

ХИМИЧЕСКАЯ ФИЗИКА

УДК 541.124.7.519.6

H. A. Jalali

**Kinetic Analysis of Model of Heterogeneous Reaction between
CH₃O₂ Radicals and Organic Compounds**

(Submitted by academician I.A. Vardanyan 19/I 2011)

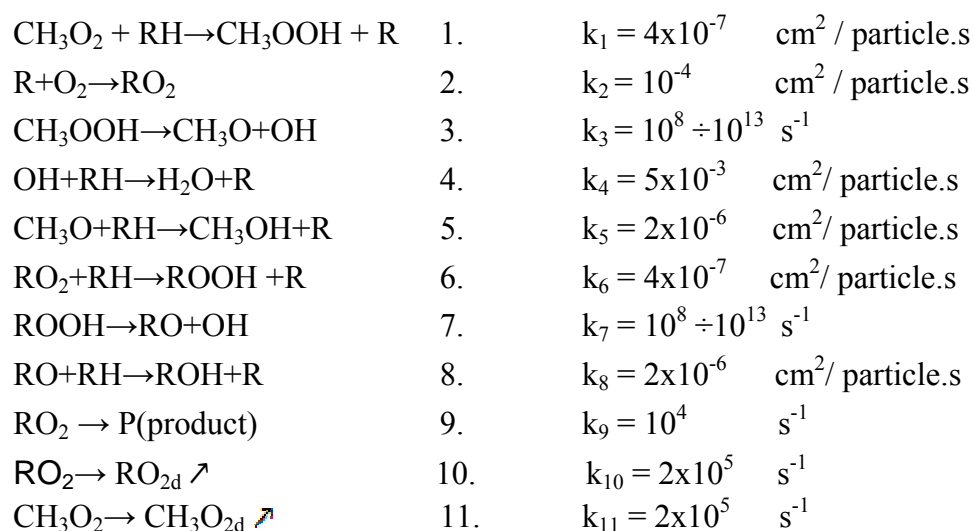
Key words: *modeling, peroxy radical, organic compound, heterogeneous*

Introduction. Earlier using kinetic method combined with ESR spectrometer the interaction of CH₃O₂ radicals with methane on TiO₂ surface [1] in flow at low pressure and room temperature under the conditions, excluding the homogeneous reactions, has been studied. During the heterogeneous reactions it has been observed not only radicals consumption as on the KCl [2] and NaCl [3] surface but also the radicals multiplication. At definite experimental conditions the concentration of radicals exceeded the initial one. The reaction was followed by radical consumption and their detection in the volume in the freezing unit. The information on the concentration of radicals, obtained by the help of the above mentioned method did not allow the identification of various types of peroxy radicals in the complex peroxy radicals spectrum.

The multiplication of radicals was ascribed to the additional organic compound consumption, initiated by heterogeneous radical decay of peroxide, which is formed during the interaction of CH₃O₂ radicals with methane. The data indicated that the mechanism of studied reaction is complex. Later [4] on the basis of these representations we have offered the model well describing the multiplication of radicals during the study of interaction of CH₃O₂ radical with organic compound in the presence of oxygen traces on the surfaces containing oxygen [1].

In this paper we consider the situation in the absence of oxygen. It is supposed, that process proceeds in an adsorbed layer in Langmuir-Hinshelwood approach on active sites of a surface. The computational methods are similar to [4]. Values of rate constants were evaluated on the basis of the data [5] with a few permissible variations. VALKIN Computer program [6, 7] on the basis of subroutine program ROW-4 [8] was used.

Below the model of heterogeneous degenerate chain branching interaction of CH_3O_2 radicals with RH offered in [4] is shown.



RH-aldehyde, hydrocarbon, RO_{2d} and CH_3O_{2d} -desorbed RO_2 and CH_3O_2 radicals, accordingly.

Initial conditions are as: $[\text{RH}]_0 = 5 \times 10^{10} \div 5 \times 10^{12}$, $[\text{CH}_3\text{O}_2]_0 = 3 \times 10^{11}$, $[\text{O}_2]_0 = 0$, $\text{particle} \cdot \text{cm}^{-2}$ and room temperature.

In Fig.1 the kinetic curves of RH and CH_3O_2 radicals consumptions are shown. As it is seen from the comparison of these curves in the mentioned range of time the consumption of organic compound proceeds faster than radicals indicating the chain consumption of organic reagent.

At small time of reaction when the quantity of CH_3OOH is small the difference will be smaller.

In Fig. 2 the dependence of desorbed radicals $[\text{CH}_3\text{O}_{2d}]$ on $[\text{RH}]_0$ at $t = 1 \times 10^{-6}$ s is shown.

As it is seen from the figure the quantity of radicals decreases with rise of initial quantity of organic compound and does not exceed the initial quantity of radicals. In

the experiments such picture is detected only during the reaction on salt surfaces [2, 3]. As seems the presence of oxygen is necessary for the multiplication of radicals in the experiment as it was on the TiO_2 surface [1].

