SENSITIZED PHOTOISOMERIZATION OF PYRIDYLHYDRAZONES

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Summary

The *syn–anti* isomerizations of benzaldehyde-2-pyridylhydrazone and pyridine-2-aldehyde-2-pyridylhydrazone by triplet energy transfer were investigated. The pyridylhydrazone of pyridyl-2-aldehyde underwent reversible isomerization without side reactions; the triplet states implied in the process were found to be quenchable by azulene and their lifetime was determined. For the pyridylhydrazone of benzaldehyde, isomerization and secondary photolysis reactions occurred simultaneously regardless of the nature of the sensitizer. A comparison of previous results with these indicates that the pathways of the direct and sensitized isomerizations do not involve intersystem crossing.

1. Introduction

Recent findings [1] in our current investigation [2 - 4] of the mechanism of photoisomerization about the azomethine bond have shown that for direct irradiation the 2-pyridylhydrazones of benzaldehyde and pyridine-2-aldehyde undergo isomerization via the minimum of the lowest excited singlet state without triplet states being involved.

With the aim of providing information about the reaction occurring from these triplet states, in this work we investigated the isomerization process following the excitation of the compounds by energy transfer from suitable sensitizers.

2. Experimental

2.1. Materials

syn-Benzaldehyde-2-pyridylhydrazone (*syn* I) and *syn*-pyridine-2-aldehyde-2-pyridylhydrazone (*syn* II) were prepared and purified by classic

methods. *anti*-Benzaldehyde-2-pyridylhydrazone (*anti* I) and *anti*-pyridine-2-aldehyde-2-pyridylhydrazone (*anti* II) were obtained photochemically as reported in a previous paper [1].

Fluorene, benzophenone, benzil and crystal violet (Baker) were suitable for "sensitizer use". Eosin y (C. Erba) was recrystallized from ethanol before use. Azulene (Fluka) puriss. was used. The benzene was of spectroscopic grade. All other common chemicals were reagent grade.

2.2. Apparatus and procedures

The experimental equipment for irradiation, for measurements of the incident light and for spectrophotometric measurements were the same as those described previously [5].

The radiations of 365, 405 and 436 nm were isolated from a mercury vapour lamp (Hanau Q 400) by means of interference filters (Zeiss Jena). The radiation of 578 nm was obtained from a tungsten incandescent lamp (Philips Attralux Spot 150 W) using interference filters (Zeiss Jena).

Samples of the substrate–sensitizer system in benzene as solvent were introduced into standard spectrophotometric cells, were deoxygenated with pure nitrogen, were thermostatted at 25 °C and were irradiated at the desired wavelength. The substrate concentration was in the range 10^{-4} - 10^{-3} M. The concentrations and the irradiation wavelengths for various sensitizers were as follows: fluorene, 0.2 M, λ_{exc} = 365 nm; benzophenone, 0.025 M, λ_{exc} = 365 nm and λ_{exc} = 313 nm; benzil, 0.02 M, λ_{exc} = 405 nm; eosin y, saturated solution in CH_3CN, λ_{exc} = 436 nm; crystal violet, 0.02 M, λ_{exc} = 578 nm. The experimental conditions used for all the systems are the optimum for reducing the light absorption from the substrate to a minimum and for following the kinetics spectrophotometrically at the most suitable wavelength.

The benzil phosphorescence was recorded at 554 nm by excitation with radiation of 410 nm. The quencher concentration was in the range 10^{-5} - 10^{-4} M.

3. Results

Preliminary tests were necessary to choose the most suitable sensitizers for carrying out an isomerization study. Because the 2-pyridylhydrazones investigated showed no phosphorescence emission and no information about lower triplet state energies was obtainable from this source, we considered sensitizers of triplet energy in the range 69 - 39 kcal: benzophenone (69 kcal), fluorene (68 kcal), benzil (54 kcal), eosin y (43 kcal) and crystal violet (39 kcal).

