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Kinetic Mechanism of Solid Alkanes Oxidation in the Troposphere. EPR Study.

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A special type of flow tube reactor was developed for online EPR registration of solid alkoxy radicals, which were formed in reaction of H + O_2. These alkanes coated the aerosil surfaces. The total surface area of coating was approx. 10^3 cm^2. After switching on the H atom discharge flow, the alkoxy radical concentration increases linear with time. After some period of time the rate of reaction becomes slower and after switching off the H atom flow, the alkoxy radicals growth stops. After additional introduction of O_2 the level of radicals falls fast.

Typical experimental conditions are:

at the beginning of RO increasing H = 5*10^{12} cm^{-3}, O_2 = 10^{13} – 10^{14} cm^{-3},

when H atoms are off: O_2 = 10^{14} – 10^{16} cm^{-3}.

The mechanisms of paraffin wax and tetracosane oxidation were studied. The rate constants of H + RH and RO + O_2 were determined: γ = (5.5 $\pm$ 0.3)*10^{-4}; k = (1.7 $\pm$ 0.3) * 10^{-17} cm^3 s^{-1}.

There were also estimated the rate constants of four reactions of R, RO, RO_2 proposed by Molina et al. for qualitative mechanism of organics oxidation [1].

We plan to develop the quantitative mechanism of solid saturated organics oxidation.

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Reference

1. M.J. Molina, A.V. Ivanov, S. Trakhtenberg, and L.T. Molina, Geophys. Res. Lett., 2004, V. 31, L22104