

AMINE ASSISTED PHOTODECHLORINATION OF 4-CHLOROBIPHENYL.

A COMMENT ON THE MECHANISM

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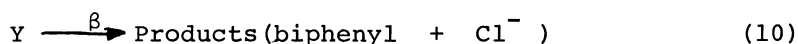
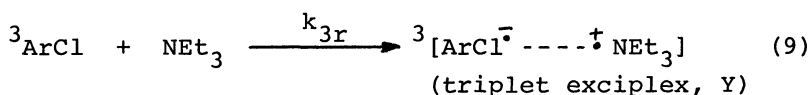
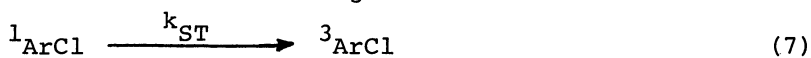
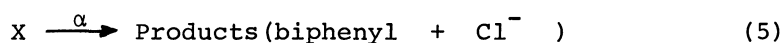
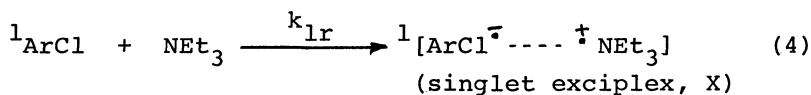
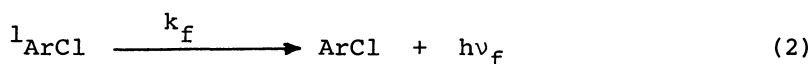
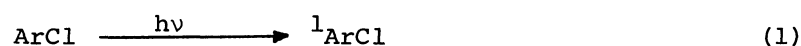
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The Stern-Volmer plot of the aliphatic amine assisted photodechlorination of 4-chlorobiphenyl was analyzed on the basis of the generalized Stern-Volmer expression for bimolecular photochemical reactions which can occur from both the excited singlet and triplet states of a reactant. This kinetic treatment showed that the reaction from the singlet state is more efficient than that from the triplet.

We reported about ten years ago that the photoreduction of 4-chlorobiphenyl by aliphatic amines proceeds from a singlet exciplex.¹⁾ As the chlorinated biphenyls are environmental pollutants, photodecompositions of those compounds have been extensively examined.²⁻⁸⁾ Bunce recently reported that the dechlorination of 4-chlorobiphenyl (ArCl) by amine assisted photolysis takes place mainly from the triplet state in contrast with our previous results.⁷⁾ We obtained the Stern-Volmer constants (k_{qT}) of 23 M^{-1} by the fluorescence quenching and of 20 M^{-1} from the plot of ϕ^{-1} vs $[\text{NEt}_3]^{-1}$, leading to a conclusion that the reaction occurs from the singlet excited state of ArCl accompanied by electron-transfer from NEt_3 . On the other hand, Bunce obtained the Stern-Volmer constants of 19.6 M^{-1} by fluorescence quenching but of 86 M^{-1} from the plot of ϕ^{-1} vs $[\text{NEt}_3]^{-1}$. He concluded, from this result, that since two different constants mean two different reactive states, the dechlorination must occur mainly from the triplet state. The contradictory conclusions by the two groups must be derived from the sets of data obtained in different experimental conditions: Bunce used GC to analyze the product, biphenyl, and discussed the mechanism based on the linear part of Stern-Volmer plot of ϕ^{-1} vs $[\text{NEt}_3]^{-1}$ where amine concentrations were below 0.05 M. We carried out, on the other hand, titration of the produced chloride anion by the Volhard method and the

mechanism was discussed based on the Stern-Volmer plot of higher concentrations of the amine (0.05-0.2 M) and ArCl (0.041 M).⁹⁾

In order to solve this discrepancy we have re-evaluated the experimental data from the both groups on the basis of the generalized Stern-Volmer expression established by Dalton and Snyder for bimolecular photochemical reactions which can occur from both the excited singlet and triplet states of a reactant.¹⁰⁾ On the analogy of the Dalton and Snyder treatment we constructed a series of reactions shown in the Scheme and derived the Stern-Volmer equation (12) for the triethylamine assisted photodechlorination which proceeds from both the singlet and triplet states of ArCl.



$$\phi^{-1} = \frac{(k_{1r}\tau_s + [\text{NEt}_3]^{-1})(k_{3r}\tau_t + [\text{NEt}_3]^{-1})}{\alpha k_{1r}\tau_s(k_{3r}\tau_t + [\text{NEt}_3]^{-1}) + \beta \phi_{ST} k_{3r}\tau_t [\text{NEt}_3]^{-1}} \quad (12)$$

$$\text{Where } \tau_s = (k_f + k_{1d} + k_{ST})^{-1}, \quad \tau_t = k_{3d}^{-1} \quad (13)$$

If only the singlet reaction takes place ($k_{3r}=0$), then

$$\phi^{-1} = \frac{1}{\alpha} \left(1 + \frac{1}{k_{1r}\tau_s [\text{NEt}_3]} \right) \quad (15)$$

While only the triplet reaction proceeds ($k_{1r}=0$), then

$$\phi^{-1} = \frac{1}{\beta\phi_{ST}} \left(1 + \frac{1}{k_{3r}\tau_t[\text{NEt}_3]} \right) \quad (16)$$