Experiments of benzil phosphorescence quenching by *syn*- and *anti*-pyridylhydrazones were carried out (Fig. 1). The linearity of Stern–Volmer plots, P_0/P *versus* substrate concentration, suggested that in no case did chemical reaction between sensitizer and substrate occur and that the
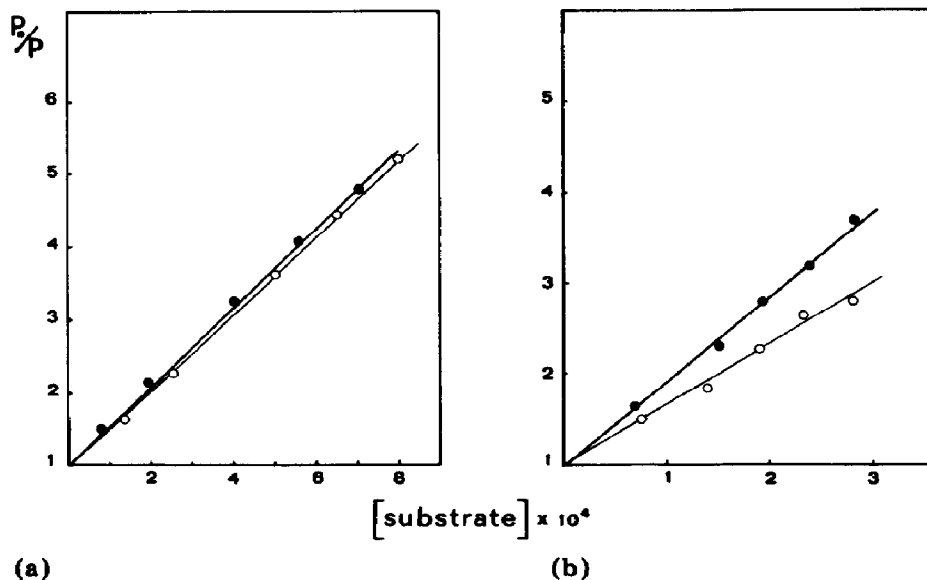
Fig. 1. Stern–Volmer plots for the quenching of the benzil phosphorescence by *syn* (O) and *anti* (●) isomers of (a) benzaldehyde-2-pyridylhydrazone and (b) pyridine-2-aldehyde-2-pyridylhydrazone.

quenching was due to energy transfer. From the slopes of the plots and from the benzil triplet lifetime (5.88×10^{-5} s) the quenching constant values were obtained (for *syn* I $k_q = 0.9 \times 10^9$; for *anti* I $k_q = 0.92 \times 10^9$; for *syn* II $k_q = 1.3 \times 10^9$; for *anti* II $k_q = 1.7 \times 10^9$). These values showed that the quenching rate of the four compounds was controlled by diffusion; therefore, benzil and even more so the sensitizers with a higher triplet energy must be considered as high energy sensitizers.

3.1. Sensitized photoisomerization of pyridine-2-aldehyde-2-pyridyl-hydrazone

Benzophenone, fluorene, benzil and eosin y were effective in bringing about *syn–anti* isomerization without side reactions, whereas crystal violet was completely ineffective for sensitization. It was evident that the reaction was independent of the chemical nature of the sensitizer and that the lower triplet reactive state lies between about 43 and 39 kcal.

The sensitization with fluorene and eosin y was not investigated quantitatively, because with these sensitizers we were necessarily operating under unfavourable experimental conditions. With fluorene the photoreaction was to a large extent due to a direct absorption of the radiation; thus, the sensitized reaction calculation became uncertain. With eosin y we had to operate in a polar solvent and so comparison with the other data — obtained in benzene — would not have much significance.

