

Kinetics of Bamberger rearrangement of N-phenylhydroxylamine in a reusable homogeneous system: CH₃CN-H₂O-CF₃COOH

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4-Aminophenol is an important raw material for several products in the field of dyes, photographs and pharmaceuticals. For instance, paracetamol (N-acetyl-4-aminophenol) a widely employed analgesic and antipyretic [1]. Bases of the present research have been the recent results in the Beckmann rearrangement of the cyclohexanone oxime to caprolactam in CH₃CN-CF₃COOH solvent catalytic system [2]. The system CH₃CN-CF₃COOH in that reaction is fully reusable because of the acidity of the CF₃COOH does not allow formation of the caprolactam salt and does not need neutralization [2]. Here we study the reactivity of the CH₃CN-H₂O-CF₃COOH system in the Bamberger rearrangement of N-phenylhydroxylamine to 4-aminophenol the former being the key intermediate in the selective hydrogenation of nitrobenzene to 4-aminophenol.

The reaction is carried out in a thermostatted reactor and the kinetics has been followed by HPLC and UV-Vis measurements. Both H₂O and CF₃COOH are in large excess and in any case an apparent first order has been observed, then a first order k_{obs} have been reported. The influence of the operative variable has been studied and in particular the influence of CF₃COOH and H₂O concentration on reaction rate is shown in Figure 1. The increase of CF₃COOH correspond to an increase of the reaction rate, on the contrary H₂O inhibits the kinetics. These results suggest that H₂O competes in one stage of the rearrangement thus reducing the overall rate, for instance, H₂O may influence protonation equilibria.

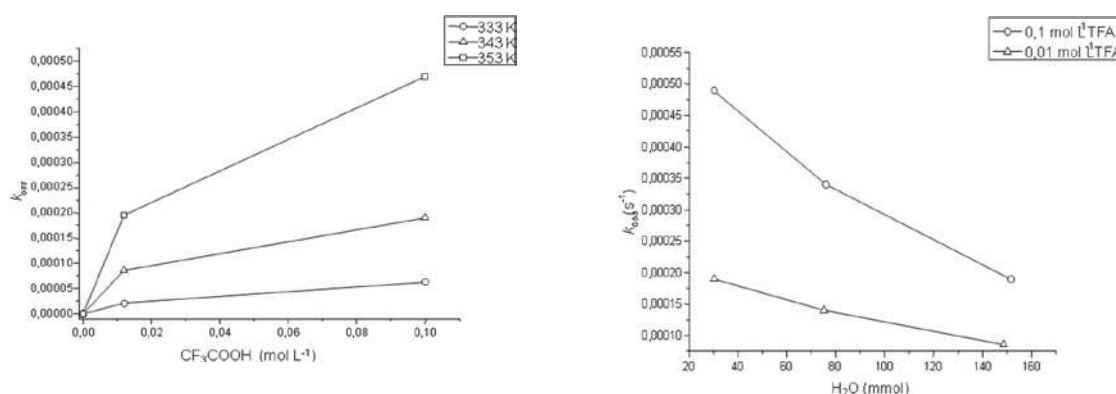


Figure 1. Influence of CF₃COOH (TFA) and H₂O on the rearrangement kinetics. Run conditions: T (343 K), N-phenylhydroxylamine (0.001 mol L⁻¹), reaction volume 25 mL.

References

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