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The Increase of the Quantum Yield of the Photoreduction of Dyes (a Catalytic Effect)

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With 3 figures

While studying the photoreduction of some dyes (D) by reducing agents (R) we observed that upon addition of a third substance (C), the quantum yield of the photoreduction increases considerably, whereas it is very small when the dye is photoreduced by C alone[1]. Some systems which exhibit such behaviour are summarized in Table 1.

The system thionine (D), allylthiourea (R), and azulene (C) was investigated in detail using both flash photolysis and continuous illumination. On photolysis, thionine is converted into its photo-reduced

Table 1. *Some systems which exhibit the catalytic effect*

D (Dye)	R (Reducing agent)	C (Catalyst)
Thionine	ATU or ascorbic acid	Azulene or thiobenzophenone
Toluidine blue	ATU (allylthiourea)	Azulene or 9.10-dimethyl-anthracene
Cresyl blue	ATU	Azulene
Lumiflavin	Mandelic acid	Fluoranthen or triphenylene or phenanthrene
Safranine	ATU	9.10-dimethylanthracene or dimethylaniline

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[1] Paper presented at the Sixth International Conference on Photochemistry, September 6—9, 1971, at Bordeaux, France; H. E. A. Kramer, M. Hafner, U. Steiner, and S. Schreiner, Ber. Bunsenges. physik. Chem. **76** (1972) 1108.

form, leucothionine TH_2. (The photoreduction of thionine by allylthiourea has been studied extensively[2,3].) In the concentration range studied there is no interaction of azulene with thionine in its ground state (no change of the absorption spectrum detected) nor in its first excited singlet state (no quenching of the fluorescence observed).

Continuous illumination experiments

Fig. 1 shows the quantum yield of the thionine photoreduction in dependence on the azulene concentration at four different ATU concentrations. The quantum yield increases with the azulene concentra-

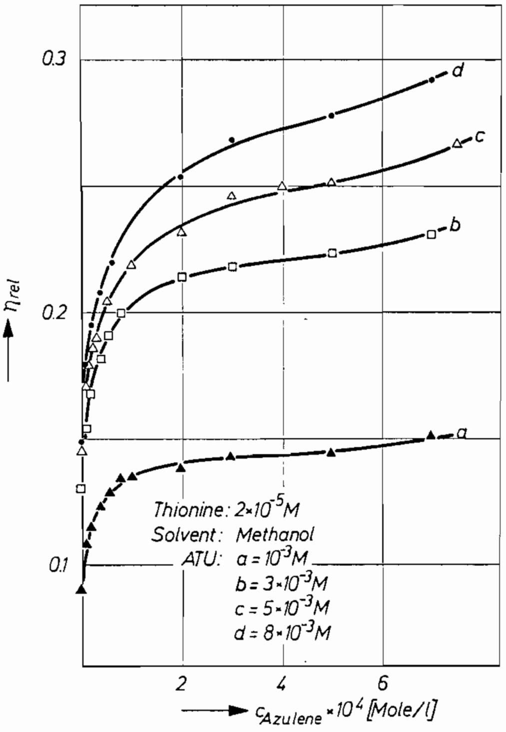

Fig. 1. Relative quantum yield of the thionine photoreduction in dependence on the azulene concentration. Thionine: 2×10^{-5} M; solvent methanol; oxygen free. The ATU concentration is for curve $a = 10^{-3}$ M; curve $b = 3\times10^{-3}$ M curve $c = 5\times10^{-3}$ M; $\lambda_{excit} = 578$ nm

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[2] Hermann Fischer, Z. physik. Chem. Neue Folge **43** (1964) 177. — H. Fischer, H. E. A. Kramer and A. Maute, Z. physik. Chem. Neue Folge **69** (1970) 113.

[3] H. E. A. Kramer and A. Maute, Photochem. Photobiol. **15** (1972) 15, 25. — M. Zügel, Th. Förster and H. E. A. Kramer, ibid. **15**, 33 (1972).

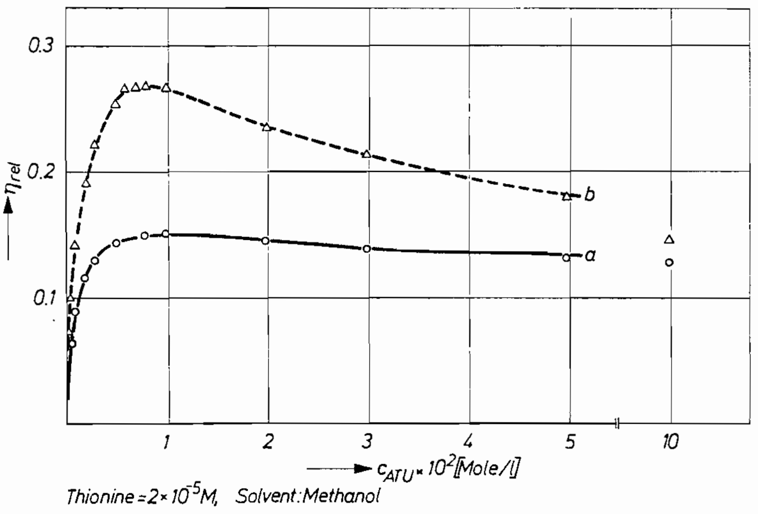

Fig. 2. Relative quantum yield of the thionine photoreduction in dependence on the ATU concentration; curve *a* without azulene; curve *b* with azulene 3×10^{-4} M. Thionine: 2×10^{-5} M; solvent methanol; oxygen free; $\lambda_{\mathrm{excit}} = 578$ nm

tion. It is also found to vary with the ATU concentration; this dependence is shown more explicitly in Fig. 2.

