

COMPARATIVE KINETIC STUDY OF THE REACTIVITY OF MOLECULES IN THEIR EXCITED SINGLET AND TRIPLET STATES IN THE CASES OF AN ELECTRON ABSTRACTION AND AN INTRAMOLECULAR PHOTOCYCLIZATION REACTION.

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Summary- Two photochemical reactions are considered, illustrating quantitatively the differences in rate constants for chemical and physical deactivating processes from excited singlet and triplet states, in each case, for the identical photochemical reaction. Firstly we have determined the rate constants of electron abstraction, k_e , and quenching, k_q , of oxonine singlet and triplet states by EDTA in aqueous solution. The rate k_{Se} for the singlet state, is found to be about ten times larger than k_{Te} for the triplet state, whereas k_{SG} is 10^3 to 10^4 faster than k_{TG} . Secondly, in the case of the intramolecular photocyclization of 1-(orthodiphenyl)-1-phenyl ethylene in cyclohexane, a common intermediate X is found for the singlet and triplet pathways. The rate constant k_{SX} is found to be 150 times faster than an apparent rate k_{TX} whereas the non radiative (nr) rate constant k_{Snr} is about 10^3 times faster than k_{Tr} .

INTRODUCTION

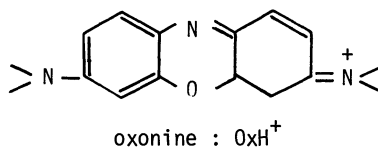
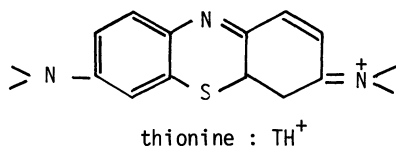
There has been intense interest in recent years in getting clear evidence for different pathways in photochemical processes involving the first excited singlet and lowest triplet states of molecules. This is a difficult matter to approach since in addition to the multiplicity effect one must also take into account differences in state lifetime, state energy level, geometrical configuration ... etc. A valid way to deal with this problem is to measure specific rate constants for singlet and triplet reactions.

During the past years we have looked in detail into two reactions of widely different interest : an electron abstraction reaction by a dye in aqueous solution and a photocyclization reaction of a vinyl-biphenyl derivative, giving a fairly complete reaction scheme, with most rate constants determined. Both reactions occurring via the singlet & triplet pathways, they will illustrate the possibilities and limits of chemical kinetic methods to the contribution of a better knowledge of photochemical reactivity.

1 - COMPARATIVE STUDY OF ELECTRON ABSTRACTION AND DEACTIVATION QUENCHING OF EXCITED AND TRIPLET STATES OF OXONINE.

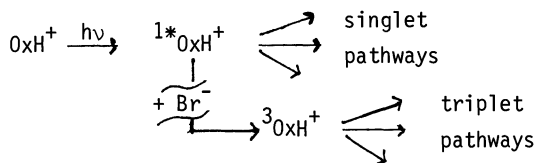
After considering a number of possible photoredox couples we chose the oxonine-EDTA (ethylene diaminetetraacetic acid) system in aqueous solution (1) (2) (3) for the following reasons :

- oxonine is a dye very similar to thionine which has been extensively studied :



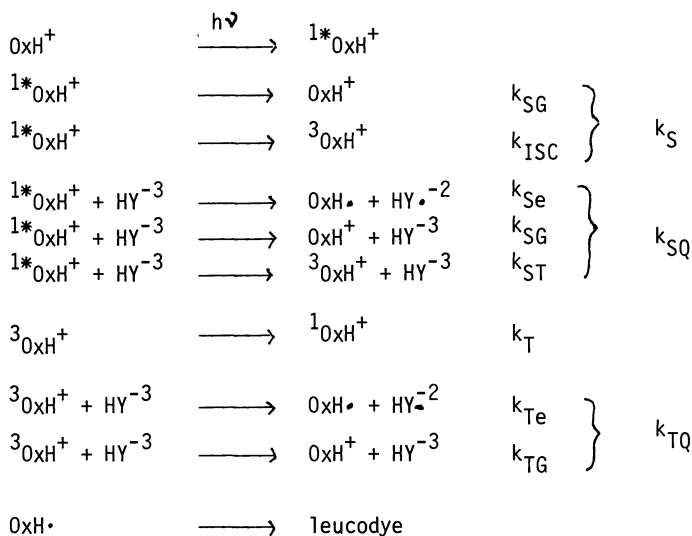
- oxonine is highly fluorescent and its rate of intersystem crossing under normal condition being very small, the excited singlet state can easily be studied,

