# ՀԱՅԱՍՏԱՆԻ ՀԱՆՐԱՊԵՏՈՒԹՅԱՆ ԳԻՏՈՒԹՅՈՒՆՆԵՐԻ ԱԶԳԱՅԻՆ ԱԿԱԴԵՄԻԱ

# НАЦИОНАЛЬНАЯ АКАДЕМИЯ НАУК РЕСПУБЛИКИ Армения

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# TO THE MECHANISM OF THERMAL OXIDATION OF METHANE

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<u>Abstract.</u> The influence of the nature of the surface of the reaction vessel on the kinetics of methane oxidation in the gas phase has been explained by a heterogeneous-homogeneous mechanism, involving reactions of radicals not only in the gas phase but also on the solid surface.

# INTRODUCTION

The search of alternative fuels different from petroleum and less polluting was the reason for the new series of investigations devoted to the methane oxidation. The new interesting result obtained in this area was the observation of multistage low temperature ignition, single and multiple cool flames, region of negative temperature coefficient (NTC) of the maximum rate of the reaction [1]. For the  $C_2H_5CHO$  oxidation reaction we have shown that the surface of the reaction vessel and the heterogeneous reactions of radicals play a significant role for the NTC phenomenon [2].

On the basis of a study of the kinetics of  $CH_3CHO$  and  $C_2H_5CHO$  oxidation reactions in the gas phase and their dependence on the nature of the reaction vessel surface it has been concluded [3,4] that the surface takes part not only in the chain termination but also in the chain propagation. This conclusion is based on the following results. The  $CH_3CHO$  and  $C_2H_5CHO$  oxidation reactions were studied under conditions excluding homogeneous reactions of peroxy radicals. Experiments were

carried out at 453 K in a "capillary" reaction vessel at very low pressures  $(P \equiv 2 \times 10^{-1} kPa)$  and residence times  $(t \sim 10^{-3} s)$ . Under such conditions the oxidation of aldehydes leads to acids and traces of peracids as final products. Peroxy radicals were also discovered in the gas phase. Under experimental conditions used the formation of peroxy radicals and peracids can be only the result of heterogeneous consumption of aldehydes. It was concluded that the heterogeneous consumption of aldehydes proceeds with the participation of peroxy radicals.

This conclusion was proved upon a direct investigation of the interaction of peroxy radicals with the aldehyde on the surface of  $SiO_2$  and  $KCI/SiO_2$  [3]. The reaction of the  $CH_3O_2$  radicals with adsorbed  $C_2H_5CHO$  was investigated by IR spectroscopy and mass-spectrometry. In addition, the reaction of adsorbed  $CH_3CO_3$  radicals with  $CH_3CHO$  was studied by ESR spectrometry. In both cases direct evidence was found for the interaction of peroxy radicals with aldehyde on the surface.

During the study of the kinetic behaviour of  $C_2H_5$ CHO oxidation in the gas phase [4] at 803 K extraordinary results depending on the surface to volume ratio (S/V) have been received: a remarkable increase of the maximal rate of aldehyde consumption and  $H_2O_2$  concentration but a decrease of HO<sub>2</sub> radicals concentration in the volume with increasing of S/V. Usually in such chain processes a proportional dependence between the rate of the aldehyde consumption and the concentration of radicals in the volume has been observed. The data were explained by the existence of the heterogeneous interaction of HO<sub>2</sub> radicals with aldehyde resulting in the formation of  $H_2O_2$ .

These data also provided the background for a second look at the mechanism of methane oxidation [2,5,6]. To illustrate the new point of view we consider the results of the gas phase oxidation of methane [5,6].

## **EXPERIMENTAL RESULTS AND DISCUSSION**

Our experiments [5,6] were carried out in a quartz vessel (l = 17 cm, d=7 cm) at atmospheric pressure in flow conditions using the radical freezing methods, combined with ESR spectrometry. The temperature range was 713-785 K. The methane concentration was varied from 33-80% in the gas flow and that of O<sub>2</sub> from 7 to 20%. The major products of methane oxidation were CO and H<sub>2</sub>O. In the reaction vessel treated with boric acid the intermediate peroxy compound, methylhydroperoxide – CH<sub>3</sub>OOH and hydrogen peroxyde – H<sub>2</sub>O<sub>2</sub>, responsible for the chain

branching, were observed. As leading active centers of methane oxidation reaction,  $HO_2$  radicals were detected. The maximum concentration of  $HO_2$  radicals was ~10<sup>13</sup> particles/cm<sup>2</sup>. The [CH<sub>2</sub>O]/[CH<sub>3</sub>OH] ratio was less than or equal to one.

In a reaction vessel treated with KBr the methane oxidation proceeds very slowly and no peroxy radicals and peroxy compounds are detected. Detectable quantities of the products are found only at the highest temperature (762 K).  $[CH_2O]/[CH_3OH]$  ratio was in excess of 1.

To develop the new point of view let us consider here for example the kinetics of methane oxidation at 738 K in a reaction vessel treated with boric acid (Fig.1). The mixture composition is  $CH_4:O_2:N_2=33:20:47$ . In Fig.2 the dependence of maximum concentrations of intermediates and  $HO_2$  radicals on methane and oxygen concentrations is shown. We see that the increase of the  $CH_4$  and oxygen concentration as a rule leads to the increase of the  $CH_3OOH$  concentration and the  $[CH_3OH]/[CH_2O]$  ratio. The increase of concentration of  $CH_3OOH$  was very significant, and only slight changes of  $[H_2O_2]$  and  $[HO_2]$  were observed.



