259. A Re-investigation of the Wavelength-dependent Photoreduction of 1-Piperidinoanthraquinone: Evidence for a Mechanism of Impurity Sensitization

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Summary

The reported wavelength-dependence of the photoreactivity of 1-piperidinoanthraquinone (1-PAQ) in hydrogen-donor solvents is ascribed to a chemical sensitization by trace amounts of 1-chloroanthraquinone, as the action spectrum for photoreactivity of the former matches the absorption spectrum of the latter. The photochemistry and photophysics of 1-PAQ seem therefore not to violate the *Kasha-Vavilov* rule, *i.e.* its photoreactivity does not involve an upper n – π^* triplet state.

Introduction. – The photoreduction of 1-piperidinoanthraquinone (1-PAQ) in hydrogen-donating or electron-donating media is thought to provide one of the very few examples of a bimolecular photochemical reaction originating from an upper excited state [1], thus violating the generally observed *Kasha-Vavilov* rule for molecules in condensed phase. This unusual mechanism is based on the observed wavelength-dependence of the photoreduction quantum yield, which is reported to be nil for irradiation in the first absorption band of 1-PAQ (> 420 nm), but to be of the order of 10^{-2} for irradiation in the UV (*e.g.* at 313 nm). The mechanism suggested to explain this behaviour involves a rapid intersystem crossing from one of the upper singlet states to an upper triplet state of n – π^* type, thought to have an unusually long lifetime in view of the large energy gap between it and the lowest triplet state.

An alternative mechanism, which has obviously not been properly considered, involves chemical sensitization by a photoreactive impurity absorbing only in the UV; such a mechanism has been shown to operate, for example, in the photoreduction of acridine 'sensitized' by benzophenone [2]. This paper shows that such a radical sensitization mechanism is most probably operating in the present case.

Results. – The obvious photoreactive impurity in 1-PAQ is 1-chloroanthraquinone (1-CAQ) which is the starting material for its synthesis. 1-CAQ possesses both the spectroscopic and photochemical properties required for the sensitization process: *i.* its lowest triplet level is of n – π^* type ($E_T \simeq 260$ kJ mol^{-1}), with a high reactivity (near unit quantum yield) towards photoreduction [1a]; *ii.* its absorption spectrum starts at around 420 nm ($\log \varepsilon \simeq 2.0$ at 400 nm), rising steadily in the UV ($\log \varepsilon \simeq 3.7$ at 330 nm, $\log \varepsilon \simeq 4.7$

at 260 nm); *iii.* its primary photoreduction product is a relatively stable semiquinone radical.

Photoreactivity of 'Purified' and 'Sensitized' 1-PAQ Solutions. When a 'purified' sample of 1-PAQ (*ca.* 10^{-4} M) in deoxygenated ethanol is irradiated, we observe a wavelength-dependent photoreaction in agreement with previous reports [1]: no reaction for irradiation wavelength greater than 420 nm, a very slow reaction at $\lambda = 406$ nm, rapid photoreaction at $\lambda = 365$, 313 and 265 nm. The spectral change corresponds to that reported earlier. Complete recovery of the original spectrum of the irradiated sample is obtained when oxygen is admitted into the cell.

The addition of small amounts of 1-CAQ to 'purified' 1-PAQ results in a rapid increase in the rate of reaction, without any change in the spectrum of the irradiation products. This suggests that the reaction mechanism is the same in the 'purified' samples and in those where 1-CAQ-sensitizer was deliberately added. *Table 1* shows the effect on the reaction rate of various amounts of added 1-CAQ-sensitizer (*i.e.* 'impurity').

Table 1. *Quantum Yields Φ for the Disappearance of 1-PAQ in EtOH as a Function of Added 1-CAQ* (in weight-%) *at 313-nm Irradiation*

1-CAQ	Φ
0	1×10^{-3}
0.02	8×10^{-3}
1	10×10^{-3}
10	39×10^{-3}

The decrease in absorbance of 1-PAQ at 510 nm as a function of irradiation time is *linear* down to over 50% conversion of the original reactants.

