



## An EPR Study of Heterogeneous Reaction of $\text{CH}_3\text{O}_2$ Radicals with Organic Compounds: Effect of Organic Compound and Surface Nature

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### Abstract

The reaction of  $\text{CH}_3\text{O}_2$  radicals with acetaldehyde on the solid surface of  $\text{NH}_4\text{NO}_3$  has been studied in a flow capillary reactor at low pressure and room temperature. The experiments were performed using EPR spectrometer combined with the kinetic method of radicals freezing. Peroxy radicals revealed an oscillation complex behavior during the process regarding to the phenomenon of radicals multiplication. The kinetic peculiarities of process depend intensively on the concentration and the nature of organic compound and aerosol surface. The increase of mass percentage of oxygen of the aerosol substances can be responsible for increasing the amplitude of radicals oscillation behavior.

**Keywords:** EPR; Peroxy Radical; Organic Compound;  $\text{NH}_4\text{NO}_3$ ; Heterogeneous Reaction

### 1. Introduction

The aerosol particles play a key role in the atmosphere, not only affecting the atmospheric heterogeneous processes but also impacting local and global climate [1, 2]. Now, it is well known that peroxy radicals ( $\text{HO}_2$ ,  $\text{RO}_2$  with R being an organic group, e.g.  $\text{CH}_3$ ) are the key reactive intermediates/chain propagators.

The investigation of the photochemical degradation of volatile organic compounds (VOCs) in the smog chamber in the presence of aerosols [3] revealed that the reaction between any environmentally important trace gases such as  $\text{CH}_4$ , CO with OH and  $\text{HO}_2$  ( $\text{RO}_2$ ) radicals can proceed not only in the gas

phase [4] but also on the surface of aerosols. The reactions of  $\text{CH}_3\text{CO}_3$  and  $\text{CH}_3\text{O}_2$  radicals with  $\text{CH}_3\text{CHO}$  and  $\text{C}_2\text{H}_5\text{CHO}$  on the surface of  $\text{SiO}_2$  and  $\text{KCl/SiO}_2$  were studied by EPR and IR spectroscopy methods [5, 6].

The study of methane oxidation in a reactor treated with boric acid suggested that methyl hydroperoxide ( $\text{CH}_3\text{OOH}$ ) is formed during the interaction of  $\text{CH}_3\text{O}_2$  radicals with methane on the surface [7].

The participation of radicals in the multistep transformations of organic compounds, in particular ketones, proposed that the free radical pathways involving both organoperoxy and superoxide radicals can be responsible for the thermal and photodecomposition of ketones over  $\text{TiO}_2$  [8].

In a similar work, the formation of stable surface peroxyacyl radicals was observed

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during the co-adsorption of aldehydes with  $O_2$  and subsequent UV irradiation on the reduced  $TiO_2$  surface at 100 K [9]. Also, it was proposed that the  $TiO_2$  surface can participate in both the initiation and propagation stages of aldehyde photo-oxidation.

An EPR study of the reaction of  $CH_3O_2$  radicals with  $CH_4$  and  $NO_2$  on the surfaces of the alkali metal salts [10, 11] with a composition similar to that of atmospheric particles and aerosols revealed a considerable consumption of peroxy radicals while the behavior of radicals was entirely different and complex on the  $TiO_2$  surface regarding to occur the wonderful phenomenon of radicals multiplication [12, 13].

These results were used in a heterogeneous model describing the peculiarities of reaction mechanism of peroxy radicals with organic compounds [14, 15].

This paper reports and describes the results of the reaction between  $CH_3O_2$  radicals and organic compounds (methane and acetaldehyde) on the different surface such as

$NH_4NO_3$ ,  $TiO_2$ ,  $NaCl$ ,  $KCl$ .

