

**REACTIVITY OF *trans*- β -STYRYLNAPHTHALENE
PHOTOSENSITIZED BY TRIS(2,2'-BIPYRIDINE)CHROMIUM(III)**

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Summary

On photosensitization by tris(2,2'-bipyridine)chromium(III), *trans*- β -styrylnaphthalene undergoes geometrical isomerization and (in the presence of dioxygen) oxidation to benzaldehyde and naphthaldehyde. Whereas oxidation seems to be due to attack by singlet oxygen, isomerization originates from a cationic radical of the olefin, formed in an electron transfer to the excited complex. The reactivity of such a radical is compared with those of triplet excited states and anionic radicals of stilbene derivatives.

1. Introduction

Stilbene-like molecules exhibit a very complex photochemical behaviour. Depending on the experimental conditions, *trans* isomers may undergo direct photodimerization and/or geometrical photoisomerization, whereas *cis* isomers may exhibit isomerization and/or intramolecular cyclization to phenanthrene derivatives. *Cis*-*trans* isomerization is also induced by triplet sensitization from energy donors; in this case, the photostationary ratio between the two isomers depends on the energy of the donor. *Cis* \rightarrow *trans* isomerization of a styrylpyridinium cation was recently photo-induced through the photochemical formation of a reduced radical of the olefin [1]. This catalytic mechanism, however, seems to be unable to induce the reverse *trans* \rightarrow *cis* isomerization [1, 2] with comparable efficiency. In the framework of a study on the reactivity of double bonds photosensitized by coordination compounds, we have attempted to induce the isomerization of *trans*- β -styrylnaphthalene (*t*-StN) by means of the photochemical formation of a cationic radical. The direct photoisomerization of this molecule is in fact affected by the presence of either electron donors [3] or electron acceptors [4] in a complex way. As a potential excited state electron acceptor we have used the tris(2,2'-bipyridine)chromium(III) ($\text{Cr}(\text{bpy})_3^{3+}$)

complex. Some experiments were also performed with $\text{Os}(\text{phen})_3^{2+}$ (phen \equiv 1,10-phenanthroline) as a photosensitizer, to clarify the reaction mechanism.

2. Experimental section

2.1. Materials

t-StN and *cis*- β -styrylnaphthalene (*c*-StN) [5] were kindly supplied by Professor G. Galiazzo and Professor U. Mazzucato and $\text{Cr}(\text{bpy})_3(\text{ClO}_4)_3$ and $\text{Os}(\text{phen})_3(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ were prepared by procedures described in the literature [6, 7]. All the other chemicals were of reagent grade.

2.2. Apparatus

The reduction and oxidation potentials were measured by means of an Amel model 448 apparatus for cyclic voltammetry. The emission intensities were measured by means of a Perkin-Elmer MPF-3 spectrofluorometer using an R 955 phototube. The lifetime measurements were performed with a flash spectroscopy apparatus equipped with a JK 2000 series DLPY 4 neodymium laser ($\lambda = 355 \text{ nm}$). The optical density measurements were performed with a Cary 219 spectrophotometer. The irradiation sources were a medium pressure mercury lamp, filtered with a band filter centred at 402 nm (half-width of transmission band, 10 nm) or a Novamat 520 slide projector equipped with a 150 W halogen lamp and a cut-off filter which was transparent to light above 400 nm. For the mercury lamp source, the intensity of the incident light, which was measured by means of a ferric oxalate actinometer [8], was $6 \times 10^{-7} \text{ einsteins min}^{-1}$. Gas chromatographic analyses were carried out with a Carlo Erba HRGC Fractovap 4160 series gas chromatograph, equipped with a flame ionization detector and a OV1 column (length 15 m; film thickness, 0.1 - 0.15 μm).

