Substituent Effects on the Hydrolysis of *p*-Substituted Benzonitriles in Sulfuric Acid Solutions at (25.0 ± 0.1) °C

Khamis A. Abbas

Department of Chemistry, Yarmouk University, Irbid, Jordan

Reprint requests to K. A. A.; E-mail: kaabbas19@hotmail.com or kabbas@yu.edu.jo

Z. Naturforsch. **63a,** 603 – 608 (2008); received February 27, 2008

The rate constants of the hydrolysis of *p*-substituted benzonitriles with sulfuric acid solutions (18.2 M to 10 M) have been determined spectrophotometrically at (25.1 ± 0.1) °C. It was found that the catalytic activity of sulfuric acid was strongly inhibited by water. The logarithms of the observed rate constants were correlated with different substituent inductive (localized) and resonance (delocalized) constants. The results of the correlation studies indicated that the rate-determining step of the hydrolysis of benzonitriles in 18.2 M sulfuric acid was the addition of a nucleophile, and the hydrolysis was clearly enhanced by the electron-withdrawing inductive effect, while the rate-determining step of the hydrolysis of *p*-substituted benzonitriles in 10.0 M sulfuric acid was most probably the protonation of benzonitriles, and the rate constants increased by both electron-donating resonance and inductive effects. A mixture of the two mechanisms most probably occurred in 15.3 to 17.0 M sulfuric acid. HSO_4^- rather thanwater most probably acted as nucleophile in the hydrolysis of benzonitriles especially at high concentrations of sulfuric acid solutions.

Key words: Sulfuric Acid; Benzonitriles; Hydrolysis; Rate Constants; Inductive Effect; Resonance Effect.