Pure isomerization conditions could not be obtained when benzophenone was used; however, an evaluation of the sensitized reaction was
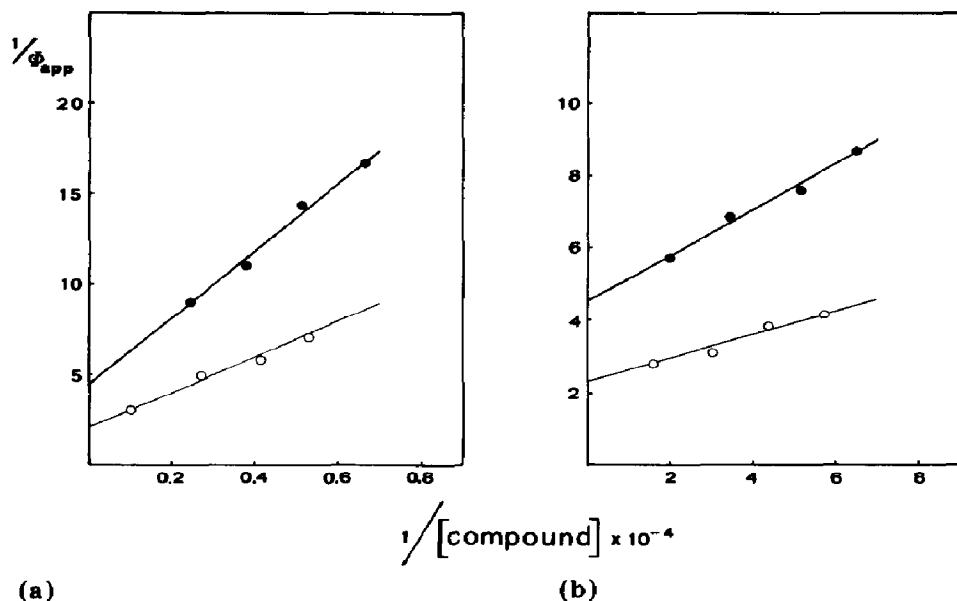
Fig. 2. The isomerization of pyridine-2-aldehyde-2-pyridylhydrazone photosensitized by (a) benzophenone and (b) benzil: ○, $syn \rightarrow anti$; ●, $anti \rightarrow syn$.

available after correction for direct radiation absorption. It was found that the quantum yields of the sensitized isomerization were dependent on the initial substrate concentration. Plots of $1/\Phi_{app}$ versus $1/[compound]$ were good straight lines (Fig. 2) from which the quantum yield limit was calculated; $\Phi_{s-a} = 0.49$, $\Phi_{a-s} = 0.22$. From the intercept-to-slope ratio and from the lifetime of benzophenone (1.9×10^{-6} s) the energy transfer constants ($k_s = 1.1 \times 10^9$ for syn and $k_s = 1.3 \times 10^9$ for $anti$) were obtained. Because these values were about the same as the k_q values obtained in quenching experiments of benzil phosphorescence, the same behaviour of the two sensitizers (benzophenone and benzil) was confirmed.

Benzil was the sensitizer which provided the best investigation conditions because it allowed us to operate under pure sensitization conditions, with quantum yields which reached constant values at substrate concentrations around 10^{-3} M. Experimentally, the following yield limiting values were found: $\Phi_{s-a} = 0.41 \pm 0.005$; $\Phi_{a-s} = 0.20 \pm 0.005$. The equilibrium state found, $[anti]_e/[syn]_e = 2.03$, was in good agreement with the ratio of the quantum yields. The theoretical values of the quantum yield limits obtained from the plots of $1/\Phi_{app}$ versus $1/[compound]$ (Fig. 2) are $\Phi_{s-a} = 0.50$ and $\Phi_{a-s} = 0.25$. In this calculation we took into account the intersystem crossing efficiency of benzil ($\eta = 0.89$).

With the aim of obtaining information about the lifetimes of the triplet states implied in the isomerization process, experiments of benzil sensitization in the presence of azulene were carried out. As a preliminary it was necessary, by means of phosphorescence-quenching experiments, to deter-
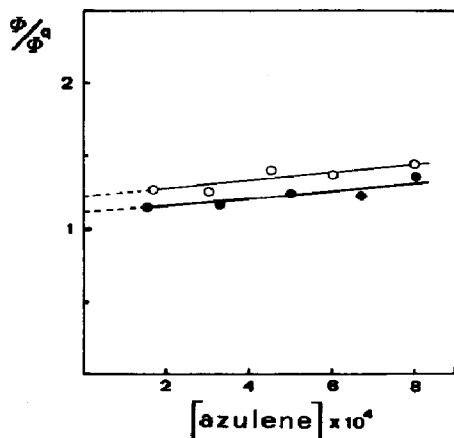
Fig. 3. The effect of azulene on the sensitized photoisomerization of pyridine-2-aldehyde-2-pyridylhydrazone: O, *syn → anti*; ●, *anti → syn*.

