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

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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 $CH_3CHO + O_2$ 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 CH_3O_2 radicals with methane on the TiO_2 surface [19]. In contrast with the free oxygen saltsurface, 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.

$$CH_3O_2 + RH \rightarrow CH_3OOH + R \quad (1)$$
$$k_1 = 4\times10^{-7} \quad cm^2 \,/\, particle.s$$

$$R + O_2 \rightarrow RO_2 \quad (2)$$
$$k_2 = 10^{-4} \quad cm^2 \,/\, particle.s$$

$$CH_3OOH \rightarrow CH_3O + OH \quad (3)$$
$$k_3 = 10^8 \div 10^{13} \quad s^{-1}$$

$$OH + RH \rightarrow H_2O + R \quad (4)$$
$$k_4 = 5\times10^{-3} \quad cm^2\,/\, particle.s$$

$$CH_3O + RH \rightarrow CH_3OH + R \quad (5)$$
$$k_5 = 2\times10^{-6} \quad cm^2\,/\, particle.s$$

$$RO_2 + RH \rightarrow ROOH + R \quad (6)$$
$$k_6 = 4\times10^{-7} \quad cm^2\,/\, particle.s$$

$$ROOH \rightarrow RO + OH \quad (7)$$
$$k_7 = 10^8 \div 10^{13} \quad s^{-1}$$

$$RO + RH \rightarrow ROH + R \quad (8)$$
$$k_8 = 2\times10^{-6} \quad cm^2\,/\, particle.s$$

$$RO_2 \rightarrow P \,(product) \quad k_9 = 10^4 \; s^{-1} \quad (9)$$

$$RO_2 \rightarrow RO_{2d} \quad k_{10} = 2\times10^5 \; s^{-1} \quad (10)$$

$$CH_3O_2 \rightarrow CH_3O_{2d} \quad k_{11} = 2\times10^5 \; s^{-1} \quad (11)$$
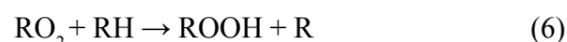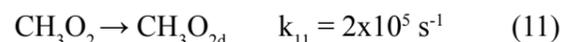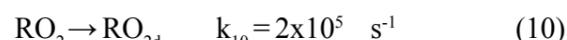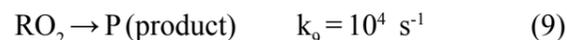
RH – hydrocarbon or aldehyde, RO2d and CH3O2d – the desorbed RO2 and CH3O2 radicals, accordingly.

In Fig. 1 the kinetic curves of RH and CH_3O_2 radicals consumption and the accumulation of the sum of $[RO_{2d} + CH_3O_{2d}]$ radicals at the initial conditions: $[RH]_o = 10^{12}$, $[CH_3O_2]_o = 3\times10^{11}$, $[O_2]_o = 10^{12}$, 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 $8 \times 10^{-7} - 1 \times 10^{-6}$ s the change of RH concentration equals to $\Delta[RH] = 6.3 \times 10^{12}$ molecules.cm^{-2} while for the case of radicals $\Delta[CH_3O_2] = 1.8 \times 10^{12}$ 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 $[RO_{2d} + CH_3O_{2d}]$ radicals is small