## 2. Experimental

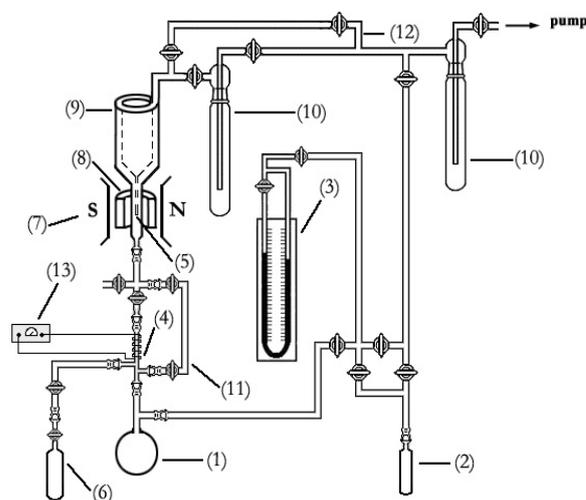
The heterogeneous interaction of peroxy radicals  $CH_3O_2$  with selected organic compound (methane) on the surface of  $NH_4NO_3$  representing solid aerosol has been studied. For this purpose a new complex method was developed. All of the experiments were carried out using EPR spectroscopy combined with the radicals freezing kinetic method in a flow capillary reactor coated by the different substances. The experiments were carried out by the laboratory apparatus, shown schematically in Fig. 1.

The  $CH_3O_2$  radicals were obtained by the heterogeneous radical decomposition of peroxyacetic acid in the presence of trace  $O_2$  in a quartz flask (1) *via*;



The injection of  $CH_3CO_3H$  vapor was carried out with the help of the liquid peracid vessel (2) and dosed with a manometer (3). Under the experimental conditions the quantity of peracid was between 2 – 6 torr in the gas phase.  $CH_3CO_3H$  was adsorbed at  $T = 78$  K on the inner surface of the quartz flask (1) with  $d = 3.8$  cm, previously treated with a saturated water solution of cobalt oxide.

$CH_3O_2$  radicals were generated into the gas phase by heating the adsorbed peracid on a water bath with heating intervals 1 – 1.5 min. The important difference between the present and previous set-up is the modification of  $CH_3O_2$  radicals source (1). The radical decay of  $CH_3CO_3H$  was carried out on the surface treated not by boric acid as before [10] but by cobalt oxide. This allows to decrease the temperature of radicals generation source from 513 – 543 K to 340 – 370 K. As a result



**Fig. 1.** Principle scheme of the set up (1) quartz flask for the adsorption of peracid, (2) vessel of peracid, (3) manometer, (4) reactor, (5) freezing unit, (6) vessel for gas reagents ( $CH_4$ ,  $CH_3CHO$ ), (7) Magnet, (8) resonator of the EPR spectrometer, (9) quartz Dewar vessel, (10) trap for analysis of gas products, (11), (12) bypass, (13) electrical furnace with power supply unit.

the greater activity of the treated surface in the reaction of radical decay of peracetic acid and replacing the oil bath with the more harmless water bath which promoted the safety of the work achieved.

The change of the radical yield ( $\Delta[\text{RO}_2]\%$ ) from the heterogeneous peracid decomposition on the cobalt oxide was plotted as a function of the bath temperature in Fig. 2. The optimal temperature for the source of  $\text{CH}_3\text{O}_2$  radicals is 333 K.

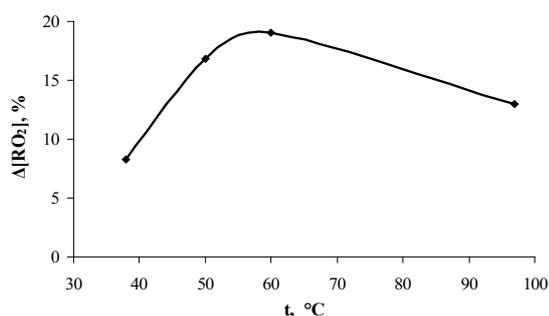


Fig.2. Temperature dependence of radical yield of peracid decomposed on the surface of CoO.

For minimizing the homogeneous interaction the experiments were performed in a flow pyrex capillary reactor (l= 2 cm, d= 0.15 cm) at low partial pressures of reagents ( $10^{-1} - 10^{-2}$  torr). The geometrical surface of the capillary reactor was approximately  $0.94 \text{ cm}^2$ .