- adding bromide ions to the aqueous solution "catalyzes" the triplet yield (4) of oxonine to the point where the triplet pathways becomes the important deactivating process of the excited dye



- the ionic species of EDTA, HY^{-3} most abundant in the pH range 7 to 9 is a good one-electron donor to excited dyes and the reverse reaction is apparently slower than the deprotonation of the amino radicals that leads irreversibly to the oxidation product of EDTA. Thus the quantum yield of formation of the semireduced dye reflects precisely the overall quantum yield of photoreduction.

The mechanism of the photobleaching reaction of oxonine (OxH^+) by HY^{-3} has been established to be the following (5) :



We want to compare on the one hand, k_{Se} and k_{Te} which measure the rates of electron abstraction by oxonine in its excited singlet and triplet state respectively and on the other hand k_{SG} and k_{TG} , the quenching processes that bring back the excited states to the ground state.

These values can only be obtained if the whole kinetic scheme is unravelled. Since the details of this study has been published elsewhere (5) only the main features and the results here will be given.

Based on the kinetic scheme proposed above the quantum yield of semireduced $\text{OxH}\cdot$ radical is given by the following expression :

$$\phi = \frac{k_{\text{Se}} [\text{HY}^{-3}]}{k_{\text{S}} + k_{\text{SG}} [\text{HY}^{-3}]} + \frac{k_{\text{ISC}} + k_{\text{ST}} [\text{HY}^{-3}]}{k_{\text{S}} + k_{\text{SQ}} [\text{HY}^{-3}]} \times \frac{k_{\text{Te}} [\text{HY}^{-3}]}{k_{\text{T}} + k_{\text{TQ}} [\text{HY}^{-3}]}$$

Since we know that the semireduced dye reacts to give the leuco compound with a constant yield in the case of thionine, we assume it also holds for oxonine and we can write that the quantum yield φ of leucoproduction measured under continuous irradiation is related to Φ by $\varphi = \rho \Phi$

The information needed to get the rate constant k_{Se} , k_{Te} , k_{SG} and k_{TG} can be obtained from the following experiments :

- 1°) fluorescence lifetime measurements,
- 2°) fluorescence quenching by EDTA,
- 3°) triplet lifetime measurement by flash photolysis,
- 4°) quantum yield measurements of bleaching as a function of EDTA concentration.

k_S - the fluorescence lifetime of oxonine in water being 2.6 ns one deduces that $k_S = 3.85 \times 10^8 \text{ s}^{-1}$.

k_T - adding sodium bromide to the solution to enhance the intersystem crossing the decay time of triplet triplet absorption observed at 780 nm by flash photolysis yields the value :

$$k_T = 8.3 \times 10^{13} \text{ s}^{-1}$$

k_{SQ} - adding increasing amounts of EDTA to the oxonine solution quenches the fluorescence of the dye and allows to determine the following relation $k_{SQ} = 16 k_S$ and therefore :

$$k_{SQ} = 6.16 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

k_{ISC} , k_{ST} - by laser flash photolysis it is possible to estimate these two constants that govern the triplet build up under normal conditions :

$$k_{ISC} \approx 10^6 \text{ s}^{-1} \quad k_{ST} \approx 1.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$

φ - quantum yield data are plotted in figure 1 as a function of HY^{-3} concentration. For large values of HY^{-3} , the product $k_{TQ} \text{HY}^{-3}$ is larger than k_1 and the quantum yield expression becomes more simply :

$$\varphi = \rho \Phi = \rho \frac{k_{ISC} \eta_T}{k_S + k_{SQ} [\text{HY}^{-3}]} + \rho \frac{(k_{Se} + k_{ST} \eta_T) [\text{HY}^{-3}]}{k_S + k_{SQ} [\text{HY}^{-3}]}$$

with $\eta_T = k_{Te}/k_{TQ}$ which measures the chemical efficiency of electron abstraction by the triplet state molecules.

