

PHOTOPROCESSES OF INDOLIC COMPOUNDS IN SOLUTION

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Vavilov's rule is not obeyed for indole and other aromatic compounds in aliphatic hydrocarbon solvents and in water (e.g. /1,2,3/). Since the fluorescence quantum yield Q_F from the indolic S_1 (1L_a , 1L_b) state is considerably smaller upon irradiation into the S_2 (1B_b) band there must be processes competing with the $S_2 \longrightarrow S_1$ internal conversion with a quantum yield $\beta = Q(S_2)/Q(S_1)$. For phenols a concomitant increase at shorter wavelengths of the formation of H-atoms in hydrocarbon solvents and of solvated electrons (e_{aq}^-) in water has been reported /4,5/.

For 5-methoxyindole in cyclohexane β is smaller than for indole, whereas in aqueous solution the β -values are comparable for both compounds. On the other hand, N-methylindole in cyclohexane shows no wavelength effect on β , but its behaviour in water is similar to that of indole.

The irradiations were performed with low pressure mercury (254 nm), cadmium (299 nm) and zinc lamps (214 nm), generally at 30°C, if not stated otherwise. The formed gaseous products were collected on a vacuum line and analyzed by gas chromatography.

In the following table the wavelength dependence of Q_F and Q_H in cyclohexane is given.

	$Q_H(254)$	$Q_H(214)$	α_H	β
Indole	6.6×10^{-3}	0.17	0.17	0.30
5-Methoxyindole	0.007	0.095	0.092	0.45
N-Methylindole	$\leq 10^{-3}$	$\leq 10^{-3}$	$\leq 10^{-4}$	1

If H-atom split is the only process in apolar solvents competing $S_2 \longrightarrow S_1$ internal conversion, $\alpha_H = Q_H(S_2) - \beta Q_H(S_1)$ should equal $(1-\beta)$. However, α is smaller than $(1-\beta)$. This is probably explained by a nonhomogeneous recombination process between $H\cdot$ and the remaining indole radical. In order to test this assumption the effect of temperature on α and β was investigated. As expected α increases with temperature whereas β is T-independent. Within the error limits $1/Q_H$ gives a straight line against $\sqrt{T/\eta}$ (η = solvent viscosity), according to nonhomogeneous kinetics. On the contrary Q_H is smaller in n-heptane and iso-octane (for indole $Q_H = 0.14$ in n-heptane and 0.11 in iso-octane) in spite of the lower viscosities of these solvents. Specific solvent-solute interactions may be an explanation.

Upon addition of methanol (1-5 v/v %) both α_H and $(1-\beta)$ decrease, most probably because of formation of H-bonds to the NH group, preventing N-H cleavage.

In water as a solvent with strong hydrogen bonds the quantum yield of H_2 -formation is very small ($Q_H \leq 10^{-2}$ at 254 and 214 nm; H-atoms were scavenged by 1 M methanol. Appropriate corrections for the reaction $H + \text{indole}$ were applied). On the other hand e_{aq}^- are formed (measured by scavenging with N_2O and determination of the N_2 -yield), their quantum yield depends on excitation wavelength (for indole: $Q_{254} = 0.12$, $Q_{229} = 0.17$, $Q_{214} = 0.24$). In aqueous solutions $\beta = 0.62$. As in hydrocarbon solutions the increase in the measured photochemical yields cannot fully account for the decrease of the fluorescence quantum yield in water ($\alpha(e_{aq}^- + H) = 0.17$, whereas $(1-\beta) = 0.38$). Most probably the difference is again due to inhomogeneous recombination reactions, which are presently under investigation.

References

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