The flow of radicals was forwarded via the reactor (4) into freezing unit (5) placed in the resonator of the EPR spectrometer. The quantity of radicals accumulated in the detection freezing unit was of order of  $10^{15}$  particles.

In addition, the temperature in the capillary reactor zone ( $20 \text{ }^\circ\text{C}$ ) was usually lower than the temperature of the radical generation zone. Therefore, the role of secondary processes in the reactor was minimized. The reactor was washed previously with the acid and the distilled water and then its inner surface was covered by the thin film of substance such as  $\text{TiO}_2$  and  $\text{NH}_4\text{NO}_3$  by treating with a 10% aqueous solution. The reagents were injected

from the vessel (6) both through the reactor entrance and bypass (11) for controlling the homogeneous reaction. Methane and acetaldehyde purity were 99.99%. The purity of the  $\text{TiO}_2$  and  $\text{NH}_4\text{NO}_3$  powder (rutile) and  $\text{NH}_4\text{NO}_3$  were marked as "pure for analysis".

The procedure of experiments consists of three steps; firstly, it was registered the initial quantity of peroxy radicals fed into the reactor, secondly it was fed the mixture of  $\text{CH}_3\text{O}_2$  radicals and organic compound into the reactor and finally it was only fed the  $\text{CH}_3\text{O}_2$  radicals into reactor for controlling the reproducibility of results. The interaction of radicals with various reactants was quantified by measuring the consumption of  $\text{RO}_2$  radicals in relation to their initial quantity. The reproducibility of experimental results was satisfactory.

### 3. Results and discussion

The absence of the interaction of peroxy radicals with reagents in the capillary reactor was established by the following calculations and the special experiments which the reagents forwarded directly into a bypass (11). These experiments showed that the radicals were not consumed when methane was introduced in the stream after the reactor. The principle condition for the reaction (3) is  $\tau < \tau_1$ .



Where  $\tau$  is the residence time of reacting mixtures,  $\tau_1$  is the time of the homogeneous interaction in the reactor and RH is methane or acetaldehyde.

The average pressure of reagents mixture at the input and output of reactor was calculated 6.3 torr and measured  $8 \times 10^{-2}$  torr respectively. The times  $\tau$  and  $\tau_1$  is defined by the following expression;

$$\tau = P_r \cdot V_r / W \cdot P_o \quad (1)$$

$$\tau_1 = 1/k_{\text{hom}} [\text{reagent}] \quad (2)$$

Where  $P_r$  is the average pressure in the

reactor,  $V_r = 3.5 \times 10^{-2} \text{ cm}^3$  is the volume of the reactor,  $P_0$  is the average pressure at the entrance of reactor,  $W = 1 \text{ cm}^3 \text{ s}^{-1}$  is the flow velocity through the reactor.  $P_r = 0.7 \text{ torr}$  was calculated assuming that the value of  $P_0$  in the reactor is decreased by the exponential law. Thus, using equation (1)

$$\tau = 3.9 \times 10^{-3} \text{ s}$$

The calculations based on the mathematical approach of the vacuum technique [16] showed that the process proceeds in molecular – viscosity regime and the value of  $\tau$  obtained consequently;

$$\tau = 2.5 \times 10^{-4} \text{ s}$$

The time of  $\tau_1$  was calculated using the rate constants for methane and acetaldehyde homogeneous reaction [17] at room temperature according to

$$k_{\text{hom}(\text{CH}_4)} = 10^{-27.8} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$$

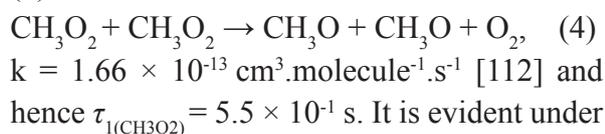
$$k_{\text{hom}(\text{CH}_3\text{CHO})} = 2 \times 10^{-20.3} \text{ cm}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$$