mine under our experimental conditions the constant of the benzil—azulene energy transfer. We found k_q = 1.3 × 10^9. The initial quantum yields Φ^q_{s-a} and Φ^q_{a-s} of the sensitized isomerization in the presence of the quencher were determined as functions of azulene concentration in the range 10^{-3} - 10^{-4} M, but with a constant ratio [compound]:[azulene] of 9:1. It was found that the quantum yields decreased with increasing quencher concentration and the ratio Φ/Φ^q was a linear function of azulene concentration (Fig. 3). The values of the slopes and of the intercepts, calculated by extrapolation, for the plots of Φ_{s-a}/Φ^q_{s-a} and Φ_{a-s}/Φ^q_{a-s} *versus* azulene concentration are respectively 325 and 1.18, and 230 and 1.12. It was observed that the addition of azulene shifted the equilibrium state of the two isomers reached in sensitization experiments to higher concentrations of the *syn* isomer. Unfortunately the data cannot be evaluated quantitatively because of slow decomposition side reactions which are brought out by prolonged irradiation.
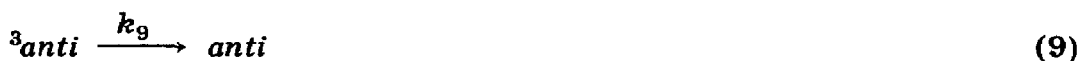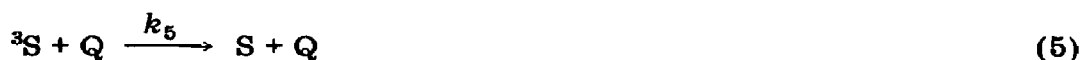
3.2. Sensitized photolysis of benzaldehyde-2-pyridylhydrazone

Benzophenone, fluorene, benzil and eosin y were effective in bringing about a reversible *syn—anti* isomerization, but at the same time a photodecomposition reaction was detected in all cases. The secondary compound formed initially was tested by spectrophotometric and chromatographic methods, and its nature was independent of the sensitizer used. The identification of this compound was difficult because it underwent photolysis as soon as its concentration was sufficient for it to compete with the substrate in absorbing irradiation or in the transfer of energy. A dimer of an azo compound was detected as the final product of the photodecomposition.

An investigation has been started to elucidate in greater detail the sensitized photolysis of benzaldehyde-2-pyridylhydrazone.

4. Discussion

The sensitized photoisomerization of pyridine-2-aldehyde-2-pyridyl-hydrazone can be interpreted using the following scheme, where S denotes sensitizer (benzil) and Q denotes quencher (azulene):

$$S \xrightarrow{h\nu} {}^1S \xrightarrow{\eta_{ISC}} {}^3S \tag{1}$$

$$^3S \xrightarrow{k_2} S \tag{2}$$

$$^3S + syn \xrightarrow{k_3} S + {}^3syn \tag{3}$$

$$^3S + anti \xrightarrow{k_4} S + {}^3anti \tag{4}$$

$$^3S + Q \xrightarrow{k_5} S + Q \tag{5}$$

$$^3syn + Q \xrightarrow{k_6} syn + Q \tag{6}$$

$$^3anti + Q \xrightarrow{k_7} anti + Q \tag{7}$$

$$^3syn \xrightarrow{k_8} syn \tag{8}$$

$$^3anti \xrightarrow{k_9} anti \tag{9}$$

$$^3syn \xrightarrow{k_{10}} p \tag{10}$$

$$^3anti \xrightarrow{k_{11}} p \tag{11}$$

$$p \xrightarrow{k_{12}} \beta syn + (1 - \beta)anti \tag{12}$$

This scheme represents a simple mechanism [6] of isomerization in which a twisted state p of intermediate geometry is reached by decay (reactions (10) and (11)) from triplet states originally populated by sensitizer (reactions (3) and (4)) and both quenchable by azulene (reactions (6) and (7)). From the p state the molecule undergoes fast decay to syn and $anti$ forms in the ratio $\beta/(1 - \beta)$.

