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Chemical conversions of organic hydroperoxides in the atmosphere

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Organic hydroperoxides play an important role in the atmospheric chemistry, because they are not only among the principle oxidants in the chemical conversions of many compounds in the atmosphere, but also are an atmospheric sink and temporary reservoir for important oxidative radicals. The atmospheric concentrations of organic hydroperoxides are controlled by their sources and also by their atmospheric conversion mechanisms. In this study, the chemical conversions of two proto-typical atmospheric organic hydroperoxides were studied with the method of laboratory simulation. The technique of long path Fourier transform infrared (LP-FTIR) spectrometry was employed for the in-situ investigation of the chemical conversion reactions of methyl hydroperoxide (CH_3OOH, MHP) and ethyl hydroperoxide (C_2H_5OOH, EHP), including the photolysis, reactions with OH radicals, O_3 and NO_x ($NO_2$and NO). The reaction mechanisms of the photolysis and OH oxidation reactions were extrapolated in detail on the basis of the analysis results. Moreover, the rate coefficients for the reactions of these two organic hydroperoxides with OH radicals, O_3 and NO_x were determined, using the relative or absolute rate method. The atmospheric lifetimes of MHP and EHP with respect to the conversion reactions mentioned above were estimated on the basis of the rate coefficients and the concentration levels of atmospheric oxidants. In order to investigate the impact of organic hydroperoxides on the concentration level of atmospheric OH radicals, the yields of OH radicals from the photolysis of MHP and EHP were further determined.