The average concentration of  $\text{CH}_4$  or  $\text{CH}_3\text{CHO}$  equals to  $1.1 \times 10^{15} \text{ molecules} \cdot \text{cm}^{-3}$  in the reactor. Thus, using equation (2)

$$\tau_{1(\text{CH}_4)} = 9 \times 10^{11.8} \text{ s}$$

$$\tau_{1(\text{CH}_3\text{CHO})} = 4.5 \times 10^{5.3} \text{ s}$$

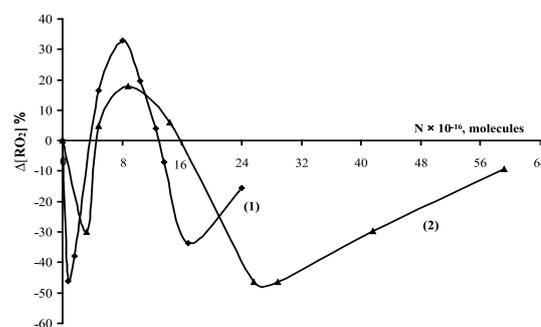
As regard the average experimental value of  $[\text{CH}_3\text{O}_2]$  was  $1.1 \times 10^{13} \text{ particles cm}^{-3}$  the value of the corresponding rate constant for reaction (4) is



### 3.1. Effect of organic compound (RH) nature

The influence of RH nature on the reaction with the adsorbed  $\text{CH}_3\text{O}_2$  radicals on the  $\text{TiO}_2$  surface has been studied. The change in the quantity of radicals ( $\Delta[\text{RO}_2]$ ) has been plotted

as a function of the initial quantity of RH ( $\text{CH}_4$  and  $\text{CH}_3\text{CHO}$ ) in Fig. 3. The “X” axis shows also the level of the initial quantity of  $\text{CH}_3\text{O}_2$  radicals. The quantity of molecular reagent was changed from  $4 \times 10^{15}$  till  $6 \times 10^{17}$  molecules. The radicals’ concentration is given in arbitrary units.



**Fig. 3.** Dependence of the change in the quantity of radicals ( $\Delta[\text{RO}_2]$ ) on the initial quantity

of  $\text{CH}_3\text{CHO}$  (curve 1) and  $\text{CH}_4$  (curve 2) ( $N \times 10^{16}$  molecules) on the  $\text{TiO}_2$  surface, 293 K,  $[\text{CH}_3\text{O}_2]_0 = 25$  arbitrary units.

At small amounts of acetaldehyde the remarkable consumption of radicals was observed, indicating the heterogeneous interaction of peroxy radicals with organic compound on the  $\text{TiO}_2$  surface. However, the further rise in the acetaldehyde quantity leads to increase the radicals quantity exceeding their initial one. For example at quantity of  $\text{CH}_3\text{CHO}$  equals to  $8 \times 10^{16}$  molecules,  $\Delta[\text{RO}_2]$  is 32% approximately. The further increase of molecular reagent quantity leads to the decrease of the radical quantity. Curve 2 (Fig. 3) also shows the behavior of radicals quantity as a function of the quantity of methane [13]. Comparing the curves it is evident that their qualitative picture is the same, indicating the similar complex oscillation behavior of radicals in the case of other class of organic compound.

However, the quantitative picture is different. Not only the decrease of  $\Delta[\text{RO}_2]$  in the case of

acetaldehyde (46%) is higher than methane (32%) but also its degree of the radicals multiplication (32%) is also more than the case of methane (18%). one of the reasons can be a better acetaldehyde adsorption on the surface compared to methane.

The second one is the higher rate constant of the heterogeneous interaction of peroxy radicals with acetaldehyde than methane. It results not only in the highest rate of the initiation stage but also the further chain branching consumption of organic compound. The ratio of possible values of the effective rate constants of reaction between  $RO_2$  radicals and organic compounds in the point of maximal consumption of radicals can be estimated by the next expression;

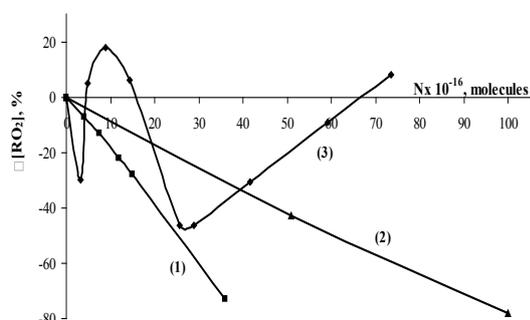
$$\Delta[RO_2] / [RO_2]_{RH} = k_{RH} \times \Delta t \times [RH] \quad (3)$$

