A DESCRIPTION OF THE COOXIDATION KINETICS OF TERNARY SYSTEMS USING AN EQUATION FOR BINARY MIXTURES

R. V. Kucher, I. A. Opeida, and A. G. Matvienko

UDC 541.127

An investigation of the cooxidation of various organic substances by oxygen in the liquid phase is of great theoretical and practical importance. Although the theory of such processes has been developed for systems containing any number of components [1], because of the complexity of the final equation obtained, the investigations are usually confined to binary systems.

The scheme for the cooxidation of a binary mixture can be written in the form

\[ R_1H + R_2H \rightarrow R_1 + R_2 \]  
\[ R_1 + O_2 \rightarrow R_1O_2 \]  
\[ R_2 + O_2 \rightarrow R_2O_2 \]

\[ R_1O_2 + R_1H \rightarrow R_1O_2H + R_1 \]  
\[ R_2O_2 + R_2H \rightarrow R_2O_2H + R_2 \]

\[ R_1O_2 + R_1H \rightarrow R_1O_2H + R_1 \]  
\[ R_2O_2 + R_2H \rightarrow R_2O_2H + R_2 \]

\[ 2R_1O_2 \rightarrow \text{inactive products} \]  
\[ \text{inactive products} \]

For a particular system the dependence of the cooxidation rate \( w_{O_2} \) on the composition is expressed by the relationship

\[ w_{O_2} = \frac{(r_1[R_1H] + 2[R_1H][R_2H] + r_2[R_2H])^{1/2}}{(r_1[R_1H] + 2R_1H \delta_1[R_1H][R_2H] + r_2[R_2H])^{1/2}}, \]

where \( r_1 = k_{p11}/k_{p1} \); \( r_2 = k_{p22}/k_{p2} \); \( \delta_1 = \sqrt{k_{p11}/k_{p1}} \); \( \delta_2 = \sqrt{k_{p22}/k_{p2}} \). According to the experimental dependence of the oxidation rate on the composition, it is possible by means of an electronic computer.

Fig. 1. A cross section of the Gibbs–Rozenbaum triangle for \([R_1H]/[R_1H] = K\).

to calculate the cooxidation parameters \(r_1\), \(r_2\), and \(\Phi\), from which the rate constants of individual cross reactions (6), (7), and (9) can be determined.

So far about 60 binary systems have been investigated [2] and the cooxidation parameters have been calculated for these. However, an analysis and comparison of data obtained are in many cases complicated owing to the fact that Eq. (11) is obtained for substances containing molecules with a single type of reaction center. If the molecule has several weak CH bonds with different energies and thus a different capacity for oxidation, the dependence of the oxidation rate on the composition will for a general case be described by a more complex equation. In the present investigation we have attempted to interpret the form of the effective values of the cooxidation parameters, measurable from a study of such systems, and to investigate the possibility of applying Eq. (11) to describe the oxidation kinetics of ternary systems.

In a general form, the kinetic scheme for the oxidation of multicomponent mixtures with a predominance of quadratic termination can be represented as follows:

\[
R_iO_2 + R_jH \overset{k_{pij}}{\longrightarrow} R_iO_2H + R_jO_2,
\]

\[
R_iO_2 + R_jO_2 \overset{k_{iij}}{\longrightarrow} \text{inactive products,}
\]

where \(k_{pij}\) and \(k_{iij}\) are the rate constants for the individual elementary chain propagation and termination reactions, respectively. The concentrations of radicals can readily be determined from steady-state and long chain conditions from the equation [1]

\[
R_iO_2 = C\delta_{ki},
\]

where \(\delta_{ki}\) is the algebraic complement of the element \(a_{ki}\) in the determinant

\[
| k_{pij}[R_iH] - \sum k_{pij}[R_iH] \delta_{ij} |.
\]

\(\delta_{ij}\) is the Kronecker symbol, and

\[
C = \left[ \frac{w_i}{\sum k_{iij}A_{ki}A_{kj}} \right]^{1/2}.
\]

In a general case the oxidation rate is described by the expression

\[
W_{\alpha} = C \sum k_{pij}A_{ki}[R_iH],
\]

a particular case of which is Eq. (11).

We will examine certain particular cases of cooxidation in three component systems with components \(R_1H\), \(R_2H\), and \(R_3H\). It is especially interesting to investigate the dependence of the oxidation rate on composition in relation to a cross section \(M_{12}-R_3H\) through one of the apices of the Gibbs–Rozenbaum triangle (see Fig. 1). Such a section corresponds to the case of cooxidation in a binary system in which one of the components has two reaction centers.

We carried out the following calculated experiment: For the cross section \(R_2H-M_{12}\) when \(R_2H/R_1H = 0.9\) and the concentrations of pure components are \([R_1H] = 6.0M, [R_2H] = 9.0M, [R_3H] = 8.0M, and \(w_1 = 1 \times 10^{-6}M \cdot \sec^{-1}\), the oxidation rate \(W_T\) was calculated over equal intervals at nine points from Eq. (15). Values chosen for the elementary reaction rate constants were close to those determined in real mixtures.