or} \quad t_i = \frac{a[\mathrm{I}]_0}{w_0}. \tag{3}$$

Relations (2) and (3) are used to determine the rate of the chain initiation process ([1–3]). In doing so, it is assumed that the initiation reaction

chain is an elementary reaction and, consequently, should not change upon the introduction of a small addition of inhibitor into the system. Since the rate of initiation, as the rate of an elementary process, must be proportional to the product of the concentrations of the substances participating in the initiation process, the dependence of w_0 on the concentrations of the reagents present in the system can be used to judge the mechanism of the initiation process.

With the commonly used method of introducing the inhibitor into the initial system, the rate of initiation measured in this way refers to the initial moment of time.

If, however, the inhibitor is introduced in the course of the process, then by an analogous method one can obtain the rate of initiation at any stage of it. In particular, for oxidation processes in which the principal mass of radicals in the developing process is produced as a result of degenerate chain branching, it is of interest to try, using the inhibitor method described, to obtain information about the rate and mechanism of degenerate branching.

Fig. 1. Kinetic curves of hydroperoxide accumulation during oxidation of n-decane at 130°: 1—without inhibitor, and 2-7 in the presence of α-naphthol ($2 \cdot 10^{-6}$ M/ml) when it is introduced at different times. The time of inhibitor introduction is indicated by arrows.

In the present work we applied the inhibitor method to measure the rate of degenerate branching of chains in the oxidation reaction of n-decane in the liquid phase.

Fig. 2.

Figure 2: Fig. 2.

Oxidation of n-decane was carried out in an oxidation cell ([4]) in a stream of oxygen; the rate of oxidation was followed from the accumulation of hydroperoxides, whose concentration was determined iodometrically. As the inhibitor, α-naphthol was chosen; its concentration was determined spectrophotometrically after extraction from the samples with $1N$ NaOH and coupling with diazotized sulfanilic acid, at the absorption maximum of the azo compound formed (520 mμ).

Figure 1 gives the kinetic curves of hydroperoxide accumulation during oxidation of n-decane at 130° in the presence of α-naphthol in an amount of $2 \cdot 10^{-6}$ M/ml, when it is introduced at different times. The corresponding curve for the case in which the inhibitor is introduced into the initial decane is not shown, since the induction period in this case is extremely long. Even at an α-naphthol concentration of $0.5 \cdot 10^{-6}$ M/ml it amounts to 20 h. This indicates a sharp acceleration of free-radical formation in the initial period of the reaction. The later the inhibitor is introduced, the shorter is the induction period of the oxidation process.

Introduction of α-naphthol into oxidizing n-decane is accompanied by gradual yellowing of the solution. If α-naphthol is introduced at comparatively deep stages, even precipitation of a brown-colored solid is observed. The compound formed has a characteristic spectrum in the visible region with an absorption maximum at 420 mμ. Figure 2 gives the changes in the concentration of hydroperoxide, α-naphthol, and the optical density of the solution at 420 mμ upon introduction of $2 \cdot 10^{-6}$ M/ml α-naphthol into oxidizing decane 50 min after the start of the oxidation process. The optical density of the solution passes through a maximum and then decreases. This indicates that the coloration of the solution is due to some intermediate compound,

formed with the participation of α-naphthol. Addition of a precipitate of this compound to fresh n-decane showed that the intermediate compound we had detected has an inhibiting action.

The consumption of α-naphthol follows a zero-order reaction only up to $\sim 70\%$ conversion, after which distinct deviations from the first-order equation are observed. This is possibly connected with the fact that, as the inhibitor concentration decreases, relation (2) becomes inapplicable and the more rigorous relation (1) must be used; and also with the fact that some of the free radicals begin to react not with α-naphthol, but with the new intermediate product. In view of these circumstances, formula (3) proves inapplicable in our case, and we calculated the branching rate only by formula (2), using the linear portion of the inhibitor-consumption curve to determine $d[I]/dt$.

Fig. 2. Change in the concentrations of hydroperoxide (1), α-naphthol (2), and

Fig. 3.

Figure 3: Fig. 3.

the optical density of the solution at $\lambda = 420$ mμ (3) when α-naphthol ($2 \cdot 10^{-6}$ M/ml) is introduced into oxidizing n-decane 50 min after the start of oxidation. Temperature 130°.

Fig. 3. Dependence of the branching rate on the hydroperoxide concentration in the oxidation reaction of n-decane at 130°.

In the calculation we assume that $a = 2$, by analogy with phenols and β-naphthol, for which this quantity has been determined experimentally (5). Since the reaction of degenerate branching leads to the formation of two free radicals, we considered that $w_0 = 2w_p$. Hence

$$w_p = -\frac{1}{2} d[I]/dt.$$

The rate of inhibitor consumption in oxidizing n-decane at 130°, hydroperoxide concentration 0.02 M/l, and different inhibitor concentrations proved to be as follows:

$[I]_0 \cdot 10^3$, M/l	1.1	1.7	3.1	4.4
$(d[I]/dt) \cdot 10^7$, M/l · sec	5.5	7.3	6.3	6.5

As is seen from these data, the value of $d[I]/dt$ obtained by us does not depend on the inhibitor concentration. This shows that the inhibitor does not take part in the formation of free radicals and is only an "instrument" by means of which the value of w_p is measured.

Figure 3 gives the dependence, obtained in this way, of the branching rate at 130° on the hydroperoxide concentration. It is seen that the branching rate is proportional to the hydroperoxide concentration. Consequently, it has been directly proved that hydroperoxide is the main branching agent in the oxidation reaction of n-decane. From the dependence of w_p on

the hydroperoxide concentration, the rate constant of the branching reaction was determined; at 130° it proved to be $1.9 \cdot 10^{-5}$ sec^{-1}. From the temperature dependence of w_p, the activation energy of the branching reaction was determined to be 24.8 kcal. The temperature dependence of the rate constant is written in the form

$$k = 6 \cdot 10^8 \exp(-24800/RT) \text{ sec}^{-1}.$$

The low value of the exponential factor, which is not characteristic of thermal-decomposition processes, is noteworthy.

This is perhaps explained by the fact that the pronounced branching does not proceed monomolecularly, but represents a bimolecular reaction with the hydrocarbon:

$$\mathrm{ROOH} + \mathrm{HR} \rightarrow \mathrm{RO}\cdot + \mathrm{H_2O} + \mathrm{R}\cdot$$

Such a reaction is energetically more favorable by 22 kcal (the difference between the bond energy of OH in water and C—H in *n*-decane) than direct cleavage of the O—O bond.

The value of k obtained by us differs greatly from the same value reported in Twigg' s work[6] ($8 \cdot 10^{11} \exp(-31800/RT)$). In that work, the rate of decomposition of a mixture of secondary decyl hydroperoxides was measured, and the rate constant for hydroperoxide decomposition was calculated on the assumption that, at small dilutions, the entire consumption of hydroperoxides is due exclusively to their primary decomposition at the O—O bond. Since our data, obtained by a more direct method, give a sharply different value of k, it may be considered that Twigg' s considerations are not correct.

Institute of Chemical Physics
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.