Computational Model of Reaction Mechanism of Alkyl Peroxy Radicals with Organic Compounds in the Presence and Absence of Oxygen

Hossein Jalali Jahromi a,*, Mojtaba Rahmani Nejad a, Sharare Zeyghami b

a Department of Chemistry and Chemical Engineering, Mahshahr Branch, Islamic Azad University, Mahshahr, Iran
b Department of Chemical Engineering, Science and Research Branch, Islamic Azad University, Fars, Iran

Abstract

On the basis of experimental data a kinetic model for the heterogeneous interaction between alkylperoxy radicals and organic compounds in Langmuir-Hinshelwood approach at room temperature has been offered. The effect of oxygen on the kinetics of process in the presence, $[O_2]_o = 1 \times 10^{11} - 1.6 \times 10^{12}$ molecules.cm$^{-2}$, and absence of oxygen has been analyzed. Over time the chain degenerate branching mechanism of the process is accompanied by the increase of the radicals concentration in the presence of oxygen. However, in the absence of oxygen the radicals are consumed continuously and the length of chains becomes shorter. In this situation the phenomenon of radicals multiplication does not take place attributed to decrease the chain consumption rate of organic compound reagent.

Keywords: Kinetics Model, Mechanism, Alkylperoxy Radical, Organic Compound, Rate Constant

1. Introduction

The reaction of active particles (atoms and radicals) on the surface of aerosols has the potential to play a major role in determining the composition of the gaseous troposphere and should be included in models for understanding this region and assessing the effects of anthropogenic emissions [1-4].

The explanation of the peculiarities of chemical processes mechanism and the establishment of its connection with the dynamic behavior of system has been successfully applied by the mathematical modeling [5-10].

The mathematical modeling of methane thermal oxidation has been performed in [7]. It has been confirmed the conclusions made on the basis of experimental data concerning the nature of the leading active centers and the products.

The participation and influence of the heterogeneous radical stages on the dynamic regimes of methane and acetaldehyde oxidation using a mathematical modeling have been studied [11 - 15].

A significant rate of heterogeneous reaction of OH radicals with CO has been established on the solid surface of NaCl in the flow condition using the laser-induced fluorescence (LIF) method [16]. These results were used in a heterogeneous – homogeneous model describing the concentration oscillations in CH$_3$CHO + O$_2$ system [17].

A series of radical intermediates, with general formula RCO and RCO$_3$, have been observed on the TiO$_2$ surface during the oxidative
decomposition of various ketons [18]. An interesting result has obtained during the reaction of CH₃O₂ radicals with methane on the TiO₂ surface [19]. In contrast with the free oxygen salt surface, on the surface of titanium oxide the dependence of radicals concentration on the initial concentration of organic reagent has a complex character. On the titanium oxide surface under some conditions not only the decrease, but also the remarkable increase of radicals concentration was discovered.

For the first time in this study, the method of mathematical modeling is used to analyze the role of oxygen on the peculiarities of heterogeneous reaction of alkylperoxy radicals with organic compounds. It is important also to find out the adequacy of the representations incorporated in model considering the experimental data, not to concentrate the chemical interactions in details.

2. Methodology

It is supposed that the process proceeds in an adsorbed layer in Langmuir - Hinshelwood (LH) approach on the active sites of a surface. In the LH mechanism of surface-catalyzed reactions, the reaction takes place by the collisions between molecules and molecular fragments adsorbed on neighboring surface sites.

Concerning the opportunity of the heterogeneous stages included in a model there are some appropriate experimental data [19-24]. It is assumed that the heterogeneous elementary stages are similar to the homogeneous reaction taking place in the gas phase.

The values of rate constants were optimized on the basis of the data in [25]. VALKIN computer program [8, 26] on the basis of subroutine program ROW-4 [27] was used.

3. Results and discussion

Below the model of degenerate chain branching reaction carrying out during the heterogeneous interaction of peroxy radicals with organic compounds in the presence of oxygen traces has been considered.