2.3. Procedures

All the experiments were performed in CH_3CN solution at room temperature. Generally the irradiation was carried out in standard spectrophotometric cells (thickness, 1 cm; capacity, 3 ml). Standard spectrophotometric cells of different path lengths (0.1, 0.2 and 0.5 cm) were also used to study the effect of the *t*-StN concentration on the photochemical reaction. For the gas chromatographic analyses, 400 ml of a solution containing $2.4 \times 10^{-4} \text{ mol}$ of $\text{Cr}(\text{bpy})_3^{3+}$ and $1.2 \times 10^{-4} \text{ mol}$ of *t*-StN were irradiated at a wavelength greater than 400 nm for 6 h in a cylindrical glass cell. The irradiated solutions were then evaporated to dryness and the residue was dissolved in the minimum volume of *n*-heptane to eliminate the chromium complex and to concentrate the reaction products before the analyses. Thin layer chromatography was performed on SiO_2 plastic sheets (Merck Kieselgel 60F 254) using a 9:1 (by volume) hexane:ether mixture as eluent. When necessary, deaeration was carried out by the freeze-pump-thaw

method. Parallel analyses were always performed on samples maintained in the dark to provide a control for the thermal reactions.

3. Results

3.1. Electrochemical measurements

From the cyclic voltammograms it is seen that *t*-StN undergoes a reversible reduction at -1.1 V (measured with respect to a saturated calomel electrode (SCE)) and a slightly irreversible oxidation at $+1.4$ V. Both processes are independent of the substrate concentration (2×10^{-5} - 6×10^{-4} M). For the *cis* isomer, reversible reduction occurs at -0.9 V and irreversible oxidation at $+1.6$ V.

3.2. Emission quenching experiments

$\text{Cr}(\text{bpy})_3^{3+}$ shows emission ($\lambda_{\text{max}} = 728$ nm) from its lowest 2E_g excited state in fluid solution at room temperature [9]. In CH_3CN solution, the emission lifetime is 34 ± 2 μs and 48 ± 3 μs in air-equilibrated and deaerated solutions respectively. Both the intensity and the lifetime of this emission are quenched by *t*-StN (complex concentration, 1×10^{-3} M; excitation at 400 nm for the intensity measurements) in a parallel way; the quenching effect increased linearly with the quencher concentration (7×10^{-6} - 8×10^{-5} M), according to a bimolecular quenching constant k_q^t of $(8 \pm 1) \times 10^8$ $\text{M}^{-1} \text{s}^{-1}$ in both air-equilibrated and deaerated solutions.

$\text{Cr}(\text{bpy})_3^{3+}$ emission is also quenched by *c*-StN (1×10^{-4} - 2×10^{-3} M); under the same experimental conditions as above, we obtained $k_q^c = (5 \pm 1) \times 10^7$ $\text{M}^{-1} \text{s}^{-1}$.

No quenching effect by *t*-StN (1×10^{-5} - 2×10^{-3} M) was observed on the emission of $\text{Os}(\text{phen})_3^{2+}$ ($\lambda_{\text{max}} = 730$ nm; $\tau = 260$ ns) [10].

3.3. Continuous photolysis experiments

The continuous photolysis of solutions containing $\text{Cr}(\text{bpy})_3^{3+}$ and *t*-StN was performed by exciting with 405 nm light, which is only absorbed by the chromium complex. The concentration of *t*-StN was varied in the range 4×10^{-5} - 4×10^{-4} M and that of $\text{Cr}(\text{bpy})_3^{3+}$ was always twice as large. (The use of higher concentrations was prevented by the upper limit of the photometric range of the spectrometer.)

In air-equilibrated solutions, the spectral changes caused by irradiation (e.g. Fig. 1(a)) are characterized mainly by a progressive and permanent decrease in the absorbance in the 250 - 360 nm range. No spectral variation was observed above 360 nm. The effect of the concentration of *t*-StN on the rate of decrease in the absorbance was determined by using cells of different optical paths to compensate for the change in concentration of $\text{Cr}(\text{bpy})_3^{3+}$ and to maintain the amount of the absorbed exciting light constant. Under these conditions, we found that the change in absorbance at 318 nm caused by a 20 min irradiation decreases as the concentration of *t*-StN increases (Fig. 2).