Linear extrapolation of the curve on figure 1 to $[\text{HY}^{-3}] = 0$ yields :

$$\rho \eta_T k_{ISC} = 2 \times 10^{-3} k_S \quad \text{from which} \quad \rho \eta_T \text{ is found to be } 0.7 + 01$$

From this value, and knowing k_{SQ} the ratio $\rho \eta_T k_{ISC} / (k_S + k_{SQ} [\text{HY}^{-3}])$ can be calculated for different values of the EDTA concentration and plotted as a function of $[\text{HY}^{-3}]$ (fig. 1)

The difference between the experimental data φ and the calculated ratio, yield the values of the last term of $\rho \Phi$ which can be written as

$$\frac{1}{\rho \Delta \Phi} = \frac{k_{SQ}}{k_{Se} + \eta_T k_{ST}} + \frac{k_S}{(k_{Se} + \eta_T k_{ST}) [\text{HY}^{-3}]}$$

plotting $\frac{1}{\Delta \Phi} = f\left(\frac{1}{\text{HY}^{-3}}\right)$ a good straight line is obtained (figure 2) whose slope yield :

$$(k_{Se} + \eta_T k_{ST}) = 0.294 k_S$$

Assuming a value of $\rho = 0.8^*$ all the constants of the reaction scheme can be determined and in particular :

$$k_{Se} = 1.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{SG} \approx 6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{Te} \approx 1.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{TG} \approx 3 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$

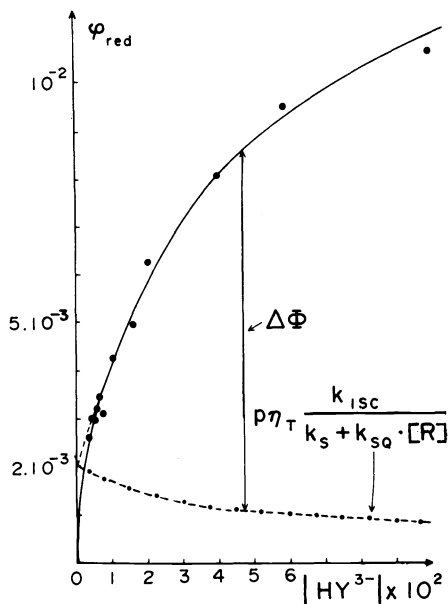


Figure 1 : Variations, as a function of the HY^{-3} concentration, of the measured quantum yield of photoreduction of oxonine (● — ●) and of the calculated value of the ratio (See text).

