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Reactivity of Orthophthalaldehyde with Aliphatic, Alicyclic and Aromatic Primary Diamines: Electrochemical Study and Mechanistic Considerations

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Abstract:

The reactions of OPA with eight primary diamines were electrochemically monitored and the main products were isolated and identified. Various types of diamines were used: two non-vicinal α, ω -diaminoalkanes, four vicinal 1,2-diamino(cyclo)alkanes and two aromatic diamines. The results showed three electrochemical patterns: α, ω aliphatic diamines and both aromatic diamines exhibited only consumption of the parent OPA without observation of any electroactive intermediate or product; aliphatic and alicyclic vicinal diamines react with OPA under fast formation of reducible intermediate and its slow follow-up reaction yielding reducible product. A special case represents 1,2-*trans*-diaminocyclohexane exhibiting different products with regard to its *cis*-isomer. The main reaction products in all cases are derivatives of indano[1,2-a]benzimidazole and not bis-Schiff bases discussed in the literature.

It has been found that the reaction of non-vicinal diamines with OPA is much faster than that of the vicinal diamines. The UV-vis monitoring revealed that the reaction of OPA with vicinal, as well as non-vicinal diamines results in the same type of product, hence the mentioned difference in the electrochemical pattern is caused by different kinetics. The slower reaction rate can be caused by lower nucleophilicity of vicinal diamines, where stronger electronic communication of vicinal amino groups takes place. This effect manifests itself as larger difference between the first and second pKa of the two amine groups and the comparison of HOMOs supported this interpretation.

Keywords: Orthophthalaldehyde, Diamines, Electrochemistry, Mechanism, Reaction products.

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