too, being less than $[CH_3O_2]_o$. At greater times the concentration of radicals becomes more than $[CH_3O_2]_o$ approximately on 20 percent, testifying the multiplication of radicals in the system. At the initial times of reaction when the quantity of CH_3OOH is small the difference between rate consumption of RH and radicals is smaller (Fig. 2).
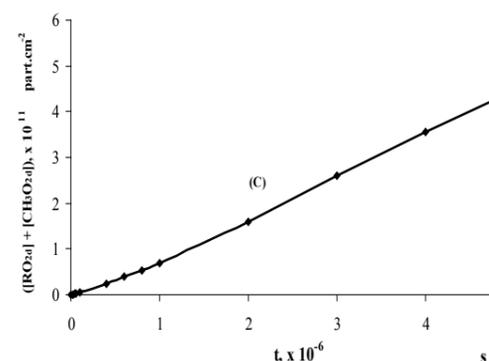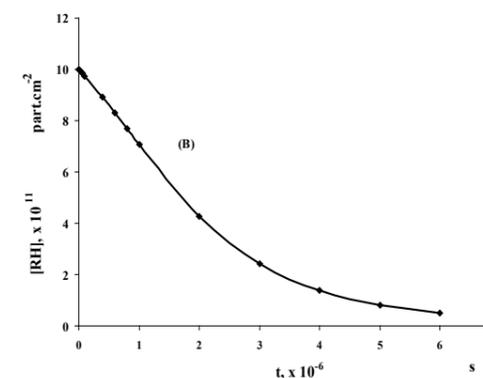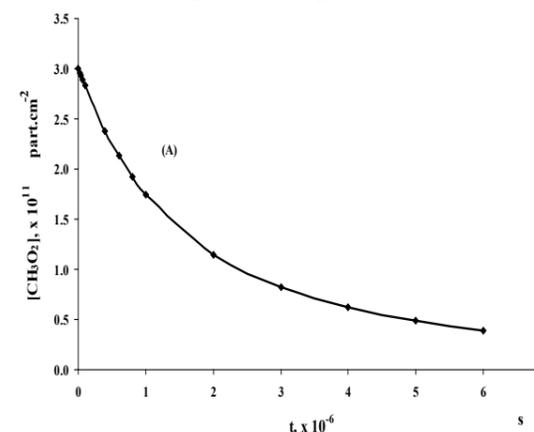
Fig.1. Kinetic curves of CH_3O_2 radicals (A), RH (B) consumption and (RO2d + CH3O2d) radicals accumulation (C). $[CH_3O_2]_o = 3\times10^{11}$, $[RH]_o = 10^{12}$, $[O_2]_o = 10^{12}$, particle.cm^{-2}.
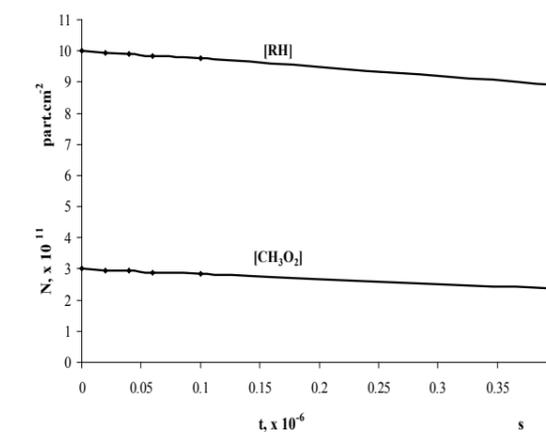
Fig. 2. Kinetic curves of RH and CH_3O_2 radicals consumption at the small times.

In Fig. 3 the kinetic curves of RH and CH_3O_2 radicals consumptions in the absence of oxygen have been shown. The initial conditions are as: $[RH]_o = 5\times10^{10} \div 5\times10^{12}$, $[CH_3O_2]_o = 3\times10^{11}$, $[O_2]_o = 0$, particle.cm^{-2} and room temperature.
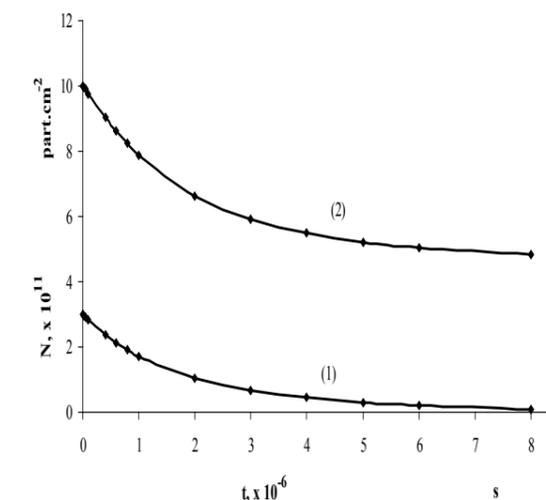
Fig. 3. Kinetic curves of CH_3O_2 radicals (1) and RH (2) consumption, $[O_2] = 0$.

