CHEMISTRY LETTERS, pp. 93-94, 1978. Published by the Chemical Society of Japan

QUENCHING OF THE BENZENE FLUORESCENCE BY PYRIMIDINE IN CYCLOHEXANE

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Studies were made on the quenching of the benzene fluorescence excited with 254 nm radiation by pyrimidine in cyclohexane. The value of quenching constant is larger by a factor of 7 than that expected for diffusion-controlled process.

Rate constants of energy transfer from an excited singlet state of benzene to various acceptor molecules have been studied.[1] For example, when biacetyl was used as an acceptor, the transfer process has been found to be diffusionally controlled.[2] In this communication, pyrimidine was used as an acceptor.

The decrease in quantum efficiency of the benzene fluorescence was found in the presence of pyrimidine using cyclohexane as a solvent. The quenching rate constant for pyrimidine was calculated from the Stern-Volmer equation:

$$I_0 / I = 1 + k_q \tau [Q]$$

where I_0 is the intensity of the benzene fluorescence in the absence of pyrimidine, I is the fluorescence intensity in the solution containing pyrimidine, k_q is the energy transfer rate constant, and τ is the lifetime of excited singlet benzene in the absence of quencher Q. A figure shows the I_0 / I as a function of pyrimidine concentration. From the initial slope of the Stern-Volmer plot, we obtain $k_q = 5.5 \times 10^{10}$ l / mol sec, using the value of $\tau = 29$ ns.[3] The rate constant (k_d) of the bimolecular process controlled by diffusion is calculated from the equation:

$$K_d = 8RT / 3000\eta$$

where R is the gas constant, T is temperature, and η is the solvent viscosity. The expected rate is $k_d^{25°C} = 7.5 \times 10^9$ l / mol sec. The value of k_q / k_d ratio is 7.3. In this experiment, a rather high concentration of benzene was used in order that more than 99 % of the incident light may be absorbed by benzene. So, the decrease of the benzene fluorescence in the presence of pyrimidine is regarded not due to the light absorption by pyrimidine. The nonlinear Stern-Volmer plot and the large value of k_q / k_d suggest that the diffusionally controlled process is not the only way of quenching the electronic excitation energy. Further detailed studies on the mechanism of energy transfer in these systems will be reported elsewhere.

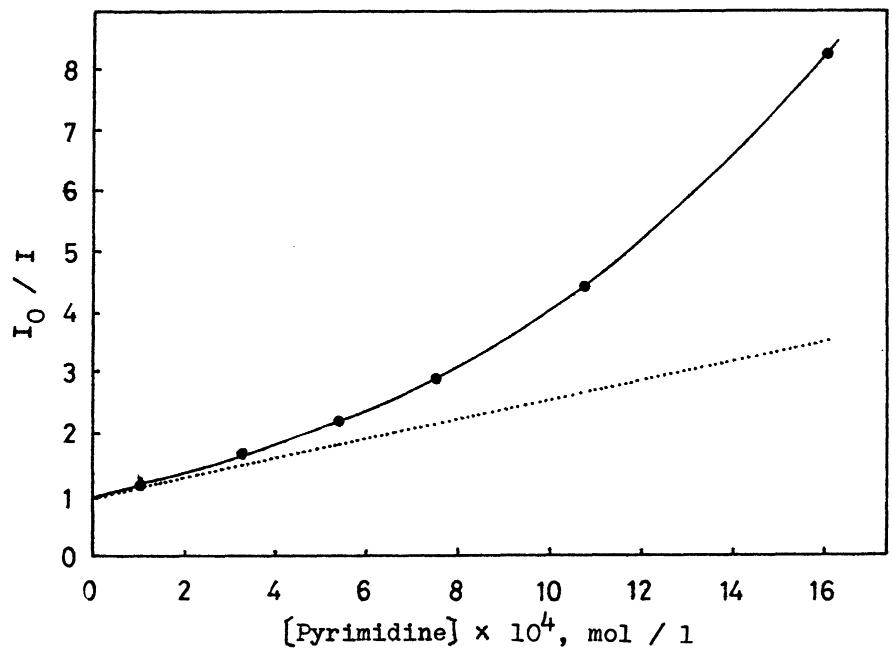

Figure. Stern-Volmer diagram for the quenching of the benzene fluorescence by pyrimidine in deaerated cyclohexane at 25°C.

References

1) W. Augustyniak, E. Wiechowicz and J. Wojtczak, J. Photochem., 6, 229 (1976/77).

2) J. T. Dubois and F. Wilkinson, J. Chem. Phys., 38, 2541 (1963).

3) I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules", Academic Press, New York (1965).

(Received November 9, 1977)