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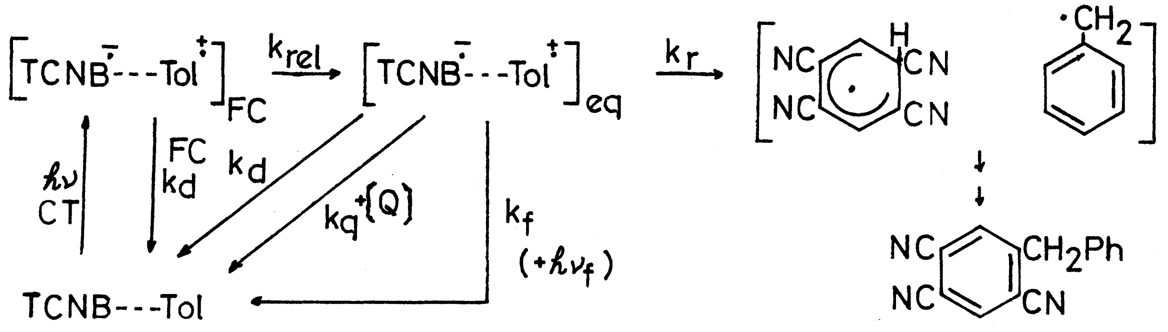
THE ROLE OF THE CT FLUORESCENT STATE IN THE PHOTOSUBSTITUTION OF 1,2,4,5-TETRACYANOBENZENE-TOLUENE COMPLEXES

Mamoru OHASHI and Noboru NAKAYAMA
Department of Materials Science, The University
of Electro-Communications, Chofu, Tokyo 182

The Stern-Volmer treatments of the photosubstitution of charge-transfer complexes of TCNB-toluene systems using trifluoroacetic acid as a quencher indicated that the reaction proceeds via the CT fluorescent state and that the rate constants of quenching and reaction were estimated to be 10^9 and $2\mathrm{x}10^5$ $M^{-1}s^{-1}$ respectively.

In previous papers we described a novel substitution of several charge-transfer complexes of 1,2,4,5-tetracyanobenzene(TCNB)-substituted toluenes on irradiation within their charge-transfer absorption bands and proposed a mechanism consisting of electron-transfer followed by proton-transfer, radical coupling and then elimination.[1)] Recently Mataga et al. clarified that on charge-transfer excitation of the TCNB-toluene complex in polar solvents, ionic dissociation proceeds not through the CT fluorescent state but from the excited Franck-Condon state.[2)] A question then arose whether the substitution proceeds via the fluorescent state or directly from the excited Franck-Condon state.

In order to clarify this point the Stern-Volmer treatments by the use of trifluoroacetic acid as a quencher of both of the CT fluorescence and the reaction were carried out. If the reaction proceeds via the CT fluorescent state, the processes shown in the scheme must be taken into account, whereby the Stern-Volmer expressions (1) and (2) are derived, and the $k_q\tau$ value in Eq.(2) caluculated from the fluorescence quenching must be the same as that from the reaction quenching.



$$1/\Phi_r=[k_{rel}/(k_d^{FC} + k_{rel})][1 + (k_f + k_d)/k_r + k_q[Q]/k_r] \qquad (1)$$

$$\Phi_f^0/\Phi_f=\Phi_r^0/\Phi_r=1 + k_q\tau[Q], \quad \tau=1/(k_f + k_d + k_r) \qquad (2)$$

The CT fluorescence(500 nm, excitation at 366 nm) quenching was measured in a toluene solution of TCNB(10^{-3}M) in the presence of various amounts of trifluoroacetic acid(0.001-0.01 M) as a quencher. Then a $k_q\tau$ value of 130 M^{-1} was obtained from the resulting Stern-Volmer plots.

For the study of the reaction quenching, a solution of TCNB in toluene(2.2×10^{-3}M) was irradiated externally with a medium pressure mercury arc for 4 h in the presence of various amounts of trifluoroacetic acid(0.001-0.01 M) using a "merry-go-round" apparatus(conversion; less than 10%). Quantitative analyses of the product were carried out by means of high pressure liquid chromatography with p-aminobenzophenone as an internal standard. From the resulting Stern-Volmer plots a $k_q\tau$ value of 110 M^{-1}, very close to that from the fluorescence quenching, was obtained. The proximity of the both $k_q\tau$ values obtained by the two independent methods indicates that the reaction proceeds via the fluorescent state. The τ value of the CT fluorescent state was already reported by Nagakura et al.[3)] and Mataga et al.[4)] to be 120-100 ns. By substituting those values in Eq.(2) we obtained the approximate k_q value to be 1×10^9 $M^{-1}s^{-1}$.

The quantum yield of the reaction was estimated by the use of a high pressure mercury arc(500 W) with a filter system of Corning glass 7-39 and 0-52(transparent only between 360 and 380 nm). A value, $\Phi_r^0=0.024$, was obtained by ferroxalate actinometry. If $k_{rel} \gg k_d^{FC}$ is assumed as is the case of an excited singlet state in solution, then we obtain an approximate k_r value of 2×10^5 $M^{-1}s^{-1}$.

When acetonitrile was used as the solvent(toluene:acetonitrile=1:2), the CT fluorescence was completely quenched, whereas the reaction proceeded even faster (about tenfold) than in the TCNB-toluene system. In this case, as shown by Mataga et al. in the flash photolytic investigations,[2)] ionic dissociation proceeds obviously not through the CT fluorescent state but directly from the excited Franck-Condon state. Consequently the essential step of the reaction does not exist in the CT fluorescent state but in the ionic dissociation leading to a solvated ion pair.

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