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Hydrolysis, alcoholysis and aminolysis of *N*,*N*′-malonyldiimidazole

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Abstract

The achievements of molecular biology, biochemistry and bioorganic chemistry are largely due to the methods of organic chemistry, in particular chemistry *N*-azolides over the past twenty years. Imidazolides are not the most reactive group of compounds among heterocyclic amides, however, it is interesting for preparative purposes because of the availability of imidazole. It is known that compounds of this class are widely used as specific condensing agents in the synthesis of a number of biologically active substances. The investigation of the physicochemical properties of *N*-azolides is of great interest.

According to well-known kinetic studies, the aminolysis and the alcoholysis of *N*-azolides proceed according to the addition-elimination mechanism. The hydrolysis of *N*-azolides of sterically hindered carboxylic acids proceeds according to the mechanism of monomolecular nucleophilic substitution. These conclusions are based on the study of the dependence of the rate constants and the activation energy of the acyl residue. Differences in the reactivity of *N*-azolides with different acyl residues are quite pronounced.

In this work, the reactions of hydrolysis, alcoholysis and aminolysis of *N*,*N*′-malonyldiimidazole were studied by an HPLC method on an isocratic pump chromatograph, with a UV spectrophotometric detector with a wavelength range of 190–600 nm. A polar chromatographic column with a particle size of 5 μm was used. Acetonitrile eluent (CH_3CN) was used as the mobile phase. The speed of the mobile phase was 1,000 ml/min. Before the experiment, air was removed from the mobile phase by degassing into an ultrasonic bath.

We used the program "Open LAB" for processing the results. Chromatography was carried out in isocratic mode at a wavelength of 280 nm. After a certain period of time, chromatography was carried out and a decreasing peak area of the starting dionicid of malonic acid was noted.

The kinetics of the processes of hydrolysis, aminolysis of alcoholysis was determined during the study. The relative instability of *N*,*N*′-malonyldiimidazole and high reactivity were established because of the calculated half-life data.

References

[1] H.A. Staab, W. Rohr. *Newer Methods of Preparative Organic Chemistry*. **1967**. Vol.53. P.61-108.
[2] P.V. Sklyuev, Z.P. Belousova, Yu.P. Zarubin, and P.P. Purygin. Synthesis and antibacterial activity of 1-[alkyl(aryl)sulfonyl]-1*H*-azoles. *Butlerov Communications*. **2011**. Vol.25. No.6. P.47-54. ROI: jbc-02/11-25-6-47
[3] A. Chikkulapalli et al. *Tetrahedron Lett.* **2015**. Vol.56. No.24. P.3799-3803.
[4] P.Y. Wang, S.W. Tsai, T.L. Chen. *Biotechnology and Bioengineering*. **2008.** Vol.101. No.3. P.460-469.
[5] P.P. Purygin, V.Yu. Alekseev, I.N. Alekseev, E.A. Agapova, and Yu.P. Zarubin. Preparation of *N*,*N*'-oxalyldiimidazole and investigation of its interaction with alkylamines and succinic acid. *Butlerov Communications.* **2018**. Vol.54. No.6. P.111-115. DOI: 10.37952/ROI-jbc-01/18-54-6-111