In the case of normally photoreactive samples of moderate optical density ($D < 0.5$) at the irradiation wavelength, the rate of reaction d[A]/dt decreases with time as the fraction of light absorbed decreases with the concentration of the absorbing photoreactive species. On the other hand, in the case of a sensitized reaction the absorption by the sensitizer may even increase slightly with time as the inner filter effect of the major (sensitized) component decreases. The observed (linear) variation of concentration [1a] in the case of 'purified' 1-PAQ samples is therefore consistent with a mechanism of photosensitization by 1-CAQ present in trace amounts.

Action Spectrum of the Photoreduction of 'Purified' 1-PAQ. If a sensitizer impurity S is present in the sample of the amine A, then the rate of reaction measured as d[A]/dt at $t = 0$ is proportional, for irradiation at a wavelength λ, to the incident light intensity $I_0(\lambda)$ and to the fraction f of light absorbed by S. Since the concentration [S] is expected to be very small, this fraction f is practically proportional to the optical density $D_S(\lambda)$. Hence, the action spectrum |d[A]/dt| *vs.* λ, when corrected for the variation of incident light intensity with wavelength and for the inner filter effect of the major component A, must then correspond to the absorption spectrum of the sensitizer S.

The optical density of the solution $D(\lambda)$ at a wavelength λ is related to the concentrations c_A and c_S of the major component A and of the sensitizer S as

$$D(\lambda) = c_A\,\varepsilon_A(\lambda) + c_S\,\varepsilon_S(\lambda) = D_A(\lambda) + D_S(\lambda) \qquad (1)$$

If $I_0(\lambda)$ is the incident light intensity on the sample, the intensity absorbed by S at $t = 0$ is

$$I_S(t = 0) = \frac{D_S}{(D_A + D_S)} I_0 (1 - 10^{-(D_S + D_A)}) \tag{2}$$

In the present case $D_S \ll D_A$, but the absorption by the photoproducts P at $t > 0$ cannot be neglected. The intensity of light absorbed by S at $t > 0$ therefore becomes

$$I_S(t) = \frac{D_S}{(D_A + D_P)} I_0 (1 - 10^{-(D_S + D_P)}) \tag{3}$$

For a small conversion from reactants to products (*ca.* 10%) it is permissible to consider that the *average* intensity $\bar{I}_S$ of light absorbed by S is the arithmetic mean of $I_S(t = 0)$ and $I_S(t)$:

$$\bar{I}_S = \frac{I_0}{2} \left[\frac{D_S}{D_0} (1 - 10^{-D_0}) + \frac{D_S}{D_f} (1 - 10^{-D_f}) \right] \tag{4}$$

where $D_0 = D_A$ is the optical density at time $t = 0$ and $D_f = D_A + D_P$ is the final optical density after an irradiation time t.

If we now assume that the rate r of the reaction is proportional only to its quantum yield Φ and to the intensity of light absorbed by the sensitizer we obtain

$$r = \frac{\mathrm{d}[A]}{\mathrm{d}t} = -\Phi \bar{I}_S = -\frac{\Phi I_0}{2} D_S \left[\underbrace{\frac{(1 - 10^{-D_0})}{D_0} + \frac{(1 - 10^{-D_f})}{D_f}}_{\text{inner filter effect factor } \chi} \right] \tag{5}$$

If the quantum yield Φ is independent of the irradiation wavelength, the proportionality between the reaction rate r and the optical density of the sensitizer in the sample is

$$r(\lambda) = -D_S(\lambda) \left[\frac{\Phi I_0(\lambda) \chi}{2} \right] \tag{6}$$

or

$$|r(\lambda)| \propto D_S(\lambda) \quad \text{q.e.d.} \tag{7}$$

Under our experimental conditions a Hg/Xe arc was used with a high-radiance grating monochromator to isolate the intense lines at 435, 406, 365, 313 and 265 nm, yielding 5 points in the action spectrum. In *Table 2* the results are compared with the absorption

Table 2. *Comparison of Action Spectrum for Disappearance of 'Purified' 1-PAQ Samples at Various Wavelengths with the Absorption Spectrum of 1-CAQ*

λ [nm]	ε(1-CAQ) [$M^{-1} cm^{-1}$]	Relative optical density of 1-CAQ	Observed relative rate of disappearance of 'purified' 1-PAQ
365	1×10^3	1	1
313	3.4×10^3	3.4	3.2
296	2.37×10^3	2.37	2.1
265	20.5×10^3	20.5	22

spectrum of 1-CAQ. It is noteworthy that the two spectra essentially overlap. This is the strongest piece of evidence for the involvement of 1-CAQ as a photosensitizing impurity in the photoreduction of 1-PAQ.