\[
\begin{align*}
\text{CH}_3\text{O} + \text{RH} & \rightarrow \text{CH}_3\text{OOH} + \text{R} \quad (1) \\
\text{R} + \text{O} & \rightarrow \text{RO} \quad (2) \\
\text{CH}_3\text{OOH} & \rightarrow \text{CH}_3\text{O} + \text{OH} \quad (3) \\
\text{CH}_3\text{O} + \text{RH} & \rightarrow \text{CH}_3\text{OH} + \text{R} \quad (5) \\
\text{RO}_2 + \text{RH} & \rightarrow \text{ROOH} + \text{R} \quad (6) \\
\text{ROOH} & \rightarrow \text{RO} + \text{OH} \quad (7) \\
\text{RO} + \text{RH} & \rightarrow \text{ROH} + \text{R} \quad (8) \\
\text{RO}_2 & \rightarrow \text{P (product)} \quad (9) \\
\text{RO}_2 & \rightarrow \text{RO}_2 \quad (10) \\
\text{CH}_3\text{O}_2 & \rightarrow \text{CH}_3\text{O}_2 \quad (11) \\
\text{RH} & \rightarrow \text{hydrocarbon or aldehyde, RO}_2 \text{d and CH}_3\text{O}_2 \text{d – the desorbed RO}_2 \text{ and CH}_3\text{O}_2 \text{ radicals, accordingly.}
\end{align*}
\]

In Fig. 1 the kinetic curves of RH and CH₃O₂ radicals consumption and the accumulation of the sum of [RO₂ + CH₃O₂] radicals at the initial conditions: [RH] = 1 × 10¹², [CH₃O₂] = 1 × 10¹², [O₂] = 10¹², particle cm⁻² has been shown. As seen the kinetic curve of RH consumption has a more steep character than that found for the radicals. This testifies that the rate of RH consumption is several times more than radicals as a result of the additional chain consumption of RH during the process. For example at interval \(8 \times 10^{-7} - 1 \times 10^{+4}\) s the change of RH concentration equals to \(\Delta[\text{RH}] = 6.3 \times 10^{+4}\) molecules cm⁻² while for the case of radicals \(\Delta[\text{CH}_3\text{O}_2] = 1.8 \times 10^{+3}\) particle cm⁻². It means the decrease in the organic compound concentration is 3.5 times more than in the radicals concentration.

At the initial times of reaction when hydroperoxide concentration is small, the output of \([\text{RO}_2] + [\text{CH}_3\text{O}_2]\) radicals is small too, being less than \([\text{CH}_3\text{O}_2]\). At greater times the concentration of radicals becomes more than \([\text{CH}_3\text{O}_2]\) approximately on 20 percent, testifying the multiplication of radicals in the system. At the initial times of reaction when the quantity of CH₃OOH is small the difference between rate consumption of RH and radicals is smaller (Fig. 2).

In Fig. 3 the kinetic curves of RH and CH₃O₂ radicals consumptions in the absence of oxygen have been shown. The initial conditions are as: [RH] = 5 × 10¹⁰ ÷ 5 × 10¹², [CH₃O₂] = 3 × 10¹⁰, [O₂] = 0, particle cm⁻² and room temperature.
As seen from the comparison of these curves in the mentioned range of time, the consumption of organic compound is a little greater than the radicals regarding to the additional chain consumption of organic reagent.

The comparison of figures 1 and 3 shows that the consumption of organic reagent in the absence of oxygen (Fig. 3) is slower than in the presence of oxygen (Fig. 1). It testifies that the process proceeds with a shorter chain branching mechanism in the absence of oxygen. In this situation, alkyl radicals formed in the reaction (1) cannot produce peroxy radicals initiator (R + O₂ → RO₂). It is clear that the existence of these radicals is essential to produce ROOH (RO₂ + RH → ROOH) followed by its decay in the branching stage (7).

Therefore, under this condition the process proceeds with the shorter chains by only the decomposition of a small quantity of CH₃OOH formed by reaction (1). However, the change in the decrease of CH₃O radicals concentration in the absence (Fig. 3 curve 1) and presence of oxygen (Fig. 1 curve A) is the same approximately. Because of CH₃O radicals consumption takes place only through one channel (1) independently. Therefore, it is clear why the presence or absence of oxygen practically does not influence on the consumption rate of peroxy radicals.

Below the model of short chain branching mechanism of the interaction between CH₃O₂ radicals and organic compounds in the absence of oxygen has been represented:

CH₃O₂ + RH → CH₃OOH + R

In Fig. 4 the dependence of the desorbed radicals concentration [CH₃O₂] on [RH], in the absence of oxygen at t = 1x10⁻⁶ s is shown.

As seen from Fig. 4 the radicals concentration decreases with the increase of the organic compound concentration and does not exceed the initial concentration of radicals. In the experiments such picture was detected only during the reaction on the free oxygen salt surfaces [21, 22]. As seems the presence of oxygen is necessary for the multiplication of radicals in the experiment as it was on the TiO₂ surface [19, 24].

Therefore, under this condition the process proceeds via the chain branching mechanism however with a shorter length of chains.

References