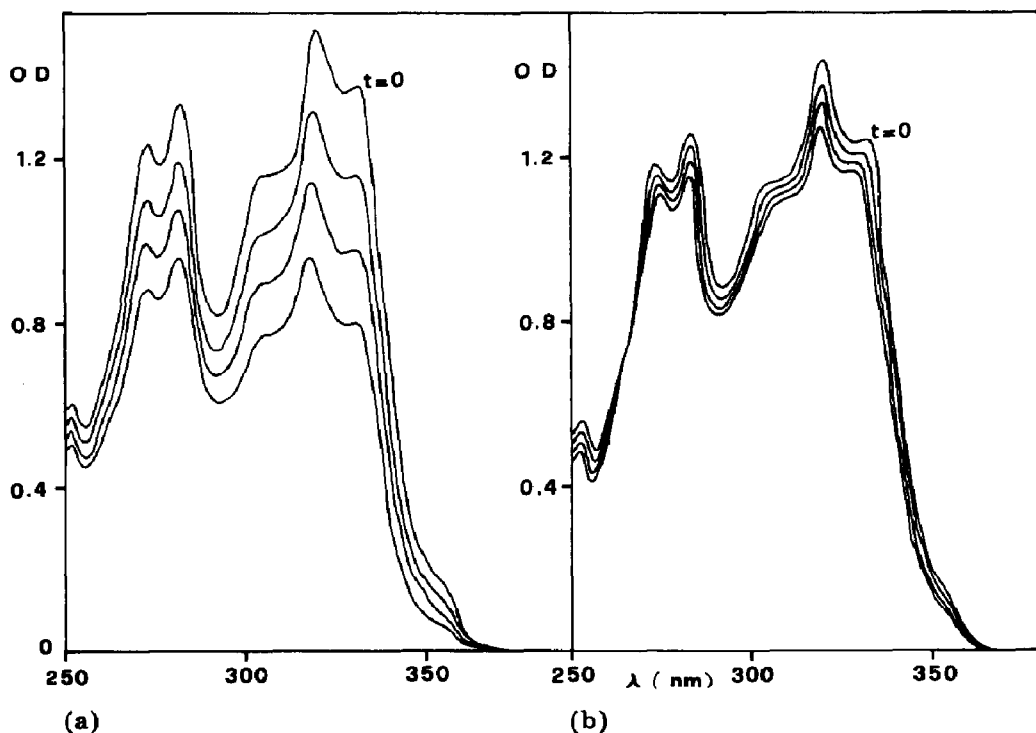


Fig. 1. Spectral changes caused by irradiation (0, 40, 100 and 180 min) on solutions containing 4×10^{-5} M *t*-StN and 8×10^{-5} M $\text{Cr}(\text{bpy})_3^{3+}$ (relative to 8×10^{-5} M $\text{Cr}(\text{bpy})_3^{3+}$; OD, optical density): (a) air-equilibrated solution; (b) deaerated solution.

In contrast, a greater decrease in the absorbance was observed for oxygen-saturated solutions with respect to air-equilibrated solutions (Fig. 2).

Thin layer chromatography of the irradiated air-equilibrated solutions revealed the presence of *c*-StN, benzaldehyde and 2-naphthaldehyde in addition to the original organic reactant. The production of the carbonyl compounds was confirmed by gas chromatography analyses.

A reliable quantitative determination of the various products was prevented by the limit in the initial concentration of *t*-StN imposed by the kinetic behaviour of the reaction. However, a lower limit for the quantum yield for the disappearance of *t*-StN could be evaluated from the initial spectral changes at 316 nm on the assumption that the products do not absorb at this wavelength; the values are 3×10^{-3} and 6×10^{-4} for $[\textit{t}\text{-StN}] = 4 \times 10^{-5}$ M and $[\textit{t}\text{-StN}] = 4 \times 10^{-4}$ M respectively.