Other Substituted Anthraquinones. Under the same conditions, the photoreduction of 2-PAQ is sensitized very inefficiently by 2-CAQ. On the other hand 2-aminoanthraquinone (2-AAQ) can be sensitized in this manner by added anthraquinone (AQ).

Discussion. – *General Reaction Mechanism.* The mechanism of the photosensitized reduction of a major species A by a sensitizer S can be described by the following essential steps:

1. $S^* + ZH \rightarrow \dot{S}H + \dot{Z}$ Primary photoreaction of sensitizer
2. $\dot{S}H + A \rightarrow S + \dot{A}H$ Sensitization (secondary process)
3. $\dot{R} + M \rightarrow N + \dot{R}'$ Propagation steps
4. $\dot{R} + \dot{R}' \rightarrow M\ (+ N)$ Termination steps

where $\dot{R}$, $\dot{R}'$ are radicals and M, N are closed-shell molecules. All propagation steps involve one radical and one molecule, whereas the termination steps require two radicals. It is assumed that absorption of a photon by A results in rapid deactivation and that the energy transfer $A^* + S \rightarrow A + S^*$ does not occur (this is clearly the case in the present instance), since both the lowest singlet and triplet levels of 1-PAQ (A) are considerably lower than those of 1-CAQ (S).

Dependence of Rate on Sensitizer Concentration. The remarkable efficiency of very low sensitizer concentrations must depend on the propagation reactions. It has been shown [3] that 1-PAQ reacts very rapidly with radicals such as CH_2OH; the overall quantum yield for the disappearance of A can then be considerably greater than unity. The effect of higher sensitizer concentrations becomes progressively smaller (*Table 1*). This may be due to the increasing importance of the termination reactions given that the radical concentration increases linearly with D_S for this range of [S]: the propagation steps depend linearly on the intensity of light I_S absorbed, whereas the termination steps depend on I_S^2.

It was beyond the scope of this work to attempt to unravel the (secondary) radical reactions of this sensitization process; nevertheless the *increasing* relative efficiency of the sensitization with *decreasing* [S] is noteworthy. We propose that this results from the different light intensity dependence (linear or quadratic) of the propagation and termination reactions under these experimental conditions, this light intensity dependence being therefore equivalent to a concentration dependence. Whatever the explanation for the data in *Table 1*, it is clear that in some cases even extremely low impurity concentrations can have a sensitizing effect. The quantum yield of reaction observed in a 'purified' sample, and the effect of added sensitizer, suggest that in the 'purified' sample about 10 ppm of sensitizer remain. The great difficulty in eliminating these last traces of CAQ (or AQ) from PAQ-(or AAQ-) samples is illustrated by the frequently observed AQ-like phosphorescence from such samples. Although attributed by some workers [4] to an 'anomalous' $T_n\ (n - \pi^*) \rightarrow S_0$ upper triplet emission, we consider that this emission is due to an impurity, as also argued by *Parker* [5].

Reactivity of Upper Excited States. The broader question raised by this work concerns the validity of the rather generally observed *Kasha-Vavilov* rule that 'only the lowest excited state of any multiplicity takes part in photochemical reactions'. The validity of this rule depends on the relative rates of deactivation and chemical reaction from upper excited states. In general the rate of deactivation is very much larger (*e.g.* $10^{12}\,s^{-1}$) than the rate of reaction [6], so that the quantum yields of both luminescence and chemical reaction from such upper excited states are expected to be very small (*e.g.* $< 10^{-4}$). Exceptions could be found in theory in cases where the deactivation rate is much smaller than $10^{12}\,s^{-1}$ (by a factor of 10^{-3} for example). In view of the energy gap law [7] which is thought to dominate the rate of radiationless transitions, the necessary condition would be a large energy gap between the reactive upper state and the nearest lower lying state of the same multiplicity. Such a situation was thought to apply to 9-anthraldehyde [8] where the $n - \pi^*$ triplet (expected to be reactive in photoreduction processes) is well separated from the lowest $\pi - \pi^*$ anthracene-like triplet. Later work has established, however, that the reactive state is S_1 in this case [9], in agreement with the *Kasha-Vavilov* rule.