For curve *b* the azulene concentration is 3×10^{-4} M whereas for curve *a* azulene is absent. The fact that curve *b* goes through a maximum (at [ATU] $\sim 10^{-2}$ M) and decreases again at very high ATU concentrations excludes the possibility that the effect is due to a reaction between the intermediately formed semiquinone of the dye and azulene since the concentration of the semiquinone rises with increasing ATU concentration. Thus the thionine triplet is the only remaining possible reaction partner of azulene.

Flash photolysis experiments

In this study, the mechanism of the catalytic effect was investigated by flash photolysis. It could be shown that azulene undergoes a very fast reaction ($k_K = 1.5 \times 10^9$ M^{-1} sec^{-1}) with the basic thionine triplet $^3TH^+$; it should be emphasized that this reaction is about 300 times faster than the corresponding reaction between ATU and the basic thionine triplet k_7 (see Fig. 3). In both systems (thionine/AZ and thionine/ATU) the same intermediate spectrum (semithionine, TH·) is obtained. From this it can be concluded that azulene and ATU react in the same way with the thionine triplet, that is, by electron

Reaction Scheme

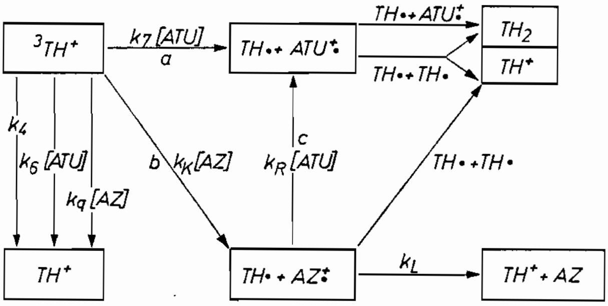

Fig. 3. General reaction scheme. In the upper half the mechanism of the thionine photoreduction by ATU which is already known from earlier investigations[2] is reproduced in as much detail as is necessary here. The lower half shows the modification of the mechanism in the presence of azulene. $^3TH^+$ denotes the basic form of the thionine triplet, $TH\cdot$ the basic form of the semithionine radical, TH_2 leucothionine, ATU/ATU$^{+\cdot}$ allylthiourea and corresponding radical, AZ/AZ$^{+\cdot}$ azulene and corresponding radical

transfer to the thionine triplet. (In both cases it was possible to demonstrate definitely that electron transfer and protonation are consecutive reactions and therefore the transfer of an H-atom does not take place). The only difference is the *absolute value* of the rate constants and the *yield* of the electron transfer process. With azulene the yield amounts to 1, while only 0.5 is found for ATU (reaction path *a*, Fig. 3), since in the case of ATU the reduction competes with a bimolecular radiationless deactivation of thionine triplet.

This offers an explanation of the catalytic effect of azulene: Due to its high reactivity, only azulene is able to react with thionine triplet in methanolic solution containing both azulene and ATU ($[\mathrm{ATU}] < 100 \times [\mathrm{AZ}]$). Therefore at moderate ATU concentration it is only azulene that determines the yield of the reduction process (reaction path *b*, Fig. 3). The reaction products are semithionine TH· ($\lambda_{\mathrm{obs}} = 400$ nm) and a positive azulene radical AZ$^{+}\cdot$ (which, however, has not yet been identified spectroscopically). When ATU is absent, most of these radicals revert to thionine and azulene (k_L, Fig. 3). In the presence of ATU the azulene radicals AZ$^{+}\cdot$ are reduced by ATU with concomitant formation of a corresponding amount of ATU$^{+}\cdot$ radicals (reaction path *c*, Fig. 3). This was shown by an indirect method which involved monitoring the regeneration of *thionine* from semithionine TH· ($\lambda_{\mathrm{obs}} = 590$ nm).

Both the rate and yield of the thionine regeneration from the radical pair $TH\cdot/AZ^{+}\cdot$ are higher than from the radical pair $TH\cdot/ATU^{+}\cdot$. With increasing ATU concentration, the characteristic thionine regeneration curve belonging to the radical pair $TH\cdot/AZ^{+}\cdot$ is converted into that of the radical pair $TH\cdot/ATU^{+}\cdot$. This conversion takes place at such a low ATU concentration that the primary reaction still takes place between thionine triplet and *azulene* (reaction path *b*, Fig. 3). At very high ATU concentration ($\sim 10^{-1}$ M), however, the process involving azulene cannot effectively compete for the thionine triplet and, therefore, the effect disappears, as shown in Fig. 2 (reaction path *a* in Fig. 3).

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