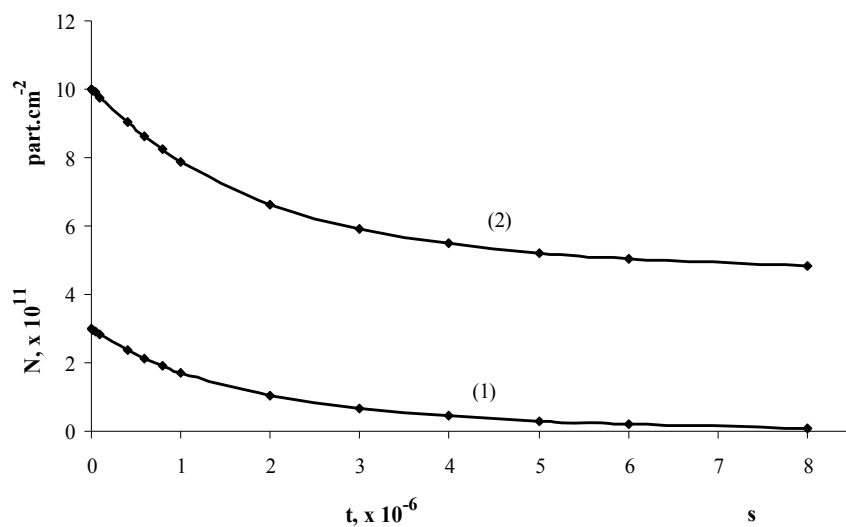


Fig. 1. Kinetic curves of CH_3O_2 radicals (1) and RH (2) consumption.

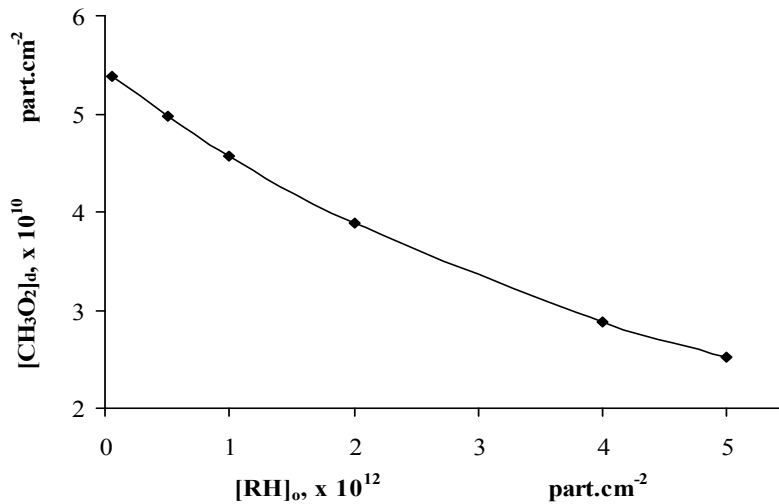


Fig. 2. Dependence of $[\text{CH}_3\text{O}_2]_t$ on $[\text{RH}]_0$, $t=1 \times 10^{-6}$ s.

On the basis of data we can conclude that the model can explain the multiplication of radicals on the surfaces containing oxygen and the absence on the salt surfaces.

Institute of Chemical Physics of NAS RA

H. A. Jalali

**Kinetic Analysis of Model of Heterogeneous Reaction
of CH_3O_2 Radicals with Organic Compound**

In Langmuir-Hinshelwood approach a model of heterogeneous reaction of CH_3O_2 radicals with organic compound in the absence of oxygen using VALKIN Computer program had been considered and analyzed. It is shown that the model can explain the multiplication of radicals on the surfaces containing oxygen and the absence on the salt surfaces.

Х. А. Джалали

**Кинетический анализ модели гетерогенной реакции
радикалов CH_3O_2 с органическим соединением**

Рассмотрена кинетическая модель реакции гетерогенного взаимодействия радикалов CH_3O_2 с органическим соединением в отсутствие кислорода в приближении Лэнгмюра – Хиншельвуда с использованием вычислительной программы VALKIN.

Показано, что модель объясняет наблюдаемое в эксперименте размножение радикалов на кислород содержащей поверхности и отсутствие его на солевой поверхности.

Հ. Ա. Ջալալի

**CH_3O_2 ռադիկալների հետ օրգանական միացության հետերոգեն
ռեակցիայի մոդելի կինետիկական անալիզը**

Անալիզի է ենթարկված թթվածնի բացակայությամբ CH_3O_2 ռադիկալների հետ օրգանական միացության ռեակցիայի կինետիկական մոդելը: Օգտագործվել են Լենգմյուր-Հինշելվուդի մոտավորությունը և VALKIN հաշվողական ծրագիրը: Ցույց է տրված, որ մոդելը բացատրում է փորձում դիտվող ռադիկալների բազմացումը թթվածին պարունակող մակերևույթի վրա և բացակայությունը աղային մակերևույթի վրա:

References

1. *Jalali H.A., Manucharova L.A., Tsarukyan S.V., Vardanyan I.A.* - Russian Journal of Physical Chemistry. A. 2011. V. 85. N 3. P. 483-485.
2. *Manucharova L.A., Tsarukyan S.V., Vardanyan I.A.* - International Journal of Chemical Kinetics. 2004. V. 36. N 11. P. 591-595.
3. *Манучарова Л.А., Царукян С.В., Варданян И.А.* - ДНАН РА. 2007. Т. 107. С. 239-246.
4. *Jalali H.A., Vardanyan I.A.* - XXI-st International Symposium on Combustion Processes. Miedzzydroje. Poland. Book of Abstracts. 2010. P.145-148.
5. *Крылов О.В.* В сб.: Проблемы кинетики элементарных химических реакций. М. Наука. 1973. С. 115.
6. *Тавадян Л.А., Мартоян Г.А.* Анализ кинетических моделей химических реакционных систем. Ценностный подход. Ереван, Изд-во "Гитутюн" НАН РА. 2005.
7. *Tavadyan L.A., Khachoyan A.* - Chemistry and Physics of Lipids. 2007. V. 147. N 1. P. 30-45.
8. *Gottwald B.A., Wanner G.* - Simulation. 1982. V. 38. N 2. P. 61-66.