Iminium-catalysed hydrolysis of epoxides by NH4+ in water: importance for atmospheric and green chemistry

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Iminium catalysis, which was known for a long time to be mediated by amines and amino acids, was also recently shown to be mediated by inorganic ammonium ions, NH4+. Iminium catalysis by NH4+ is potentially of great interest both for green chemistry in water and in atmospheric aerosols where these ions are abundant. In this work we investigate the hydrolysis of epoxides such as 1,2-epoxybutane, cis-2,3-epoxybutane, 2,3-dimethyl-2,3-epoxybutane, and the “isoprene-derived” cis- and trans-(2-methyloxirane-2,3-diyl)dimethanol (or “IEPOX” 3 and 4, respectively) in aqueous solutions at pH = 5-8 in the presence of NH4+. The products and kinetics of each reaction have been studied with a combination of GC/MS, GC/FID and 1H-NMR and by comparison with authentic standards. The results showed that each epoxide produced the expected diol or tetrol in large yield and that the reaction rate was much larger than when catalyzed by base or acid, confirming that NH4+ is an efficient catalyst for the hydrolysis of epoxides. Iminium catalysis by NH4+ thus provides a cheap and green alternative for the manufacturing of diols and glycols in water. In tropospheric aerosols, the hydrolysis of epoxides by NH4+ catalysis should be much faster than by acid catalysis for pH ≥ 3-4, thus in many regions except the most polluted ones.