The case of 1-PAQ is analogous. From quenching and sensitization experiments [3] the lowest triplet $\pi - \pi^*$ state is about 120 kJ mol^{-1} above the ground state, whereas the $n - \pi^*$ anthraquinone-like triplet should be well above 260 kJ mol^{-1}. On the basis of the present results, however, it appears that 1-PAQ shows no chemical reactivity under photoreduction conditions from any of its excited states.

Since the participation of an upper excited state (*e.g.* T_2) in chemical reactions depends (among other things) on the magnitude of the energy gap between T_2 and T_1, it is clearly essential to ensure that there really are no other states within the T_2/T_1 gap ('T_2' would then in fact be T_n, $n > 2$). Triplet-triplet absorption spectra are in principle the decisive proof, but care must be taken about the possible presence of weak (forbidden) $T_1 \rightarrow T_m$ transitions which may not be detectable under normal experimental conditions. In the case of 1-PAQ, the T-T spectrum is at present not available due to the extremely short lifetime of its T_1-triplet.

Conclusion. – The reported wavelength effect on the photoreduction of 1-PAQ is most probably the result of an unusually efficient sensitization (*via* a radical exchange reaction) by a reactive anthraquinone impurity (probably 1-CAQ) present in very low concentration from the synthetic process leading to 1-PAQ. The occurrence of such a sensitization mechanism should be given due consideration for any photoreaction before unusual upper excited state mechanisms are invoked solely on the basis of wavelength effects on reaction quantum yields. It should be stressed that the purity of the samples is often of critical importance in such photophysical and photochemical experiments.

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Appendix. – A referee has suggested that the level of impurity of 1-CAQ (*ca.* 10 ppm) in our 'purified' sample of 1-PAQ quoted above may perhaps be further reduced to strengthen our conclusions. Extensive chromatography on alumina yielded a fraction of 1-PAQ exhibiting, with 365 nm irradiation in deoxygenated EtOH, a 50% reduction in the quantum yield for dissappearance with respect to the original 'purified' sample. Equally, the new sample showed diminished impurity phosphorescence, which cannot, however, be assessed quantitatively as it comes very close to the detection limit of our instrument. These findings are in line with our above conclusions based on the effect of *added* alleged impurity and on its action spectrum; hence further tedious purification work does not seem justifiable as it becomes impossible to evaluate the level of impurities remaining in these samples. We thank the referee for his supporting recommendations.

REFERENCES

[1] a) *A.K. Davies, R. Ford, J.F. McKellar & G.O. Phillips,* J. Chem. Soc., Perkin Trans. 2 *1972*, 923; b) *H. Inuoe, K. Kawabe, N. Kitamura & M. Hida,* Bull. Chem. Soc. Jpn. *55*, 1874 (1982); c) *A.K. Davies, J.F. McKellar & G.O. Phillips,* Proc. R. Soc. London *A323*, 69 (1971); d) *N.J. Turro,* Modern Molecular Photochemistry, Benjamin, Menlo Park, 1978.

[2] *E. Vander Donckt & G. Porter,* J. Chem. Phys. *46*, 1173 (1967).

[3] *B.E. Hulme, E.J. Land & G.O. Phillips,* J. Chem. Soc., Faraday Trans. 1 *1972*, 1992.

[4] *N.S. Allen, B. Harwood & J.F. McKellar,* J. Photochem. *9*, 565 (1978).

[5] *C.A. Parker,* J. Photochem. *12*, 91 (1980).

[6] *N.J. Turro, V. Ramamurthy, W. Cherry & W. Farneth,* Chem. Rev. *78*, 2 (1978).

[7] *J.B. Birks,* 'Organic Molecular Photophysics', Vol. 1, Wiley-Interscience, New York, 1973, pp. 32, 153–233.

[8] *N.C Yang & R.L. Loeschen,* Tetrahedron Lett. *1968*, 2571.

[9] *P. Suppan,* Tetrahedron Lett. *1971*, 4469.