Dye-sensitized cyclization of diphenylamines

RAVINDER KUMAR GARG, KAMINI MALHOTRA and K.S. SIDHU

Department of Chemistry, Punjabi University, Patiala 147002 (India)

In contrast with some of the earlier reports on the reactivity of arylamines with excited dyes [1], for thiazine dyes we observed dehydrogenative cyclization of N-substituted diphenylamines to carbazoles with concomitant formation of leuco dyes and H^+ ions in degassed methanol and methanol–water solutions (steady illumination intensity, 1.43×10^{-4} einsteins l^{-1} min^{-1}). Molecular hydrogen is not formed and the quantum yield Φ for carbazole increases with oxygen concentration and then approaches zero at $[O_2] = 2.1 \times 10^{-3}$ M where O_2 $^1\Delta_g$ is predominantly formed ($[amine] = 10^{-5}$ M). The dye itself quenches the reaction, which is dielectric and viscosity dependent. Reversible and equilibrium-limited reactions participate in the system and a kinetic scheme in terms of the suggested mechanism is proposed for discussion.

1 R. H. Kayser and R. H. Young, *Photochem. Photobiol., 24* (1976) 403.

Measurement of quantum yields for photochemically produced solvated electrons

G. GRABNER, G. KÖHLER, J. ZECHNER and N. GETOFF

Institute for Theoretical Chemistry and Radiation Chemistry, University of Vienna, Währingerstrasse 38, 1090 Vienna (Austria)

Photolytic Cl^- ion formation in aqueous solutions of phenol and chlorinated aliphatic compounds, in particular 2-chloroethanol and the chloroacetate ion, has been studied in detail. Phenol was excited at low light intensity within the first excited singlet state. The dependence of the quantum yield $Q(Cl^-)$ on the concentration of 2-chloroethanol was investigated for concentrations over five orders of magnitude. Competition measurements with added scavengers for the solvated electron e_{aq}^- (especially H^+) and fluorescence quenching measurements were performed in order to distinguish the formation of e_{aq}^- from other Cl^--liberating processes. The method allows the determination of $Q(e_{aq}^-)$ in the limit of very low scavenger concentrations. For phenol excited at 254 nm a value of $Q(e_{aq}^-) = 0.010 \pm 0.001$ was obtained with this method.