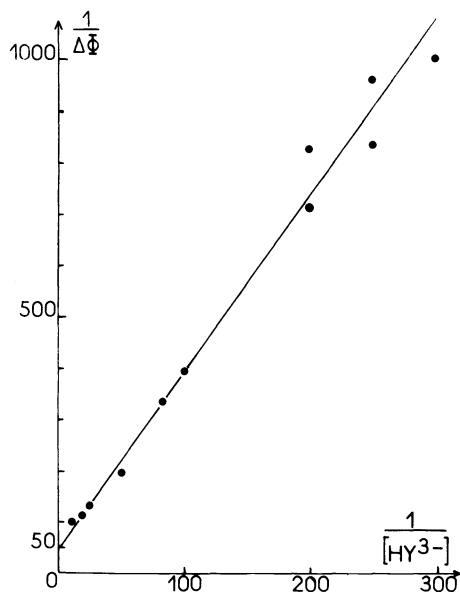


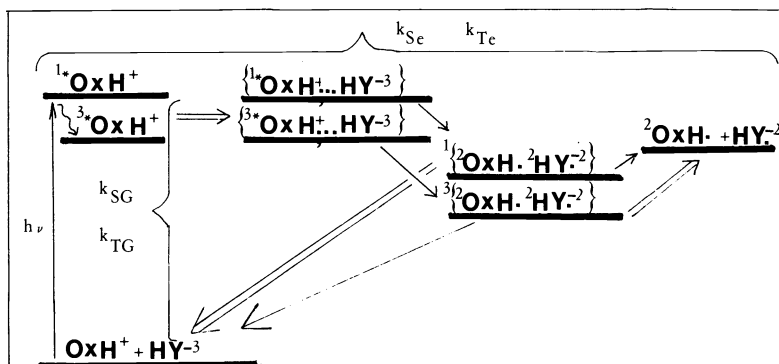
Figure 2 : Variations of the reciprocal contribution of the excited singlet state to the total photoreduction quantum yield, as a function of the reciprocal concentration of HY^{-3} .

Thus in the system we have studied large differences in rate constants are found.

On the one hand, the rate constant for electron abstraction k_e is about ten times larger for the excited singlet state than for the triplet state. This difference can be in first approximation, related to the difference in energy of the two states, which also affects the redox potential of the excited states and therefore the free enthalpy change for the electron transfer in the encounter complex between the excited state and the reducing agent (4). The rate constant for electron transfer is then determined by this free enthalpy change as shown by Rehm and Weller (6) for the excited singlet state of a series of aromatic hydrocarbons and azocompounds.

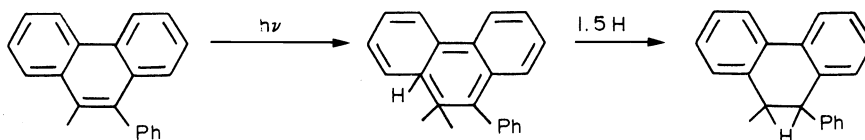
On the other hand, the rate constant for deactivation to the ground state k_g is much greater (by a factor 10^3 to 10^4) for the excited singlet than for the triplet state, because as always, intersystem crossing takes time. The ion pair has a singlet or a triplet memory. Using Weller's notation one can draw the following diagramme depicting the important steps of the mechanism in which appear the encounter complex (${}^1\text{OxH}^+ \cdot \text{HY}^{-3}$), the ion pair (${}^2\text{OxH} \cdot {}^2\text{HY}^{-2}$) and the separated ions, ${}^2\text{OxH} \cdot$ and ${}^2\text{HY}^{-2}$.

*Changes of the values of ρ and η_T between 0.6 and 1.0 do not modify the results greatly.



II - COMPARATIVE REACTIVITY OF SINGLET AND TRIPLET STATE FOR A PHOTOCYCLIZATION REACTION -

Photocyclization reactions may also occur via a triplet and a singlet pathway. We have found that 1-(orthodiphenyl)-1-phenyl ethylene (DPE) lends itself very conveniently for such a study (9). The molecule possesses an hexatriene system which has two consecutive double bonds part of benzene rings. In contrast to the isomeric stilbenes the primary product of the photocyclization leads, in the absence of oxidant, to a stable species by a thermally allowed suprafacial 1.5 hydrogen shift.



A - Laser flash spectrophotometry of DPE

Two distinct transient absorptions are observed when a cyclohexane solution of DPE (10 M) is flashed with the quadruple 264 nm radiation of a neodymium laser delivering 3 ns pulses of light.

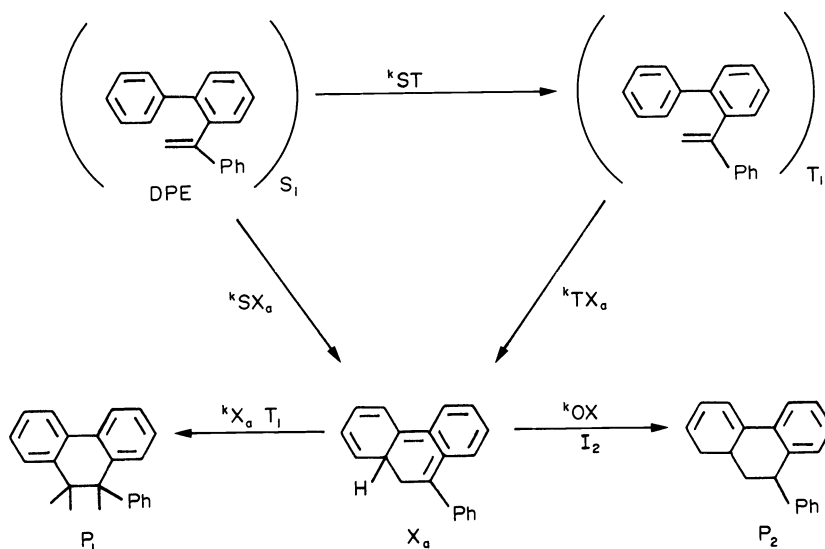
a - One having a short decay time in the microsecond range, which has a maximum at 370 nm. It disappears by a first order process with a rate constant of $5.75 \times 10^5 \text{ s}^{-1}$ in degassed solutions and is quenched by oxygen with a rate constant of $1.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This transient is formed during the laser pulse duration ($\sim 3\text{ns}$) whatever be the O_2 concentration. These data suggest that this species should be assigned to the triplet state.

