

## КРАТКИЕ СООБЩЕНИЯ

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### INTERACTION OF $\text{CH}_3\text{O}_2$ RADICALS WITH $\text{CH}_3\text{CHO}$ AND $\text{CH}_4$ ON $\text{TiO}_2$ SURFACE

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The reaction of  $\text{CH}_3\text{O}_2$  radicals with  $\text{CH}_4$  and  $\text{CH}_3\text{CHO}$  on  $\text{TiO}_2$  (rutile) surface at room temperature has been studied. It was shown that in both cases the radicals multiplication has been observed. This phenomenon was ascribed to the additional consumption of organic compound by the chain branching mechanism initiated by above mentioned reaction. It has been concluded that this phenomenon is more striking revealed in the case of acetaldehyde.

Fig. 1, references 12.

## Introduction

The Earth's atmosphere is mostly a gaseous medium with a small volume fraction of aerosols and solid particles. The impact of them on the atmosphere composition can be quite large because of some reactions, that are very slow in the gas phase, can proceed more rapidly on the surface of these particles. OH and peroxy radicals ( $\text{HO}_2$  and  $\text{RO}_2$ ) are involved as intermediates in the mechanisms of the gas phase processes of oxidation and combustion of organic compounds. Short living species, originating, e.g. from the oxidation of volatile organic compounds (VOCs) and carbon monoxide, control the removal of primary pollutants such as  $\text{NO}_x$  and VOCs, which are not only harmful to human health but are also a major contributing factor to the formation of lower-atmosphere ozone.

The use of titanium dioxide ( $\text{TiO}_2$ ) not only as one of the most important species for the degradation of aqueous pollutants [1-3], but also for its high corrosion resistance, low toxicity and particularly in the remediation of volatile organic compounds is currently a topical issue.

In the works [4-6] thermally unstable peroxyacyl and peroxy radicals on  $\text{TiO}_2$  surface following thermal and photodecomposition of several adsorbed aldehyde and ketones have been identified.  $\text{RCO}$ ,  $\text{RCO}_3$  radicals that were generated by the reaction between charge carriers in  $\text{TiO}_2$  and various reagents in the presence of  $\text{O}_2$  molecules have been observed [4].

With the help of the kinetic method of radical freezing combined with ESR and IR-spectroscopy, some experimental data showing the opportunity of the heterogeneous interaction of peroxy radicals ( $\text{CH}_3\text{O}_2$ ,  $\text{CH}_3\text{CO}_3$ ) with the organic compound (methane, acetaldehyde) on the solid surface of KCl, NaCl and  $\text{TiO}_2$  have been obtained [7-11].

In works [9-11] the mentioned reactions were investigated at low pressure ( $10^{-2}$  Torr) in the capillary tube covered by NaCl, KCl and  $\text{TiO}_2$ , available in the composition of atmospheric particles and aerosols.

It was shown that on salt surface the remarkable consumption of radicals takes place.

NaCl is more active in this process compared with KCl. The degree of the consumption increased dependent on quantity of methane.

In contrast with salt surface, on  $\text{TiO}_2$  surface the dependence of radicals quantity in flow on the initial quantity of organic reagent has complex character [11]. On titanium oxide surface under some conditions not only the decrease, but the remarkable increase of radicals quantity in relation to their initial quantity has been observed too.

This phenomenon is attributed to the additional heterogeneous chain branching radical consumption of organic compound.

Taking into consideration the above mentioned and scarce information on this problem it is became clear that obtaining new data on the heterogeneous interaction of radicals with organic compounds is very important.

The goal of the present work is to study the effect of nature of the organic compound on the kinetic peculiarities of the reaction of methylperoxy radicals with acetaldehyde and methane on  $\text{TiO}_2$  surface.

## Experimental Results and Discussion

The interaction of acetaldehyde or methane with peroxy radicals was investigated using ESR spectrometry combined with the kinetic method of radicals freezing. The description of experiments is given in the work [11]. The experiments were performed at low pressure ( $\approx 10^{-2}$  Torr) and room temperature. Heterogeneous radical decomposition of peracetic acid served as a source of  $\text{CH}_3\text{O}_2$  radicals in a quartz flask covered with cobalt oxide ( $\text{CoO}$ ). The dimensions of a quartz capillary reactor ( $l = 2$  cm and  $d = 0.15$  cm) as well as the low pressure used in experiments allowed to minimize homogeneous reactions. The residence time of reacting mixture in the capillary reactor is much less than the time of homogeneous interaction of  $\text{CH}_3\text{O}_2$  radicals with reactants (acetaldehyde, methane). The inner surface of reactor was covered with  $\text{TiO}_2$  powder (rutile, pure for analysis) by treating the surface with its 10% aqueous suspension. Then the water was evaporated and surface was covered by the thin film of  $\text{TiO}_2$ . The

concentration of the radicals was determined every time before the experiment with acetaldehyde to compare it with the concentration in the next experiment with acetaldehyde. The reproducibility of experimental data was good.

At the presence of small quantities of acetaldehyde the remarkable consumption of radicals on the  $\text{TiO}_2$  surface at room temperature has been registered, indicating the heterogeneous interaction of peroxy radicals with organic compound. In Figure (curve 1) the dependence of the difference between current and initial quantity of radicals ( $\Delta[\text{RO}_2]$ ) on the quantity of acetaldehyde is shown.