The equation (12) indicates that the ϕ^{-1} vs $[\text{NEt}_3]^{-1}$ plot will be linear with a positive slope equal to eq. (17) as $[\text{NEt}_3]$ approaches to zero, while the initial slope of the plot is equal to eq. (18) at $[\text{NEt}_3]^{-1} = 0$.

$$(k_{1r}\tau_s\alpha + k_{3r}\tau_t\phi_{ST}\beta)^{-1} \quad (\text{the final slope}) \quad (17)$$

$$\frac{1}{\alpha k_{1r}\tau_s} \left(1 - \frac{\beta\phi_{ST}}{\alpha} \right) \quad (\text{the initial slope}) \quad (18)$$

It is clear from eq. (18) that the initial slope will be negative when $\beta\phi_{ST} > \alpha$ (i.e., the triplet reaction is predominant), while it is positive when $\beta\phi_{ST} < \alpha$ (i.e., the singlet reaction is predominant). Our result shown in Fig. 1 as well as the plot of ϕ^{-1} against $[\text{NEt}_3]^{-1}$ in the Bunce paper⁷⁾ clearly indicate the positive initial slope, which safely leads to the conclusion that the reaction through the singlet exciplex is more efficient than that of the triplet. If the major reaction was from the triplet state as Bunce suggested, the ϕ^{-1} vs $[\text{NEt}_3]^{-1}$ plot would go through a minimum as Dalton and Snyder demonstrated in the typical examples.¹⁰⁾ Bunce argued the mechanism on the basis of the linear part of the Stern-Volmer plot where the slope probably corresponds to eq. (17), while in our case the slope of the plot is better expressed by eq. (18). This may account for the discrepancy of the two groups' conclusions. In the previous paper we applied eq. (15) to the

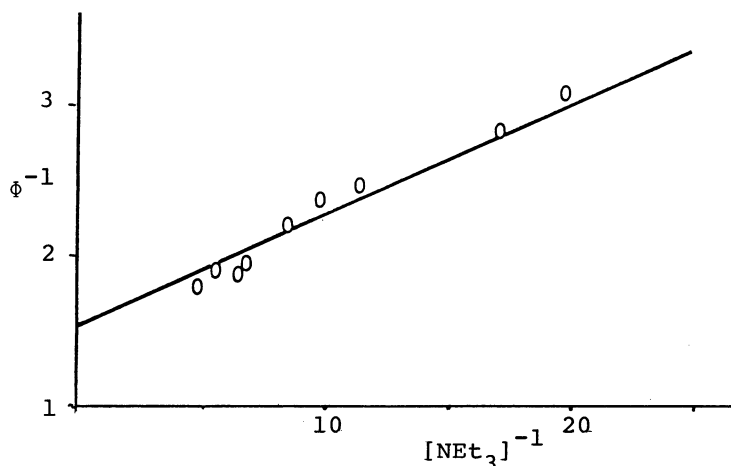


Figure 1. Plot of ϕ^{-1} vs $[\text{NEt}_3]^{-1}$ for the photolysis of ArCl with NEt_3 in acetonitrile. $[\text{ArCl}] = 0.041$ M. The product yields were titrimetrically determined by the Volhard method. Trioxalatoferate(III) actinometry was used.¹¹⁾

analysis of the Stern-Volmer plot. This, however, is probably oversimplified and the participation of the triplet state in the formation of the products as well should be taken into consideration. Nevertheless, we are convinced again that the major process of dechlorination is electron-transfer from the amine to the excited singlet state of the chlorobiphenyl at higher amine concentrations, while the triplet state, as Bunce reported, must play an important role at lower amine concentrations.¹²⁾

References

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- 9) Different analytical methods between the two groups must not be important for discussion on the multiplicity of the reactive excited state as Bunce has already discussed in his paper on various side processes.⁷⁾
- 10) J. C. Dalton, J. J. Snyder, Mol. Photochem., 6, 291(1974).
- 11) In acetonitrile, NET_3 has $\epsilon_{254}=61$, while ArCl 21,000.⁷⁾ Since the light absorption by amine gives little effect on the amount of quanta absorbed by ArCl at the concentrations of NET_3 (0.2-0.05 M) and ArCl (0.041 M), the quantum yields are not corrected.
- 12) To obtain the relationship $\phi_s > \phi_t$, the amine concentrations must satisfy the following relation of eq. (19) (ϕ_s and ϕ_t mean the quantum yields of the singlet and triplet reactions, respectively);

$$[\text{NET}_3] > (\beta\phi_{\text{ST}}k_{3r}\tau_t - \alpha k_{1r}\tau_s)(\alpha k_{1r}k_{3r}\tau_s\tau_t)^{-1} \quad (19)$$

Assuming that $k_{1r}=k_{3r}$ (the diffusion controlled rate constant), $k_{1r}\tau_s=20$ (from fluorescence quenching), $\alpha>0.7$ (from the intercept in Fig. 1 and eq. 12), $\beta\phi_{\text{ST}}<0.3$ (from eq. 18 and the slope in Fig. 1), and $\tau_t \gg \tau_s$, substitution of these values for eq. (19) will roughly tell the amine concentration as $[\text{NET}_3] > 0.02$ M. Bunce suggested that eq. (16) is applicable to the plot of ϕ^{-1} vs $[\text{NET}_3]^{-1}$ provided that $k_{\text{ST}} > k_{1r}[\text{NET}_3]$. However, this condition does not relate $[\text{NET}_3]$ to the predominant reaction process.

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