b - The other transient has "a long decay time", in the millisecond range and appears in the visible ($\lambda_{\text{max}} = 510 \text{ nm}$) and in the UV ($\lambda_{\text{max}} < 300 \text{ nm}$). It disappears by a first order process with a rate constant of $1.6 \times 10^2 \text{ s}^{-1}$ and is weakly affected by the presence of O_2 ($k_Q = 2.3 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$)

In degassed solution 80 % of this latter transient is produced during the laser pulse (from the singlet) and 20 % at a rate constant of $5 \times 10^5 \text{ s}^{-1}$ quite close to the value found for the decay of the short transient described above (the triplet). This second transient reacts with iodine giving rise to 9-phenyl phenanthrene until $[\text{I}_2] > 5 \times 10^{-4} \text{ M}$. We can assign this long lifetime transient to the primary product of the cyclisation and shall call it X_a .

B - Mechanism and rate constant for the photocyclization of DPE

Irradiations of degassed or oxygen saturated solutions of DPE lead exclusively to 9-phenyl -9,10 dihydrophenanthrene (P_1) but with a sufficient iodine concentration ($\sim 10^{-3} \text{ M}$) 9-phenyl phenanthrene (P_2) only is formed. These results together with those of laser flash photolysis allow us to propose the following reaction scheme.



We have measured, at 253,7 nm, the quantum yield of photocyclization of DPE in degassed cyclohexane solution and found. $\phi_p = 0.24$ With trans piperylene as triplet quencher, $\phi_p = 0.21$. By sensitization with benzophenone we obtained the quantum yield of the reaction via the triplet state $\phi_{TP_1} = 0.58$. We measured the lifetime of S_1 by the single photon technique and obtained $\tau_{S_1} = 4$ ns and the lifetime of T_1 has been reported above to be $\tau_{T_1} = 1.75 \times 10^{-6} \text{ s}^{-1}$. To deduce directly the rate constant of cyclization from S_1 and T_1 we had to be sure that the formation of X_a was quasi irreversible.

Indeed the quantum yield of product formation in degassed and in aerated solutions containing $5 \times 10^{-4} \text{ M}$ of iodine are almost identical: $\phi_{P_1} = 0.24$ and $\phi_{P_1} + \phi_{P_2} = 0.04 + 0.22 = 0.26$. From laser flash photolysis measurements it was found that addition of this amount of iodine decreases the lifetime of X_a by a factor of 20. If the slight increase in quantum yield with iodine was significant, it could be an effect of the reversible opening in absence of oxidizer. It must however be small since, on the basis of these data, the conversion yield of X_a to P_1 is at least 0.92 without oxidizer. Therefore we can estimate that $\phi_{X_a P_1} = 1$ and consequently:

$$\phi_{SP_1} = \phi_{SX_a} = k_{SX_a} \times \tau_S \longrightarrow k_{SX_a} = 5.2 \times 10^7 \text{ s}^{-1}$$

