MECHANISM OF OXIDATION INHIBITION BY METAL COMPLEXES

I. KINETICS OF OXIDATION OF PENTAERYTHRITE ESTERS OF MONOCARBOXYLIC ACIDS BY MOLECULAR OXYGEN


Study of the action of antioxidants in stabilizing lubricants, and the principles governing the selection of such materials, is an important scientific problem with practical applications [1]. Its solution requires data on the kinetics of oxidation in various practical systems.

It was the aim of the present work to investigate the mechanism of oxidation of the pentaerythrite esters of the monocarboxylic acids, compounds used as synthetic lubricants [2], and measure the rate constants for the various elementary reaction steps.

EXPERIMENTAL

The rate of oxidation of the C₂ - C₄ fraction (RH) of the pentaerythrite esters of monocarboxylic acids was measured at 95-210°C, either by volumetric determination of the O₂ uptake or by iodometric determination of the peroxide buildup. The RH samples (GOST 9286 - 59) were passed through a column packed with activated Al₂O₃ prior to oxidation. The purified RH had the following characteristics: d₀.996 ± 0.004 g/ml, nD₂°1.4537, mol. wt. 640 ± 15, degree of hydroxyl group esterification > 99%. The rate of free-radical formation (Wi) during thermal breakdown of the initiator in RH solution was determined by the inhibitor method, measuring the rate of α-naphthol consumption and working through the equation

\[ \Delta W_i = f \cdot \Delta [\alpha\text{-naphthol}] / \Delta t \]

\[ \Delta [\alpha\text{-naphthol}] \] designating the change in the inhibitor concentration in time \( \Delta t \), and \( f \) the stoichiometric inhibition coefficient, 2 in the present case [3].

The α-naphthol content of the system was determined colorimetrically, from the optical absorption (λ 526 nm) of the azo compound formed in reaction with p-sulfophenyldiazonium sulfate. The working conditions was so chosen that each chain could be presumed to break on an inhibitor molecule. The inhibitors used here were azocyclohexanitrile at 95-105°C, and cumene peroxide at 110-140°C. For the azocyclohexanitrile, the measured values of the initiation rate constant (k_i) at 95 and 105°C were (6.5 ± 0.5)\times10^{-5} and (1.5 ± 0.1)\times10^{-4} sec⁻¹, respectively. The mean value of k_i for cumene peroxide satisfied an Arrhenius-equation of the form

\[ \lg k_i = (14.5 ± 0.1) - (33800 ± 1000k)/4.57 T \]

The fact that the k_i values obtained here were close to those applying to nonpolar solvents [3] was an indication that solvent RH had no appreciable effect on the probability of free-radical passage into the body of the system.

DISCUSSION OF RESULTS

Oxidation of RH can be speeded up by irradiation and by the action of compounds (azocyclohexanitrile, benzoquinone, cumene peroxide) which function as initiators for free-radical reactions; it is retarded by compounds [2,4,6-tri(tert-butyl)phenol, benzoquinone, diphenylamine] which act as inhibitors for radical-chain reactions. The kinetic curves for peroxide buildup were typical of those associated with autocatalytic reactions (curve 1, Fig. 1). The rate of initiated RH oxidation ($W_0$) in anisole solution was directly proportional to $[RH]_0$ and the square root of the initiation rate, i.e., $W_0 \sim [O_2]_0 \cdot [RH]_0 \cdot \sqrt{W_i}$ (Fig. 2), but it was independent of the oxygen pressure over the interval from 0.2 to 1.0 atm. At an RH conversion $< 1 \cdot 10^{-2}$ mole/liter and a temperature less than 130°C, the $O_2$ absorption varied linearly with the time. Here the $O_2$ absorption correlated quantitatively with the peroxide formation. Thus, at 25°C and with $W_i = 4.0 \cdot 10^{-5}$ mole/liter sec, a 40-min run consumed $3.6 \cdot 10^{-3}$ mole/liter $O_2$ and produced $3.5 \cdot 10^{-3}$ mole/liter of peroxides.

The observed reaction kinetics suggest that RH oxidation proceeds through a radical-chain mechanism. The fact that $W_0$ was proportional to $W_i^{1/2}$ indicated second-power chain breaking in the peroxide radical reactions. The structure of the RH peroxide radicals is not presently known. However, according to [4] it is a $\alpha$-CH bond which is subjected to preferential oxidation in the esters of diatomic alcohols. It is obvious that the same should also be true of the esters of polyatomic alcohols, including RH.

In view of what has been said, RH oxidation can be described by the following simplified ($[R'] > [RO\_2^{-}]$)

$\begin{align*}
\text{RH} & \quad \text{Initiator, } O \quad - \quad C \quad \text{CH} \quad \text{OC(R')} \\
R' + O_2 & \rightarrow RO\_2^{-} \\
RO\_2^{-} + RH & \rightarrow ROOH + R' \\
ROOH & \rightarrow \text{Free radicals} \\
RO\_2^{-} + RO\_2^{-} & \rightarrow \text{Molecular products}
\end{align*}$

Here the rate of oxidation is given by the expression

$$W_0 = \left(\frac{k_2}{k_1^{1/2}}\right) [RH] (W_i + k_3 [ROOH])^{1/2}$$

Trustworthy values of $k_2/k_1^{1/2}$, the macrokinetic factor characterizing the RH oxidizability, were obtained by studying the initiated oxidation under such conditions that $k_1$ [initiator] $\gg k_3$ [ROOH]. Values of this ratio, applicable over the 95-140°C temperature interval, are shown in Table 1, these having been determined from either the $W_0$ vs $W_i^{1/2}$ or the $W_0$ vs $[RH]$ relation (cf. Fig. 2).