As seen from the curve 1 at low quantity of acetaldehyde the remarkable decrease of radicals was registered. However with the further increase of acetaldehyde quantity the rise of radicals quantity till the quantities exceeding the initial one has been detected. For example at  $\text{CH}_3\text{CHO}$  feed in quantity equal to  $8 \times 10^{16}$  molecules the increase of radicals quantity ( $\Delta[\text{RO}_2]$ ) is approximately 32%. The further increase of molecular reagent quantity leads to the decrease of the radicals quantity.

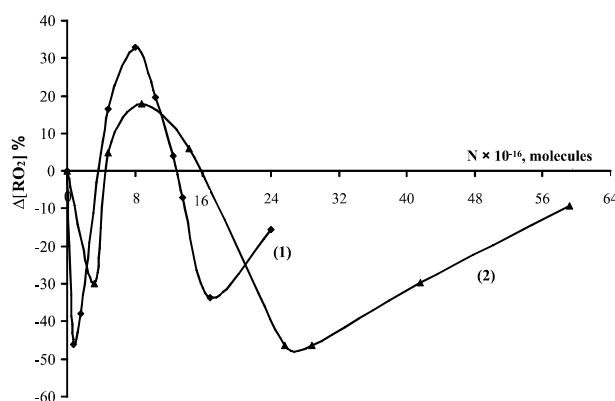


Figure. Dependence of the difference between current and initial quantity of radicals ( $\Delta[\text{RO}_2]$ ) on the initial quantity of acetaldehyde (curve 1) and methane (curve 2), at 293 K,  $[\text{CH}_3\text{O}_2]_0 = 25$  arbitrary units.

For comparison in the Figure the behavior of radicals quantity vs. methane quantity is also shown (curve 2). Comparing these two curves we can conclude that in general the qualitative picture is the same, indicating the similar complex character of the reaction in the case of other organic compound. Similar to [10, 11], the phenomenon of radicals multiplication is observed. But the quantitative picture is different. The decrease of  $\Delta[\text{RO}_2]$  in the case of acetaldehyde (46%) is higher than in the case of methane (32%). It is clear that one of the reasons can be a better acetaldehyde adsorption on  $\text{TiO}_2$  surface compared with methane.

The second conclusion drawn from the comparison of data by analogy with the homogeneous interaction is the highest rate constant of heterogeneous interaction of peroxy radicals with acetaldehyde than with methane. It results in the highest rate of the initiation of the further chain branching consumption of molecular organic reagent. Therefore the highest degree of the radicals multiplication is observed in the case of acetaldehyde.

Earlier [12] the model well describing the multiplication of radicals during the interaction of  $\text{CH}_3\text{O}_2$  radicals with organic compound (aldehyde, hydrocarbon) on the oxygen containing surfaces has been offered. It was supposed, that the interaction

proceeds in an adsorbed layer according to Langmuir-Hinshelwood approach on active sites of a surface. The goal of the calculation was to find out the adequacy of the representations incorporated in model to experimental data, without going into detailed mechanism of the chemical interaction. It was shown that the additional consumption of organic compound was explained by chain branching mechanism initiated by the radical decay of ROOH, forming during the interaction of peroxy radicals with organic compound.

Taking into account this consideration it becomes evident why the increase of radicals in the presence of acetaldehyde is observed at lower amount of the molecular product. The reason is the higher value of rate constant of the reaction of acetaldehyde with  $\text{CH}_3\text{O}_2$  radicals compared with that in the case of methane.

## Conclusion

Kinetic method of radicals freezing combined with ESR spectrometry was used to study the interaction of  $\text{CH}_3\text{CHO}$  and  $\text{CH}_4$  with  $\text{CH}_3\text{O}_2$  radicals on  $\text{TiO}_2$  surface. The multiplication of radicals for both above mentioned reactions is detected, being more apparent in the case of acetaldehyde.

The existence of radicals multiplication not only in the case of hydrocarbon, but in the case of aldehyde as well, indicates the common character of the earlier observed phenomenon.

### $\text{CH}_3\text{O}_2$ ՌԱԴԻԿԱԼՆԵՐԻ ՓՈԽԱԶԴԵՑՈՒԹՅՈՒՆԸ $\text{CH}_3\text{CHO}$ ԵՎ $\text{CH}_4$ ՀԵՏ $\text{TiO}_2$ ՄԱԿԵՐՆՈՒՅԹԻ ՎՐԱ

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$\text{CH}_3\text{CHO}$  և  $\text{CH}_4$  օրինակի վրա ուսումնասիրվել է օրգանական միացության հետ  $\text{CH}_3\text{O}_2$  ռադիկալների հետերոգեն ռեակցիան: Ցույց է տրված, որ երկու դեպքում էլ դիտվում է ռադիկալների բազմացման երևույթը, որը պայմանավորված է օրգանական միացության ծախսով շղթայական ճյուղավորված մեխանիզմով՝ հարուցված վերոհիշյալ ռեակցիայով: Նշված երևույթն ավելի ցայտուն է արտահայտված ագետալդեհիդի դեպքում:

### ВЗАИМОДЕЙСТВИЕ $\text{CH}_3\text{O}_2$ РАДИКАЛОВ С $\text{CH}_3\text{CHO}$ И $\text{CH}_4$ НА ПОВЕРХНОСТИ $\text{TiO}_2$

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На примере ацетальдегида и метана на поверхности  $\text{TiO}_2$  изучено влияние природы органического соединения на реакцию  $\text{CH}_3\text{O}_2$  радикалов с органическим соединением. Показано, что в обоих случаях наблюдается явление размножения радикалов, которое объясняется иницированием вышеуказанной реакцией расходования органического соединения по цепному разветвленному механизму. Указанное явление выражено более ярко в случае ацетальдегида.

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