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PHOTOCHEMISTRY OF 9-ANTHRALDEHYDE IN SOLUTION.

P. Suppan

Davy-Faraday Laboratory of the Royal Institution, 21 Albemarle St., London W 1.

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Reports in this Journal have described the results obtained by Yang et al.[1], and by Warwick and Wells[2], on the photochemistry of 9-anthraldehyde (9AA) in solution. These authors conclude that :

1. In suitable solvents (olefins) both the anthracene nucleus photodimerization (the 9,9',10,10' anthracene to anthracene addition) and the photoreduction of the carbonyl group (which results in the formation of pinacols or oxetanes as final products) occur, depending on irradiation wavelength.
2. The reaction can be quenched by 1-naphthaldehyde (E_T = 19700 cm^{-1}) but not by naphthalene (E_T = 21300).
3. The reaction can be sensitized by acetophenone (E_T = 25750) , xanthone (26000), and triphenylene (23500), but not by 2-acetonaphthone (E_T = 20800 cm^{-1}).

From these observations it was concluded that one or more upper triplet states of 9AA were responsible for carbonyl photoreduction.

We have examined the quantum yields and the relative product yields in various conditions. On the basis of our observations we believe that the photoreactivity of 9-AA is consistent with the lowest excited singlet state, S_1 , being responsible for both the photoreduction and the anthracene nucleus photodimerization reactions.

1. Thus, we find that when 9AA is irradiated in ethanol at wavelengths > 420 nm, at 365 nm, or at 313 nm, the reaction is one of carbonyl photoreduction, as evidenced by the appearance of a structured anthracene-like absorption from the

structureless 9AA spectrum. At [9AA] = 10^{-4}, the quantum yield of disappearance is $6.7 \cdot 10^{-4}$ in both degassed and aerated solutions.

When wavelengths above 420 nm are used, good isosbestic points are obtained throughout the irradiation. At shorter wavelengths the reaction is not so clean, probably because of further photoreactions of the products.

2. In benzene as solvent the anthracene nucleus photodimerization only is obtained, both in degassed and aerated solutions, at >420, 365, and 313 nm irradiation. The quantum yield is concentration dependent, 10^{-5} at [9AA] = 10^{-4}, 0.02 at 10^{-1}.
3. In other solvents photoreduction of the carbonyl and photodimerization of the anthracene nucleus occur in various ratios (Table 1), at 420 and 365 nm.

Table 1.

Solvent	Carbonyl reduction	Aromatic dimerization
ethanol	1.0	negligible
toluene	0.1	0.9
hex-1-ene	0.05	0.95
cyclohexane	negligible	1.0
benzene	negligible	1.0

Table 1 : Relative yields of photoproducts for 9AA concentration of 10^{-4}.

4. With 2-methyl-2-butene (2M) in benzene, the principal reaction is carbonyl photoreduction in both aerated and degassed solutions, the quantum yield being $2.8 \cdot 10^{-3}$ at [9AA] = 10^{-4}.

Quenching. 10^{-4} M 9AA in ethanol solutions were irradiated with wavelengths >420, with and without 10^{-1} M 1-naphthaldehyde added as quencher. No difference was found in the relative quantum yields within the accuracy of the experiment (around 15 % relative error).

Sensitization. Triphenylene does sensitize the photoreduction of 9AA in ethanol, and also the anthracene nucleus photodimerization in benzene.

Discussion.

As 9AA can be photoreduced in certain solvents, but can also always undergo the anthracene nucleus photodimerization reaction, it is necessary to use very low concentrations to study specifically the photoreduction.

At 10^{-4} M 9AA, we find that photoreduction occurs predominantly in ethanol, at all irradiation wavelengths. It is particularly significant that reduction does take place with wavelengths >420 nm, in accord with Yang's erratum[3] following his earlier observations.

We are in disagreement with Warwick and Wells about the possibility of quenching of the photoreactions of 9AA. Using much higher quencher concentrations we find that no quenching occurs within experimental error. The small quantum yield decreases reported by Warwick and Wells (e.g. 0.012 to 0.010) must have been based on an implied accuracy better than 5%, which appears too hopeful particularly when correction must be made for the light absorbed by the quencher.

The observations of quenching by nitroxides[4] do not distinguish between singlet and triplet reactions, we shall therefore not discuss them here.

The observation that triphenylene can sensitize both the carbonyl photoreduction and the anthracene nucleus photodimerization (depending on the solvent) points to the lowest excited singlet state, S_1 , being responsible for both reactions. This explains also the inefficacy of specific triplet quenchers and the fact that with irradiation >420 nm either reduction or dimerization can occur.

Sensitization by triphenylene is probably a sensitization of the S_1 state of 9AA, by energy transfer. The S_1 state of triphenylene is of higher energy, and its lifetime is relatively long, 35 ns in degassed solution[5]. Assuming a diffusion controlled rate for this energy transfer, the quantum yield of 9AA singlet formation is 0.7 at $[9AA] = 10^{-2}$.

When xanthone is used to sensitize the reaction of 9AA in benzene/2-methyl-2-butene, the change in absorption spectrum shows that the overall reaction is complex. A long-wavelength absorption develops in a region (>400 nm) where neither the photodimer nor the photoreduction products absorb. It is therefore probable that a chemical reaction takes place between excited xanthone and 9AA, and this is in agreement with the fact that Yang finds a much higher quantum yield for the xanthone-sensitized reaction than for direct irradiation.

The reported sensitization by acetophenone is likely to be a chemical sensitization by H atom transfer from acetophenone ketyl radical to ground state 9AA. At $[9AA] = 10^{-2}$, the quantum yield of hydrogen abstraction by acetophenone in 1 M 2-methyl-2-butene is 0.01 if quenching of acetophenone triplet by 9AA is diffusion controlled. This is approximately the figure quoted for this sensitized reaction. The chemical mechanism is also in agreement with the failure of acetonaphthome (which is unreactive) to sensitize the reaction.

References.

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