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The Kinetics of the Photochemical Reaction of Methylene Green with Methylamine and Ethylamine

Rehana SAEED, Fahim UDDIN , Zahida KHALID
Photochem Research Lab, Department of Chemistry,
University of Karachi, Karachi-75270 PAKISTAN
email: fahim_uddin01@yahoo.com

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Authors

chem@tubitak.gov.tr

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Abstract: The photochemical reduction of methylene green with methylamine and ethylamine in 50% aqueous isopropanol was studied. The photochemical reduction was carried out in a special type of optical processor associated with a deoxygenating system, a temperature controlling unit and a magnetic stirring system. A monochromatic light of 657 nm wavelength was used for irradiation of oxygen free reaction solutions in a double walled reaction cell. The transmitted light was measured and recorded in terms of electrical signals with the help of a calibrated galvanometer. Acidities of the solutions were measured with the help of a spectrophotometer based on the Hammet acidity function [H_o]. The quantum yield (φ) for the photochemical reaction of methylene green with methylamine and ethylamine was determined as a function of concentrations of methylene green, concentrations of reductants [AH_2], acidity [H_o], temperature and alkyl group associated with amine or the nature of the reductant. It was observed that the quantum yield varies with reductant concentration [AH_2] and is independent of the concentration of methylene green at specific values of acidity and temperature. The results have been interpreted in terms of the reaction mechanism. The values of specific rate constants for ethylamine were found to be relatively higher than those of methylamine, which shows that the reactivity of amines increases as the number of alkyl groups increased in amines. It was found that 2 equilibria exist: i.e. one between the triplet state of methylene green with the proton and the protonated triplet state of methylene green [MGH_{2T}^{++}], and the other between the protonated triplet state of methylene green with reductants and associated the complex of methylene green [$\{MGH\}_{2T}^{++}\ AH_2$]. Thermodynamic parameters were also evaluated as a function of the concentration of reductant, acidity and temperature.

Key Words: Photochemical reduction, methylene green, amines, kinetics, mechanism, thermodynamic parameters

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