The spectral changes caused by 405 nm light on deaerated solutions containing 8×10^{-5} M $\text{Cr}(\text{bpy})_3^{3+}$ and 4×10^{-5} M *t*-StN are reported in Fig. 1(b). With respect to the behaviour of the air-equilibrated solutions, we can note a slower decrease in the absorbance in the 270 - 360 nm region and an isosbestic point at approximately 264 nm. The spectral changes in the deaerated solutions are those expected for the conversion of *t*-StN into the *cis* isomer. The occurrence of a clean photoisomerization was

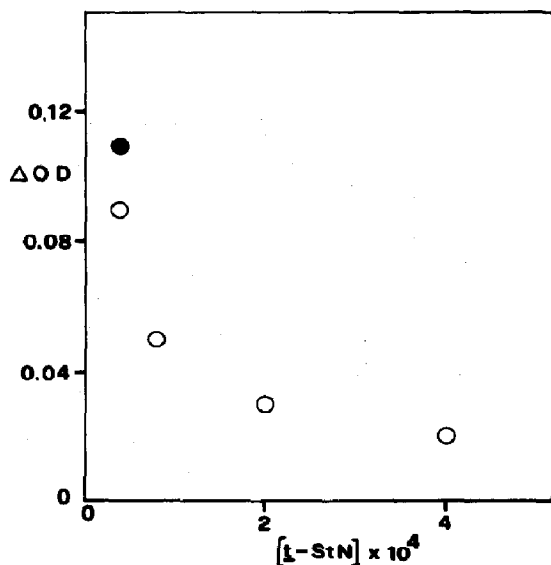


Fig. 2. Decrease in absorbance at 316 nm caused by a 20 min irradiation on air-equilibrated solutions: ●, oxygen-saturated solution.

confirmed by thin layer chromatography which revealed the presence of *t*-StN and *c*-StN alone in the irradiated solutions.

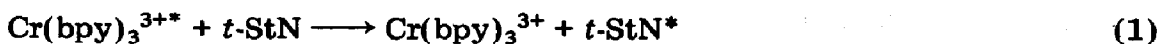
The rate of variation in the optical density was found to decrease as the irradiation time increased, and prolonged irradiation led to a photo-stationary state in which the $[t\text{-StN}]_{ss}/[c\text{-StN}]_{ss}$ ratio was 2.2 ± 0.4 .

A quantum yield for photoisomerization of $(2 \pm 0.5) \times 10^{-3}$ was calculated from the initial spectral changes at 316 nm. No reaction was observed in solutions maintained in the dark for more than 10 h.

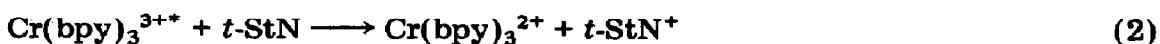
Formation of benzaldehyde and naphthaldehyde was also observed in air-equilibrated solutions containing 8×10^{-4} M *t*-StN and 2.5×10^{-5} M $\text{Os}(\text{phen})_3^{2+}$ on irradiation with light ($\lambda > 400$ nm) which was only absorbed by the complex. In contrast, no reaction was observed on prolonged irradiation of deaerated solutions. (In some experiments in which the solutions were not carefully protected from the laboratory light a small amount of *c*-StN was produced as a result of the direct photoisomerization of *t*-StN.)

4. Discussion

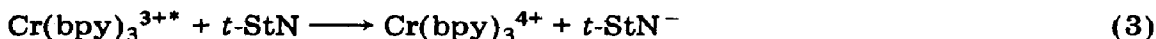
The quenching of the 2E_g excited state of $\text{Cr}(\text{bpy})_3^{3+}$ by *t*-StN can, in principle, be due to energy transfer