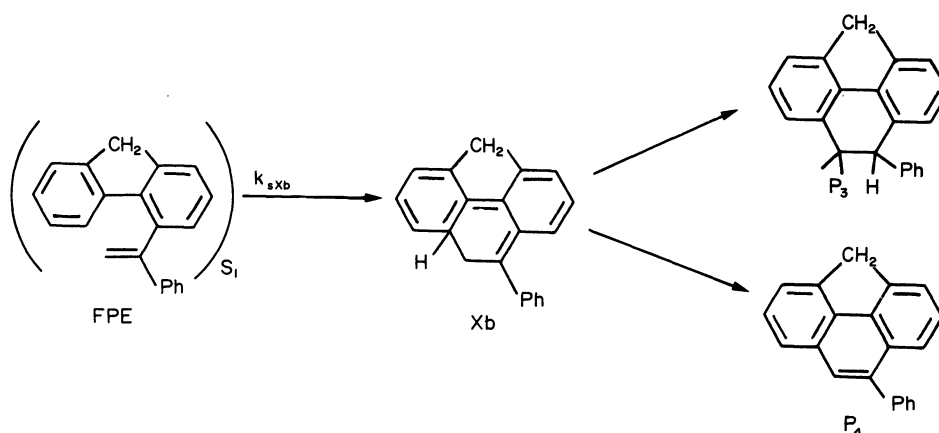
$$\phi_{TP_1} = \phi_{TX_a} \times \tau_T \longrightarrow k_{TX_a} = 3.3 \times 10^5 \text{ s}^{-1}$$

The rate constant of almost all the different processes originating from the excited DPE have been obtained but we report here only those concerned with the chemical reaction.

The main result is that the cyclisation is apparently 150 times faster from the singlet state than from the triplet state. This could be accounted for by a multiplicity or an energetic effect if the mechanism of cyclisation from S_1 and T_1 were the same but the considerations that follow seem to show that it is not the case.

C - Comparative photocyclization of DPE and FPE

Just as we have been able to measure the rate constant of the same reaction from two different excited states of DPE it was of interest to see how a geometric modification of the aromatic moiety would affect the reactivity of the two states. For this study we have irradiated 1-(4-fluorenyl)-1-phenyl ethylene (FPE); it gives exclusively P_3 in degassed solution while in aerated solution P_4 is formed predominantly.



The rate constant of cyclization by S_1 is faster than with DPE :
 $k_{S_1X_b} = 1.3 \times 10^8 \text{ s}^{-1}$ (calculated from $\phi_{S_1} = 0.33$, $\tau_S = 2.5 \times 10^{-9} \text{ s}$ and assuming as it was done with X_a that X_b is irreversible formed). This increase in rate could be related to the more rigid geometry of FPE, with regard to DPE, since a quasiplanar structure would favor the concerted cyclisation rather than the other deactivation paths. Contrasting with the higher reactivity of singlet, by direct irradiation as well as with sensitizer (benzophenone, acetone) we have been unable to observe a triplet cyclization of FPE. This finding points to a different geometric requirement for the cyclization according to the multiplicity of the reactive state as expected if the two following mechanisms occur : a concerted singlet cyclization by a planar transition state and a triplet pathway by a twisted methylene double bond.

If this interpretation is correct then the rate constant k_{TX} given above is probably wrong since it was calculated from the lifetime of a triplet species measured by flash photolysis which may not be the cyclizing species. The lifetime measured corresponds most likely to the precursor triplet state that controls reaching the orthogonal triplet that cyclizes. And therefore the quantum yield relation that should be used is

$$\phi = \frac{k_{\text{twist}}}{k_{\text{twist}} + k_{\text{deactivation}}} \times \frac{k_{\text{cyclization}}}{k_{\text{cyclization}} + k_{\text{deactivation}}}$$

From known rate of twisting of styrene type double bond, the first ratio written above can be assumed to be nearly one. Bonneau has determined for the rate of deactivation of perpendicular triplet state of styrene derivative a value of about $2 \times 10^7 \text{ s}^{-1}$. Introducing this value, k_{TX_a} becomes of the order of 2×10^7 .

In conclusion it is cleared that the measurement of rate constants can really provide the necessary information concerning the difference of reactivity between singlet and triplet pathways of photochemical reactions. However kinetics only yields the values of the rate constant for each step considered in the scheme. This means that we can only have confidence in elementary rate constant for reaction scheme that have been established very carefully.

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