Hence

$$k_{CH_3CHO} / k_{CH_4} = 5.75$$

### 3.2. Effect of surface nature

The influence of the nature of solid surface on the reaction of peroxy radical with organic compound was studied on the example of methane. In Fig. 4 the dependence of the change in the quantity of radicals ( $\Delta[RO_2]$ ) on



**Fig. 4.** Dependences of the change in the quantity of radicals ( $\Delta[RO_2]$ ) on the initial quantity of  $CH_4$  ( $N \times 10^{16}$  molecules) on the (1) NaCl, (2) KCl and (3)  $TiO_2$  surfaces, 293 K,  $[CH_3O_2]_0 = 25$  arbitrary unit.

the initial quantity of methane is shown at 293 K on the NaCl, KCl [10,11] and  $TiO_2$  surface. As seen the shape of curves (1) and (2) differ than curve (3) both quantitatively and qualitatively. In the case of oxygen free surfaces it is observed only the consumption of radicals which is much more in the case of NaCl.

However, in the case of  $TiO_2$  alongside with the consumption of radicals due to reaction (3) at small amounts of RH it is observed that the phenomenon of radicals multiplication. It is also observed that the consumption rate of radicals on the  $TiO_2$  surface is more than on the oxygen free surfaces. For example, in the fed methane quantity equals to  $3.2 \times 10^{16}$  molecules the consumption of  $CH_3O_2$  radicals is at least 30 % while on the NaCl surface is about 7 %. Obviously, it can be conclude the rate constant of process on the  $TiO_2$  surface is more than the oxygen free surfaces.

The ratio of the possible effective values of the rate constants due to the reaction of  $RO_2$  radicals with methane on the different salt surfaces can be estimated by the following expression;

$$\Delta[RO_2] / [RO_2]_{salt} = k_{salt} \times \Delta t \times [CH_4]_{salt} \quad (4)$$

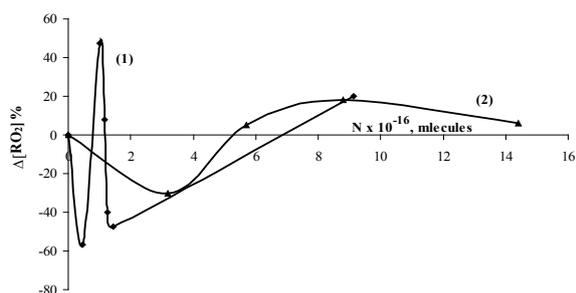
The calculations have been performed on the base of corresponding data of radical consumption quantity (Fig. 4). For the same concentration of methane and time ( $3.9 \times 10^{-3}$  s) it obtains;

$$k_{KCl} ; k_{NaCl} ; k_{TiO_2} = 0.03 ; 0.06 ; 0.3$$

It means the maximum heterogeneous consumption of peroxy radicals in the presence of the above mentioned solid surfaces was higher by factors of 1 (KCl); 2 (NaCl); 10 ( $TiO_2$ ).

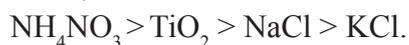
The influence of the nature of oxygen containing surface on the process was studied on the example of  $NH_4NO_3$ . The change in the quantity of radicals ( $\Delta[RO_2]$ ) has been plotted as a function of the initial quantity of methane

on the  $\text{NH}_4\text{NO}_3$  (curve 1) and  $\text{TiO}_2$  (curve 2) surfaces in Fig. 5.



**Fig. 5.** Dependence of the change in the quantity of radicals ( $\Delta[\text{RO}_2]$ ) on the initial quantity of  $\text{CH}_4$  ( $N \times 10^{16}$  molecules), on the surface of (1)  $\text{NH}_4\text{NO}_3$  and (2)  $\text{TiO}_2$ , 293 K.