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 ($R + O_2 \rightarrow RO_2$). It is clear that the existence of these radicals is essential to produce ROOH ($RO_2 + RH \rightarrow ROOH$) 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 CH_3OOH formed by reaction (1). However, the change in the decrease of CH_3O_2 radicals concentration in the absence (Fig. 3 curve 1) and presence of oxygen (Fig. 1 curve A) is the same approximately. Because of CH_3O_2 radicals consumption takes place through only 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:

$$CH_3O_2 + RH \rightarrow CH_3OOH + R \quad (1)$$
$$CH_3OOH \rightarrow CH_3O + OH \quad (2)$$
$$OH + RH \rightarrow H_2O + R \quad (3)$$
$$CH_3O + RH \rightarrow CH_3OH + R \quad (4)$$
$$CH_3O_2 \rightarrow CH_3O_{2d} \quad (5)$$
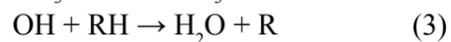
In Fig. 4 the dependence of the desorbed radicals concentration $[CH_3O_{2d}]$ on $[RH]_o$ in the absence of oxygen at $t = 1 \times 10^{-6}$ s is shown.

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 TiO_2 surface [19, 24].
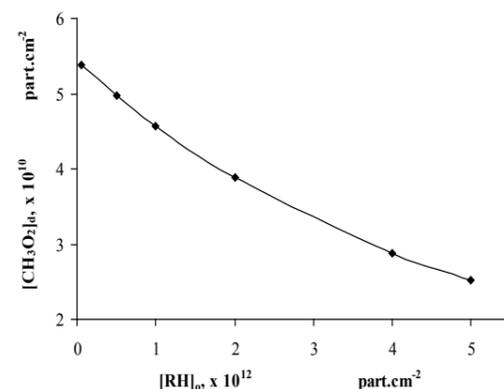
Fig. 4. Dependence of $[CH_3O_{2d}]$ on $[RH]_o$, $[O_2] = 0$, t = 1×10^{-6} s.

The wonderful phenomenon of radicals multiplication is the consequence of the additional consumption of organic compound reagent. As mentioned the additional consumption of RH is related to the association of two branching channels of hyroperoxide decay. In the absence of oxygen, the mechanism proceeds only via the first branching channel due to CH_3OOH decomposition. The participation of one channel alone cannot cause to multiply the radicals due to the fact that the additional consumption rate of RH is low. This displays the importance of the task of the second degenerate branching stage and consequently the major role of RO_2 radicals in the radicals multiplication phenomenon.

It should be highlighted that this original model was used for the first time for the simulation of reaction between peroxy radicals and organic compounds with fitting the rate constants. The experimental and simulation results qualitatively were in a good agreement with each other.

4. Conclusion

The important role of oxygen during the heterogeneous reaction of alkylperoxy radicals with organic compounds shows the possibility of products formation on the surface during

the chain radical oxidation of hydrocarbons and aldehydes.

In the presence of oxygen (or the surfaces containing oxygen) the number of active intermediate species on the surface increases during the process. Since the formed radicals also react with RH, RH consumption occurs with acceleration under the conditions of multiplication of active radicals. In the absence of oxygen (or free oxygen surfaces) the process proceeds via a shorter chain branching mechanism with a low rate of the additional chain consumption of RH. Therefore the multiplication of radicals cannot take place. It seems even in the absence of oxygen the process proceeds via the chain branching mechanism however with a shorter length of chains.

