

Effect of Aerosol Surface Nature on Phenomenon of Radicals Multiplication during Heterogeneous Interaction of Peroxy Radicals with Organic Compound

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Interest to study of heterogeneous radical reactions is stipulated by several reasons. At first, similar stages take place at gas phase oxidation of organic compounds (RH). Second, at the presence of aerosols in an atmosphere they can influence on a rate of the photochemical degradation of organic compounds and, thus, on the composition of an atmosphere.

In this work the results of the investigation of the reaction between radicals and organic compound (CH₄, CH₃CHO) at room temperature dependent on surface nature (TiO₂, NH₄NO₃, NaCl and KCl) are reported. These compounds present in the form of aerosols in atmosphere. Experiments were carried out with the help of the method designed by us using ESR spectrometer and radicals freezing. The heterogeneous radical stages in flow in a capillary glass reactor (l = 2 cm, d = 0.14 cm) at low pressures (10⁻² Torr) were studied. These experimental conditions allow to reduce the contribution of the homogeneous interaction of radicals to a minimum. The surface of a reactor was treated by solutions of indicated compounds, accordingly.

Peculiarities of the interaction of CH₃O₂ radicals with organic compound dependent on the surface nature were analyzed generally by the example of CH₄. Comparison of the regularities of the change of quantity of radicals (ΔRO_2) from a quantity of methane has shown the sharp difference both in the quantitative, and in qualitative aspect. In case of NaCl and KCl salts only the diminution of a quantity of radicals was observed, being on NaCl much more. On TiO₂ and NH₄NO₃ alongside with the more significant consumption of radicals at small amounts of methane, the multiplication of radicals with the further rise of CH₄ amount has been observed, i.e. the amount of detected radicals exceeds their initial amount (on 18 and 47 %, correspondingly). The consumption proceeds more intensively on NH₄NO₃ surface. Apparently the radicals multiplication is observed only in case of an oxygen-containing surface.

Radicals consumption is attributed to the stage $CH_3O_2 + CH_4 \rightarrow CH_3OOH + CH_3$ (1) while radicals multiplication can be attributed to the additional consumption of organic compound by the chain degenerate branching mechanism because of heterogeneous radical decay of CH₃OOH. This fact allows assuming the participation of the lattice oxygen in the interaction peroxy radicals with RH.

The model of chain consumption of organic compound, initiated by a stage (1) has been offered and analyzed in approximation both Langmuir-Hinshelwood and Readyl-Ealy at the presence of oxygen traces to the qualitative explanation of the experimentally observed phenomenon. The application limits of these approximations were established dependent on adsorption capacity of compounds and a rate constant of the stage (1).

From the obtained data follows, that at the presence of aerosols the contribution of heterogeneous reaction of radicals with various organic compounds can influence on the processes proceeding in atmosphere. Detailed elaboration of the concrete mechanism of interaction with an active site of a surface is a subject of the further investigations.