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Ph.D. Thesis

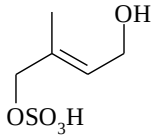
Aqueous-phase kinetics of complex reactions of isoprene for air quality modeling

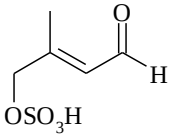
Abstract

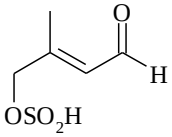
Results of laboratory study of aqueous-phase chemical kinetics, mechanisms and products of complex isoprene transformations in the presence of selected inorganic compounds present in the atmosphere – dissolved forms of SO_2 ($SO_2 \times H_2O$, HSO_3^-, SO_3^{2-}), nitrite ions/nitrous acid, oxygen and manganese(II) sulfate – is reported. Isoprene reacted with sulfoxy radical-anions, which were produced by the autoxidation of dissolved forms of SO_2 catalyzed by $MnSO_4$, also in the presence of nitrite ions and nitrous acid.

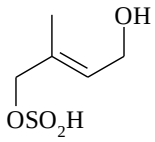
Isoprene, nitrite ions and nitrous acid, individually, exhibited the significant influence on the kinetics of S(IV) autoxidation in the way depending on the initial acidity of the reaction solutions ($pH_o = 2.2 \div 8.7$). Nitrous acid altered the rates of the transformation of isoprene during the autoxidation of S(IV) in the acidic solution.

Molecular structures of newly formed products from the reaction of isoprene with sulfoxy radical-anions were elucidated using a triple-quadruple negative electrospray mass spectrometry (–)ESI-MS/MS, nuclear magnetic resonance and UV spectroscopy, and confirmed by the comparison of their mass spectrometric behavior with that of the synthesized model compounds. Namely, the following compounds were firmly identified:

1-*O*-sulfonyl-4- hydrox-2-methylbut-2-ene 

4-*O*-sulfonyl-3-methylbut-2-enal 

4-*O*-sulfinyl-3-methylbut-2-enal 

1-*O*-sulfinyl-4-hydrox-2-methylbut-2-ene 

Quantum chemical calculations were used to assess the thermodynamic stability of novel products formed.

Mechanism of the aqueous-phase transformation of isoprene was proposed and supported, partly, with chemical-kinetic simulations.