or to either reductive electron transfer



or oxidative electron transfer



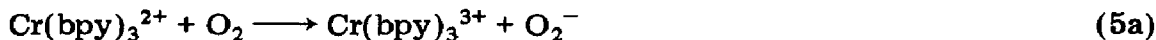
These mechanisms can be distinguished on the basis of thermodynamic considerations. The electronic energy E_{00} , the reduction potential $E(\text{Cr}(\text{bpy})_3^{3+*} | \text{Cr}(\text{bpy})_3^{2+})$ and the oxidation potential $E(\text{Cr}(\text{bpy})_3^{3+*} | \text{Cr}(\text{bpy})_3^{4+})$ of $(^2E_g)\text{Cr}(\text{bpy})_3^{3+*}$ are $13.7 \times 10^3 \text{ cm}^{-1}$, +1.45 V and less than +0.1 V respectively [9]. From a comparison of these data with the triplet energy of $t\text{-StN}$ ($(18.6 - 16.5) \times 10^3 \text{ cm}^{-1}$) [11 - 13] and its redox potentials (see Section 3), it appears that energy transfer (reaction (1)) and oxidative electron transfer (reaction (3)) are too endoergonic to give a noticeable contribution to the quenching process. However, reductive electron transfer (reaction (2)) is energetically allowed, and thus it may be considered to be mainly responsible for the quenching. Analogous arguments lead to the same conclusion for the quenching of $\text{Cr}(\text{bpy})_3^{3+*}$ by $c\text{-StN}$. The difference between k_q^t and k_q^c parallels the difference between the oxidation potentials of $t\text{-StN}$ and $c\text{-StN}$, in agreement with the suggested quenching mechanism.

We can therefore conclude that the photochemical processes that originate from the quenching of $\text{Cr}(\text{bpy})_3^{3+*}$ by $t\text{-StN}$ represent reactions of the cationic radical of the olefin. Two photochemical reactions, namely geometrical isomerization and (in air-equilibrated solutions) oxidation of the ethylenic double bond, were observed under our experimental conditions. Both these reactions cause a decrease in absorbance in the 320 nm absorption band of $t\text{-StN}$, in agreement with the experimental results. (Spectral variations analogous to those of Fig. 1 had already been observed in the UO_2^{2+} -sensitized photoisomerization of stilbene in both air-equilibrated and deaerated solutions [14].) Oxidation is expected to cause a greater decrease in absorbance than isomerization, because its products (benzaldehyde and 2-naphthaldehyde) almost do not absorb in this region. The photo-oxidation process may in principle occur through any of the following mechanisms.

(a) O_2 attacks the $t\text{-StN}^+$ produced in the primary electron transfer (reaction (2)) directly:



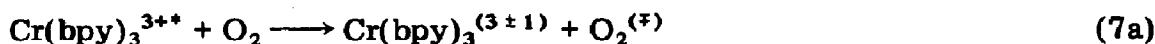
(b) Reduction of O_2 by $\text{Cr}(\text{bpy})_3^{2+}$ (formed in reaction (2)) is followed by reaction between O_2^- and $t\text{-StN}^+$ [15] or $t\text{-StN}$:



(c) Energy transfer between $\text{Cr}(\text{bpy})_3^{3+*}$ and O_2 [16] is followed by oxidation of $t\text{-StN}$ by $^1\text{O}_2$:



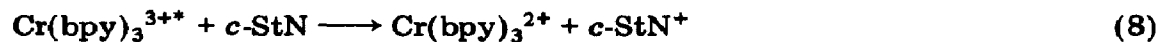
(d) Electron transfer occurs between $\text{Cr}(\text{bpy})_3^{3+*}$ and O_2 (both oxidative and reductive electron transfer cannot be excluded *a priori* [16], even if they seem to be endoergonic), and the O_2 radical reacts with *t*-StN:



The observed reduction in the rate of decrease in the optical density at 316 nm when the concentration of *t*-StN is increased is evidence against paths (4) and (5); in these two paths, in fact, both oxidation and isomerization rates would increase with increasing concentration of *t*-StN. In contrast, mechanisms (6) and (7), which involve a competition between O_2 and *t*-StN for the quenching of $\text{Cr}(\text{bpy})_3^{3+*}$, are expected to cause the observed trend in the rate of variation in the optical density. We suggest mechanism (6) as the most likely path for the photo-oxidation reaction because it is exoergonic and also because the electron transfer step (7a), if it occurs, would probably be followed by a rapid back electron transfer, as occurs with other polypyridine complexes [17, 18].

Our suggestion is supported by the presence of benzaldehyde and 2-naphthaldehyde in irradiated air-equilibrated solutions containing *t*-StN and $\text{Os}(\text{phen})_3^{2+}$. Since the excited state of the complex is not quenched at all by *t*-StN and it is known [18] to produce $^1\text{O}_2$ with high efficiency, the carbonyl compounds can only be formed through a mechanism analogous to reaction (6).

