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A Thermodynamic Assessment on the Reaction of Aromatic Amines Versus Reactivity with p-Benzoquinone from a Kinetic Study

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With 3 Figures and 3 Tables

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Abstract

The investigated aromatic amine-quinone reaction was found to proved kinetically as a second order reaction. Reactivities of amines towards addition to p-benzoquinone have been determined by individual rate measurements and carefully elucidated in terms of (i) electronic and mesomeric effects, (ii) the standard free energy change ΔG^0, (iii) the fraction of activated molecules (N^*/N): Informations streaming from different sources were found to indicate that electron repelling groups tend to increase the reaction rate, whereas electron withdrawing groups decrease it. A substituent effect ($\varrho = -1.5$) has been observed. The thermodynamic activation parameters of the reaction were determined and ΔS^+ was found to be a linear function of ΔH^+ which points to the occurance of the same mechanism for the investigated reaction using different aromatic amines.

Introduction

The kinetics and mechanism of the coupling of diazonium salts with aromatic amines have been studied by WISTAR [1], SCHMIDT [2] and VERHKOVSKYA [3]. Other kinetic studies on the acylation of arylamines by acid chloride [4] or thioacetic anhydride [5] and other reagents [6–8] were investigated. Also the addition of amines to p-tolylvinylsulphone was kinetically studied. MARTYNOFF [10] and HAROSPOOL [11] pointed out to the nature of the product of aromatic amines with p-benzoquinone reaction. Aromatic amines react quantitatively with p-benzoquinone to give 2-amino-p-benzoquinone and hydroquinone.

The present investigation presents on extended interest in elucidating the nature of the aromatic amines-p-benzoquinone reaction in terms of a thermodynamic analysis through a kinetic study.

Results and Discussion

Stoichiometry of reaction was determined by the molar ratio method [12], and the red coloured product has a maximum absorption band at λ 505 nm at molar ratio of 2 : 1 (p-benzoquinone: aniline) [13].

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