Refrences

[1] P. Wilhelm, C. Zetzsch, D. Stephan, Progress in Colloid and Polymer Science. 133. (2006) 147.

[2] L. I. Nieto-Gligorovski, S. Net, S. Gligorovski, H. Wortham, , H. Grothe, C. Zetzsch, Atmospheric Environment. 44. (2010) 5451.

[3] T. Imamura, Y. Rudich, R. K. Talukdar, R. W. Fox, A. R. Ravishankara, J. Phys. Chem. A. 101. (1997) 2316.

[4] A. R. Ravishnkara, Science. 276. (1997) 1058.

[5] G. S. Yablonsky, V. I. Bikov, A. N. Gorban, Kinetic models of catalytic reactions, Novosibirsk, Izd-Vo Nauka, Moscow, 1983, 254.

[6] S. L. Kiperman, Foundations of chemical kinetics in heterogeneous catalysis. Izd-Vo. Khimiya, Moscow, 1979, 350.

[7] I. A. Vardanyan, A. B. Nalbandyan, International Journal of Chemical Kinetics. 17. (1985) 901.

[8] L. A. Tavadyan, G. A. Martoyan, Analysis of kinetic models of chemical reaction systems. Value approach, Izd-"Gitochon", Yerevan, 2005, 278.

[9] V.S. Arutunov, M. Ja Bikhovskij, M. Ja Sineov, V. N. Korchak, Izvestija RAN, seria Khimicheskaya, 8. (2010) 1493.

[10] L. A. Tavadyan, A. Chachoyan, Chemistry and Physics of Lipids. 147. (2007) 30.

[11] I. A. Vardanyan, L. A. Manucharova, S. V. Tsarukyan, 19th international symposium of gas kinetics (Orleans, France, 2006), 232-234.

[12] I. A. Vardanyan, L. A. Manucharova, S. V. Tsarukyan , Proceedings Asme Ati Conf. Energy: Production, Distribution and Conservation (Italy, Milan, 2006), 915- 921.

[13] A. M. Arustamyan, I. A. Vardanyan, Chem. Phys. Reports. 16. (1997) 2035.

[14] Rub. T. Malkhasyan, I. A. Vardanyan, Dokl. NAN RA, 108. (2008) 229.

[15] I. A. Vardanyan, L. A. Manucharova, A. M. Arustamyan, S. V. Tsarukyan, Dokl. NAN RA, 106. (2006) 161.

[16] W. Hack, H. G.Wagner, I. A. Vardanyan, MPI, Stroemungsforschung, Report 13. (1997) 1.

[17] G. N. Sargsyan, R. S. Yessayan, I. A. Vardanyan, J. Appl. Catal. A: General. 203. (2000) 285.

[18] E. Carter, A. F. Carley , D. M. Murphy, Chemphyschem. 8. (2007) 113.

[19] H. A. Jalali, L. A. Manucharova, S. V. Tsarukyan, I. A. Vardanyan, Russian Journal of Phys.Chem. A. 85. (2011) 483.

[20] R. H. Bakchadjyan, I. A. Vardanyan International Journal of Chemical Kinetics, 26. (1994) 595.

[21] L. A. Manucharova, S. V. Tsarukyan, I. A. Vardanyan, International Journal of Chemical Kinetics, 36. (2004) 591.

[22] L. A. Manucharova, S. V.Tsarukyan, I. A. Vardanyan, Dokl. NAN RA. 107. (2007) 239.

[23] L. A. Manucharova DHAH. PA, 109. (2009) 221.

[24] H. A. Jalali, L. A. Manucharova, S. V. Tsarukyan, A. M. Arustamyan, Chemical Journal of Armenia, 63. (2010) 38.

[25] O.V. Krilov, Problems of kinetics of elementary chemical reactions, Moscow, Nauka, 1973, 115.

[26] L. A. Tavadyan, A. Chachoyan, Chemistry and Physics of Lipids. 147. (2007) 30.