Comparing these curves it is obvious that the behavior of peroxy radicals in the case of  $\text{NH}_4\text{NO}_3$  differs in relation to the free oxygen surfaces such as NaCl and KCl (Fig. 4). It is similar to the data received from the case of  $\text{TiO}_2$ . However, the amplitude of oscillations of  $\text{RO}_2$  radicals for the case of  $\text{NH}_4\text{NO}_3$  and the degree of phenomenon of radicals multiplication (curve 1) is more than the case of  $\text{TiO}_2$  (curve 2). In addition, the radicals consumption is more on the  $\text{NH}_4\text{NO}_3$  surface than on the  $\text{TiO}_2$  surface. These results indicate the possible participation of the lattice surface oxygen during the interaction of peroxy radicals with organic compound. One can be estimated the impact of oxygen on the process by considering the mass percentage of oxygen in the compounds used as a surface. For example this ratio for  $\text{NH}_4\text{NO}_3$  is 1.5 times more than for  $\text{TiO}_2$ . Thus, it is possible to arrange the sequence of the activity of substances as;



#### 4. Conclusion

The concentration and nature of organic compound play a critical role on the amplitude of radicals' oscillations and peculiarities of

the heterogeneous reaction between peroxy radicals and organic compounds such as the phenomenon of the radicals' multiplication. In addition, the surfaces nature of aerosol substances can significantly affect on the quantities of active sites and intermediates ( $\text{ROOH}$ ) formed on the surface. When they increases, the radicals generated as a result of the decomposition of  $\text{ROOH}$  react with methane in the presence of trace oxygen or surface oxygen and cause RH consumption by the short chain branching mechanism. In other words, the solid surface can participate in all stages of mechanism. The increase of mass percentage of oxygen of the aerosol substances can be also responsible for increasing the amplitude of radicals' oscillations.

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#### References

- [1] A. R. Ravishnkara, Science. 276 (1997) 1058.
- [2] M. J. Rossi, Chem. Rev., 103 (2003) 4823.
- [3] W. Behnke, W. Hollander, W. Koch, F. Nolting, C. Zetzsch, Atmospheric Environment, 22 (1988) 1113.
- [4] P. D. Lightfoot, R. A. Cox, J. N. Crowley, M. Destriau, G. D. Hayman, M. E. Jenkin, G. K. Moortgat, F. Zabel, Atmospheric Environment, 26A (1992) 1805.
- [5] R. H. Bakhchadjyan, K. G. Gazaryan, I. A. Vardanyan, Khim. Fiz., 10 (1991) 659.
- [6] R. H. Bakchadjyan, I. A. Vardanyan, International Journal of Chemical Kinetics, 26 (1994) 595.
- [7] E. G. Keheyany, I. A. Vardanyan, Chemical Journal of Armenia, 51 (1998) 177.
- [8] E. Carter, A. F. Carley, D. M. Murphy, Chem.Phys. Chem., 8 (2007) 113.
- [9] A. J. Charles, D. M. Murphy, The Journal of Physical Chemistry B, 103 (1999) 1019.
- [10] L. A. Manucharova, S. V. Tsarukyan, I. A. Vardanyan, International Journal of Chemical

- Kinetics, 36 (2004) 591.
- [11] L. A. Manucharova, S. V. Tsarukyan, I. A. Vardanyan, Dokl. NAN RA. 107 (2007) 239.
- [12] H. A. Jalali, L. A. Manucharova, S. V. Tsarukyan, A. M. Arustamyan, Chemical Journal of Armenia, 63 (2010) 38.
- [13] H. A. Jalali, L. A. Manucharova, S. V. Tsarukyan, I. A. Vardanyan, Russian Journal of Physical Chemistry A, 85 (2011) 483.
- [14] H. A. Jalali, I. A. Vardanyan, Archivum Combustionis, 30 (2010) 297.
- [15] Hossein Jalali Jahromi, Mojtaba Rahmani Nejad, Sharare Zeyghami, Journal of Physical Chemistry and Electrochemistry, 1 (2013) 179.
- [16] B. I. Korolev et al., Principles of Vacuum Technique, Energija, Moscow, 1975, 416.
- [17] V. I. Vedenev, M. Ya. Goldenberg, N. I. Gorban, M. A. Teitelboim, Kinitika i Kataliz, 29 (1998) 7.

