

QUENCHING OF THE TRIPLET STATE OF A DYE BY AROMATIC AMINES

R. CHAPELON, G. PERICHET and B. POUYET

Laboratoire de Photochimie, Université Claude Bernard Lyon I, 69621 Villeurbanne (France)

(Received April 16, 1976)

Summary

The quenching of the triplet state of a dye (erythrosin) has been studied in presence of anilines. A good correlation between the inhibition constant and the ionization energy of the quencher has been shown. An interpretation of these results has been indicated and a charge-transfer complex intermediate is propounded.

Introduction

Triplet states of many dyes are quenched by aromatic amines. For example, xanthenic dye solutions, when they are irradiated by visible light ($\lambda > 510$ nm) show dyes in the triplet state; by addition of aromatic amines the yield of the triplet state decreases [1, 2], by flash photolysis techniques. Chrysochoos and Grossweiner [3] have shown that there are two types of reactions:



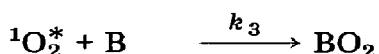
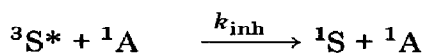
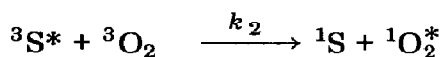
S = dye sensitizer, A = aniline.

The rate constants of these two reactions in the case of aniline and eosin solutions were determined and it was found that $k_{inh I} > 15 k_{inh II}$. The following results and discussion are restricted to reaction (I).

According to Chrysochoos and Huang [4], a complex between aniline and the ground state of eosin is involved. An attempt has been made to find a complex between aniline and dye in its excited triplet state.

Experimental

Photochemical oxidations of a substrate B (1,4-dimethoxy-9, 10-dipyridylanthracene) sensitized with dye (erythrosin) and with several aromatic amines were carried out in pyridine and from the results the following mechanism is suggested:



In a previous paper [5] it was shown that k_{inh} is obtained by drawing the curve $1/\text{BO}_2 = f(1/\text{B})$, if $1/X$ is ordinate in the absence of inhibitor and if $1/Y$ is ordinate in the presence of inhibitor:

$$\frac{k_1 + k_2({}^3\text{O}_2) + k_{\text{inh}}(\text{A})}{k_1 + k_2({}^3\text{O}_2)} = \frac{X}{Y}$$

According to Gollnick [1] $k_1 \approx 6 \times 10^3 \text{ s}^{-1}$, and in addition Foote [6] found that $k_2 = 1.2 \times 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$. On the other hand $({}^3\text{O}_2) = 5 \times 10^{-3} M$ in pyridine [7], where k_1 can be neglected compared to $k_2({}^3\text{O}_2)$, $10^3 \times k_1 < k_2({}^3\text{O}_2)$. The following inhibition constants were obtained with different anilines:

Aromatic amines	$k_{\text{inh}} \text{ (l mol}^{-1} \text{ s}^{-1}\text{)}$
Aniline	2×10^9
<i>o</i> -Toluidine	3×10^9
<i>N</i> -Methylaniline	8.5×10^9
<i>N</i> -Ethylaniline	11×10^9
<i>N,N'</i> -Dimethylaniline	30×10^9

In Fig. 1, the rate constants are plotted against the ionization potential of the anilines [8]. The good correlation between $\log k_{\text{inh}}$ and ionization energy is a temptation to interpret the quenching as a charge-transfer interaction between ${}^3\text{S}^*$ and ${}^1\text{A}$.

Discussion

Ogryzlo and Tang [9] reported similar experimental results for the reaction between singlet oxygen (${}^1\Delta_g$) and the aliphatic amines. In the present

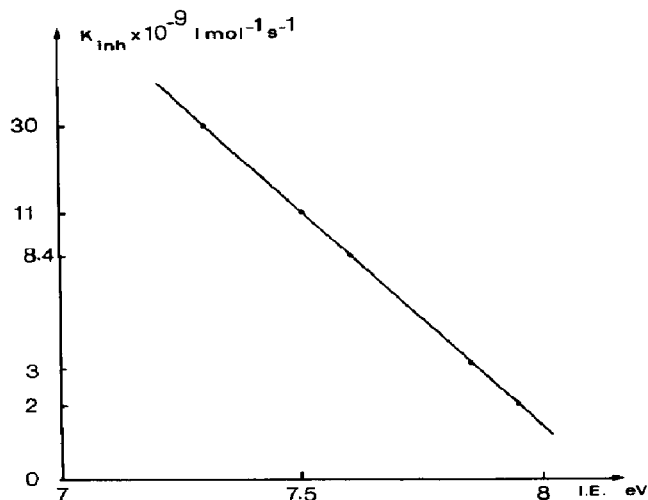
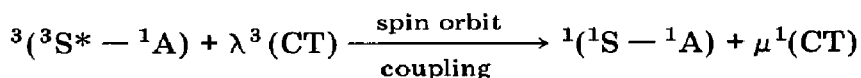


Fig. 1. Plot of rate constant vs. ionization potential of the anilines.

case it is suggested that the electronic state corresponding to a zero level of vibration of the complex formed between the aromatic amine and the sensitizer in the triplet state is the product of the non-perturbed state of the amine (1A) and the sensitizer [(^1S) and ($^3S^*$)]. The $^3(^3S^* - ^1A) \rightarrow ^1(^1S - ^1A)$ transition is theoretically forbidden by change in the multiplicity of the complex, because it is necessary to have interaction between a pair of molecules and the charge-transfer states. The initial state of the complex is (3CT) and the final state is (1CT). A low spin-orbit coupling gives the transition possible:



where λ and μ are a measure of the extent to which complexes possess charge-transfer character.

Conclusion

It has been shown that a relation exists between the inhibition constant by aromatic amines and the ionization potential of the amines. This may be interpreted by the existence of a charge-transfer complex between the dye in the excited triplet state and the aromatic amines in the ground state.

References

- 1 G. O. Schenck and K. Gollnick, *J. Chim. Phys.*, 55 (1958) 705.
- 2 K. Gollnick, *Adv. Photochem.*, 6 (1968) 1.
- 3 J. Chrysochoos and L. I. Grossweiner, *Photochem. Photobiol.*, 4 (1968) 923.

- 4 J. Chrysochoos and C. S. Huang, *Spectros. Lett.*, 1 (1968) 367.
- 5 R. Chapelon, G. Périchet and B. Pouyet, *Mol. Photochem.*, 5 (1) (1973) 77.
- 6 C. S. Foote, *Science*, 162 (1968) 913.
- 7 Gmelin, *Handbuch der Anorganischen Chemie*, 8th Edn, Verlag Chemie, Berlin, 1958.
- 8 G. Briegleb and J. Czekalla, *Z. Elektrochem.*, 63 (1959) 6.
- 9 E. A. Ogryzlo and C. W. Tang, *J. Am. Chem. Soc.*, 92 (1970) 5034.