In this model the initial quantum yield Φ_{s-a} of isomerization in the absence of quencher is

$$\Phi_{s-a} = \eta_{ISC} \frac{k_3[syn]}{k_3[syn] + k_2} \frac{k_{10}}{k_{10} + k_8} (1 - \beta)$$

and in the presence of quencher it is [7]

$$\Phi^q_{s-a} = \eta_{ISC} \frac{k_3[syn]}{k_3[syn] + k_2 + k_5[Q]} \frac{k_{10}}{k_8 + k_{10} + k_6[Q]} (1 - \beta)$$

Consequently

$$\frac{\Phi_{s-a}}{\Phi_{s-a}^{q}} = \left(1 + \frac{k_5[Q]}{k_3[syn] + k_2}\right)\left(1 + \frac{k_6[Q]}{k_8 + k_{10}}\right) \tag{13}$$

For our experimental conditions the quantum yields no longer increase with increasing concentration and are very close to the limiting value; therefore $k_3[syn] \gg k_2$. Then eqn. (13) becomes

$$\frac{\Phi_{s-a}}{\Phi_{s-a}^{q}} = \left(1 + \frac{k_5[Q]}{k_3[syn]}\right)\left(1 + \frac{k_6[Q]}{k_8 + k_{10}}\right) \tag{14}$$

By substitution of $1/(k_8 + k_{10}) = \tau_{3_{syn}}$ and by rearrangement, eqn. (14) reduces to

$$\frac{\Phi_{s-a}}{\Phi_{s-a}^{q}} = 1 + \frac{k_5[Q]}{k_3[syn]} + \left(1 + \frac{k_5[Q]}{k_3[syn]}\right)\tau_{3_{syn}}k_6[Q] \tag{15}$$

Similarly we obtain

$$\frac{\Phi_{a-s}}{\Phi_{a-s}^{q}} = 1 + \frac{k_5[Q]}{k_4[anti]} + \left(1 + \frac{k_5[Q]}{k_4[anti]}\right)k_7\tau_{3_{anti}}[Q] \tag{16}$$

Our results showed that at constant ratios [Q]/[compound] the plots of Φ/Φ^q *versus* [Q] were linear as eqns. (15) and (16) require. Also the extrapolated values of the respective intercepts were very close to those expected from the k_q values determined from the phosphorescence quenching of benzil. Given that $k_6 \approx k_7 \approx 10^9$, the lifetimes of the two isomers become of the order of 10^{-7} s ($\tau_{3_{syn}} = 3 \times 10^{-7}$ s; $\tau_{3_{anti}} = 2 \times 10^{-7}$ s).

On the basis of these lifetimes, the isomerization pathway could more probably involve intersystem crossing of the originally formed triplet states to the p state of the ground state, without needing a previous decay to the ^{3}p state for which the lifetimes observed would be very long.

The Φ_{s-a} value, very close to 0.5, suggests a unitary decay efficiency $^3syn \rightarrow$ p ($k_8 \ll k_{10}$) and a value of β of 0.5, whereas the lower value found for Φ_{a-s} can be attributed to $k_9 \approx k_{11}$.

In conclusion, the comparison of the direct and sensitized photoisomerization results points strongly to a difference in the two pathways. In fact azulene was an efficient quencher for the sensitized photoisomerization of pyridine-2-aldehyde-2-pyridylhydrazone, while no effect was found in the direct photoisomerization; therefore, quenchable triplet state participation can be ruled out in this latter process. As we have previously proposed [1], the molecule in the lower excited singlet state can undergo (1) relaxation to a minimum of intermediate geometry from which it decays to the ground *syn* and *anti* states or (2) conversion with retention of configuration. This latter was the sole pathway available for the *anti* isomer which was hydrogen bonded, whereas in the sensitized process the *anti* → *syn* reaction was possible because the hydrogen bond did not influence the triplet states [4].

The difference between the direct and sensitized reactions was more evident for benzaldehyde-2-pyridylhydrazone. In this case the triplet state

excitation by energy transfer underwent, concurrently with the isomerization, a photolysis which was not observable under direct irradiation. Because we exclude a chemical reaction between sensitizer and substrate, the triplet states must be responsible for the photolysis reaction.

Acknowledgment

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