Fig. 1. Kinetics of methane oxidation in the reaction vessel treated with boric acid at 738 K. CH<sub>4</sub>:O<sub>2</sub>:N<sub>2</sub>=33:20:47, 1 - CH<sub>2</sub>O, 2 - CH<sub>3</sub>OH, 3 - H<sub>2</sub>O<sub>2</sub>, 4 - HO<sub>2</sub>, 5 - CH<sub>3</sub>OOH, 6 - CO, 7 - CO<sub>2</sub>, 8 - H<sub>2</sub>.



Fig. 2. Dependence of maximum concentration of products on the concentration of methane and oxygen in the mixture in the reaction vessel treated with boric acid, T=738 K, 1 – CH<sub>2</sub>O, 2 – CH<sub>3</sub>OH, 3 – H<sub>2</sub>O<sub>2</sub>, 4 – CH<sub>3</sub>OOH, 5 – HO<sub>2</sub> radicals in arbitrary units.

The rise of  $CH_4$  consumption with the rise of methane concentration is accompanied with the growth of  $CH_3OOH$  concentration. The rise of  $CH_3OOH$  concentration of course is connected with the reaction of  $CH_3O_2$ radicals, the concentration of the latter is about 10 times lower compared to the concentration of  $HO_2$  radicals.

Let us estimate from the curve 5 (Fig.1) the rate of CH<sub>3</sub>OOH accumulation  $(W_1)$ 

$$W_1 = \frac{\Delta [CH_3OOH]}{\Delta t} \cong 2.6 \times 10^{14} \frac{molec}{cm^3 s}$$

and compare that with the rate of CH<sub>3</sub>OOH formation ( $W_2$ ) estimated using the published value of the rate constant k of the reaction

$$CH_{3}O_{2} + CH_{4} \longrightarrow CH_{3}OOH + CH_{3}$$
  
k = 10<sup>-13</sup> exp(-18600 / RT) cm<sup>3</sup> / molec s [7]

at T=738K with  $[CH_4]=3.1\times10^{18} particle/cm^3$ ,  $[HO_2]=2.2\times10^{12} particle/cm^3$ at time when W<sub>1</sub> reaches its maximum value. Taking into account that  $[CH_3O_2] < [HO_2]$ , let us accept  $[CH_3O_2] \cong 2.2\times10^{11} particle/cm^3$ . Hence we obtain for the rate of CH<sub>3</sub>OOH formation (W<sub>2</sub>) the following value:

$$W_2 = 3 \times 10^{-18.5} \times 2.2 \times 10^{11} \times 3.1 \times 10^{18} \equiv 2 \times 10^{11.5} \frac{molec}{cm^3 s}$$

We see that  $W_2$  is many times lower than the experimental rate of CH<sub>3</sub>OOH accumulation  $W_1$ . If we even suppose that  $[CH_3O_2] = [HO_2] = 2 \times 10^{12} \text{ particle/cm}^3$ , the rate of the gas phase formation of CH<sub>3</sub>OOH shall be lower than the experimental registered value. The conclusion doesn't change if we estimate  $W_2$  using CH<sub>2</sub>O instead of CH<sub>4</sub> as a reagent.

These data indicate that besides the gas phase formation there is another way of CH<sub>3</sub>OOH formation. Taking into consideration the experimental data for the heterogeneous formation of peroxy compounds during the oxidation of aldehydes we can confirm the presence of such a channel of methylhydroperoxide formation during the thermal oxidation of methane. The fact that the change of the reaction vessel surface from boric acid to KBr leads to the remarkable change of product concentrations, particularly such as peroxy compounds and peroxy radicals, shows that in the case of methane oxidation their formation is also connected not only with homogeneous but with heterogeneous reactions of peroxy radicals.

# CONCLUSION

The theoretical considerations made on the basis of estimation of the rate of the hydroperoxide formation and experimental data depending on the surface of the reaction vessel allow us to conclude that the sensitivity of the methane oxidation reaction to the surface of the reaction vessel can be ascribed not only to the existence of heterogeneous recombination stages of  $RO_2$  and  $HO_2$  radicals but also to the existence of the heterogeneous interaction of these radicals with methane and aldehyde (CH<sub>2</sub>O). From the new point of view the methane oxidation represents a heterogeneous-homogeneous process with the reaction of radicals in the gas phase and on the solid surface.

#### ՄԵԹԱՆԻ ՋԵՐՄԱՅԻՆ ՕՔՍԻԴԱՑՄԱՆ ՄԵԽԱՆԻՋՍԻ ՎԵՐԱՔԵՐՅԱԼ

#### Ե. Մ. ԿԵՀԵՅԱՆ և Ի. Ա. ՎԱՐԴԱՆՅԱՆ

Ռեակցիոն անոԹի մակերևույ/ժի բնույ/∂ի ազդեցուԹյունը մեԹանի գազաֆազ օջսիդացման կինետիկայի վրա բացատրված է ռեակցիայի Հետևրոգեն-Հոմոգեն մեխանիզմով, որն իր մեջ ներառում է ռաղիկալների ռեակցիաները ոչ միայն գազային ֆազում, այլ նաև պինդ մակերևույ/Թի վրա:

# К МЕХАНИЗМУ ТЕРМИЧЕСКОГО ОКИСЛЕНИЯ МЕТАНА

#### Е. М. КЕГЕЯН и И. А. ВАРДАНЯН

Влияние природы поверхности реакционного сосуда на кинетику газофазного окисления метана объяснено гетерогенно-гомогепным механизмом реакции, включающим в себя реакции радикалов не только в газовой фазе, но и на твердой поверхности.

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