



## Chemistry of Surface Organic Radicals

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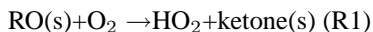
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This presentation is a review of our 6 papers published or submitted to the Russian Journal of Chemical Physics. The works were at the first time turned to obtain understanding of the mechanism of evolution of organic aerosols (OAs) in the troposphere and its impact on tropospheric composition and climate.

Main results:

- Kinetic and EPR spectroscopic evidence of surface organic radicals (SORs) formation in heterogeneous reactions of simplest gaseous radicals OH, Cl, O, H with organic films of stearic/palmitic acid (1:1) mixture and paraffin wax  $(\text{CH}_3)_2(\text{CH}_2)_n$ ,  $n=16-20$  was obtained.
- Kinetic studies were carried out by means of a mobile insert flow tube reactor combined with an EPR spectrometer or with a mass spectrometer. In spectroscopic studies organic matter was placed inside the EPR cavity held at ether room or liquid nitrogen temperature to monitor EPR spectra of SORs generating in reactions with gaseous radicals.
- In off-line experiments pyrex plates covered with organics were treated in the flow tube reactor by gaseous radicals, and the change of surface composition (XPS), roughness (profilometry), and contact angle (goniometry) were studied.
- Alkyl and alkyl peroxy radicals were detected at liquid nitrogen temperature, but at room temperature EPR spectrum of alkoxy radicals became the most intensive one.

- The initial uptake coefficients of OH and Cl on organic films are about 0.1 – 0.2 at  $[\text{OH}] \sim [\text{Cl}] \sim 10^{11} \text{ cm}^{-3}$ . The steady state values are one order of magnitude smaller. The chemical lifetime of OAs is about 5 times lower than the time of deposition.
- The rate constant of the heterogeneous reaction



is  $k \approx 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ . The following monomolecular reactions are supposed to be effective:



- The lifetime of RO(s) radicals in reaction R1 is very short in the troposphere ( $\sim 10^{-2} \text{ s}$ ). Reactions R2 and R3 should also be fast [1].
- Treatment of organic matter by active oxygen ( $\text{O}[\sim 10^{11} \text{ cm}^{-3}] + \text{O}_2$ ) was found to result in simultaneous increase of surface roughness and decrease of contact angle. This can be explained by formation of COOH and COH surface groups that increases roughness cavities, where water could flow diminishing the observed contact angle.

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1. R. Atkinson et. al., J. Phys. Chem. Ref. Data, 1997, V.26, supplement a,b, PP. 521-1011, 1329-1499.