The *trans* \rightarrow *cis* isomerization that occurs in deaerated solutions originates from the electron transfer reaction (2), and the same mechanism is probably responsible for the formation of *c*-StN in air-equilibrated solutions. When the fraction of $\text{Cr}(\text{bpy})_3^{3+*}$ quenched by *t*-StN under our experimental conditions is taken into account, the limiting quantum yield ϕ_{lim}^t of *c*-StN production (*i.e.* the value of the quantum yield corresponding to complete quenching of $\text{Cr}(\text{bpy})_3^{3+*}$ by *t*-StN) is $(3.3 \pm 0.8) \times 10^{-3}$. The photostationary state reached on prolonged irradiation probably results from the reverse isomerization induced by quenching of $\text{Cr}(\text{bpy})_3^{3+*}$ by *c*-StN:



According to this hypothesis, the limiting quantum yield ϕ_{lim}^c for the isomerization of *c*-StN evaluated by means of

$$\frac{[t\text{-StN}]_{ss}}{[c\text{-StN}]_{ss}} = \frac{k_q^c}{k_q^t} \frac{\phi_{\text{lim}}^c}{\phi_{\text{lim}}^t}$$

is 0.12 ± 0.05 . A radical cation path therefore seems to be more efficient for *cis* \rightarrow *trans* isomerization than for the reverse process. This conclusion is

consistent with the observation [19] that the *trans* radical cation is formed predominantly from electron impact of either *cis*- or *trans*-stilbene.

It is possible that our *trans* \rightarrow *cis* and *cis* \rightarrow *trans* isomerizations involve a common intermediate (e.g. a twisted perpendicular radical cation). In such a case, the intermediate should decay to *t*-StN and *c*-StN in a ratio equal to $\phi_{lim}^c/\phi_{lim}^t$, but it should be formed with an efficiency of less than unity because $\phi_{lim}^c + \phi_{lim}^t < 1$. It is possible that a rapid back electron transfer between $Cr(bpy)_3^{2+}$ and *t*-StN⁺ (or *c*-StN⁺) within the solvent cage prevails over escape from the cage and twisting of the radical.

It is interesting to compare our results with other isomerization mechanisms. Both direct excitation and triplet energy transfer of *t*-StN in CH₃CN cause isomerization with quantum yields much higher [3, 4] than our value. Moreover, the photostationary composition indicates [4, 13] that the triplet excited state decays to *trans* and *cis* ground state molecule in a 1:1 ratio. Therefore, the triplet excited state of *t*-StN seems to undergo *trans* \rightarrow *cis* isomerization more readily than the cationic radical. This last conclusion excluded the hypothesis that a radical cation mechanism could contribute to the photoisomerization of *t*-StN in the presence of the electron acceptors *p*-dicyanobenzene and bis(dicyanomethylene)-2,2,4,4-tetramethylcyclobutane; the addition of these substances was in fact found [4] to increase the quantum yield of isomerization.

Both *cis* \rightarrow *trans* and *trans* \rightarrow *cis* isomerizations of the *N*-methyl-4-(β -styryl)pyridinium ion were found [1] to be photochemically induced by zinc tetraphenylporphyrin through an oxidative electron transfer. (Analogous experiments carried out [1] with $Ru(bpy)_3^{2+}$ as the sensitizer are less significant because energy transfer and electron transfer may occur simultaneously [2].) The quantum yield ratio (about 20) was close to the $\phi_{lim}^c/\phi_{lim}^t$ value determined in this work, which suggests that anion and cation radicals of stilbene derivatives have similar properties in relation to isomerization. No other reactions, apart from isomerization, could be detected in deaerated solutions. This result is in apparent contrast with the finding [20] that dimerization of styrene derivatives may occur through a radical cation mechanism. This discrepancy can be well explained, however, by the large difference between the substrate concentrations used in our experiments and in the dimerization experiments.

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