PHOTOSENSITIZED *CIS–TRANS* ISOMERIZATION OF NITROSTILBENES IN SOLVENTS OF DIFFERENT POLARITY*

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(Received July 12, 1977)

Summary

The triplet sensitized *cis–trans* isomerization of 4-nitro-4'-methoxystilbene (NMS) in non-polar and polar solvents has been studied using 13 selected sensitizers. The photostationary *cis/trans* ratio at various triplet energies of the sensitizer and photoisomerization quantum yields are given. The fraction α' of NMS molecules in the planar and twisted triplet states decaying to the *trans* ground state is determined by two different methods. In the first α' is calculated from the *cis/trans* ratios employing high-energy sensitizers. In the second method α' is obtained from quenching measurements with ferrocene using naphthalene sensitized and directly excited photoisomerization conditions. For the latter method no assumptions about the rates of energy transfer from the sensitizer to the stilbene and about the yields of energy wastage are necessary. Results from both methods are in reasonable agreement: the value of α' increases with increasing solvent polarity.

The decrease of the quantum yield $\phi_{t \to c}$ for the direct *trans* → *cis* isomerization of NMS and of 4-nitro-4'-dimethylaminostilbene (NDMAS) with increasing solvent polarity is accounted for by an increase of α' and by a radiationless deactivation step from the excited *trans* singlet state to the *trans* ground state bypassing the triplet state. Results for 4-nitrostilbene, 4,4'-dinitrostilbene, 4-cyano-4'-dimethylaminostilbene and 4-cyano-4'-methoxystilbene in solutions of cyclohexane, benzene and/or methanol are also presented. For these stilbenes, in contrast to NMS and NDMAS, α' depends only slightly on substituents and solvents.

Introduction

The direct photochemical *cis–trans* isomerization of unsubstituted stilbene takes place in singlet states [1, 2]. In order to study the role of

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*This publication is considered to be no. VII in the series on *cis–trans* isomerization of nitrostilbenes.

triplet states in the photoisomerization process, sensitized excitation is necessary [1 - 5]. High energy triplet sensitizers transfer energy efficiently to *cis* and *trans* triplet states of stilbene [6, 7].

In the case of 4-nitro-4'-methoxystilbene (NMS), triplet sensitized *cis–trans* isomerization has been studied in benzene solutions [8] and in molten naphthalene [9] using γ irradiation. The triplet energy of the *trans* isomer was determined to be 46.5 kcal mol^{-1} and for the *cis* isomer it was estimated to be 53 kcal mol^{-1} [9].

In contrast to unsubstituted stilbene the triplet states of substituted 4-nitrostilbenes can be generated at room temperature by direct excitation [10, 11]. Nevertheless it is necessary to investigate the sensitized isomerization in order to calculate the fraction of triplet states which decay to the *trans* and to the *cis* ground states (α' and $1 - \alpha'$ respectively). A variation of α' could account for the decrease of $\phi_{t \to c}$ for NMS with increasing solvent polarity [12 - 14]. Results of α' determinations for several nitrostilbenes in various solvents are presented in this paper. A recently proposed model for the photochemical *cis–trans* isomerization of substituted 4-nitrostilbenes [11] has been used to evaluate the data obtained.

Experimental

The sensitized photoisomerization measurements were performed using excitation wavelengths of 254 nm, 313 nm and 417 nm. The 417 nm and 313 nm wavelengths were isolated from the emission of a xenon arc lamp (XBO 450 W) using interference filters (Schott) with bandwidths of almost 7 nm. The 254 nm wavelength was isolated from a low pressure mercury lamp (Gräntzel, Karlsruhe) by a reflection filter (Schott, UV-R-250).

All samples were degassed (argon bubbled through for at least 30 min) and irradiated in 1 mm Suprasil absorption cells. Two samples, one containing *cis* and the other *trans* nitrostilbene isomer, were irradiated simultaneously under the same conditions. The photostationary state was reached from both isomers in 10 - 100 min. In the case of cyanostilbenes the photostationary state was reached from the *trans* form and from a mixture of isomers containing about 80% *cis* form. The concentrations of stilbenes and sensitizers were adjusted so that the sensitizer absorbed almost 99% of the incident light intensity. Typical concentrations used were 5×10^{-2} M for sensitizers and 5×10^{-4} M for cyanostilbene or nitrostilbene isomers. It was shown that the very small direct excitation of cyanostilbenes or nitrostilbenes did not affect the sensitized isomerization measurements.

The percentages of *trans* and *cis* isomers were determined spectroscopically (at different wavelengths after given time intervals) using a spectrophotometer (Zeiss, PMQ II). In several cases the percentages of isomers in the photostationary state were also determined by gas chromatography. The quantum yields were obtained according to the method of Malkin and Fischer [5] by triphenylene sensitized photoisomerization. Potassium ferrioxalate actinometry was employed [15].

The *trans* and *cis* isomers of 4-nitro-4′-methoxystilbene (NMS), 4-nitro-stilbene (NS), 4,4′-dinitrostilbene (DNS), 4-nitro-4′-dimethylaminostilbene (NDMAS) and the *trans* isomers of 4-cyano-4′-dimethylaminostilbene (CDMAS) and 4-cyano-4′-methoxystilbene (CMS) were prepared as described elsewhere [13, 16]. For CMS and CDMAS the mixture of isomers containing about 80% *cis* form was prepared by irradiation of the *trans* form at 366 nm.

All nitrostilbenes are more than 99% pure and *trans* and *cis* isomers were found by gas chromatography to contain less than 2% of the other isomer. The sensitizers, listed in Table 1, were of the purest commercial quality available, recrystallized twice or zone refined; the purity was determined by gas chromatography.

The solvents (Merck) were of spectroscopic quality, and the ferrocene (Merck, 99.9% pure) was recrystallized twice.

TABLE 1

Sensitizer	Supplier[a]	Purity (%)
Acetophenone	Merck, Darmstadt	99.2
Anthracene	Merck (r)	99.7
Azulene	Aldrich	99.3
Benzil	Merck (z)	99.98
Benzophenone	Merck (r)	99.95
Biacetyl	Merck-Schuchardt	99.93
Chrysene	Merck (z)	98.0
Fluorenone	Merck-Schuchardt (r)	99.1
Naphthalene	Merck (z)	99.94
1-Naphthonitrile	Ega-Chemie (r)	99.8
Phenanthrene	Schuchardt (z)	98.98
Pyrene	Fluka	97.5
Triphenylene	Rütgerswerke (r)	98.1

[a]r, recrystallized twice; z, zone refined.

Results

The *cis/trans* ratios ($[c]/[t])_{sens}$ in the photostationary state under conditions of sensitized excitation have been measured for various sensitizers. The same values for ($[c]/[t])_{sens}$ were obtained within experimental error (±15%) when irradiation wavelengths of 254 nm and 313 nm were used. A wavelength of 417 nm was used when biacetyl was the sensitizer. In benzene solutions of NMS no interaction between solvent and sensitizers and no chemical reactions were observed. In cyclohexane, methanol and dimethyl-formamide solutions fewer sensitizers could be used owing to chemical side reactions [17].

In Fig. 1 plots of ($[c]/[t])_{sens}$ as a function of the triplet energy E_T of the sensitizer (Saltiel plots) are shown for benzene, methanol, cyclohexane
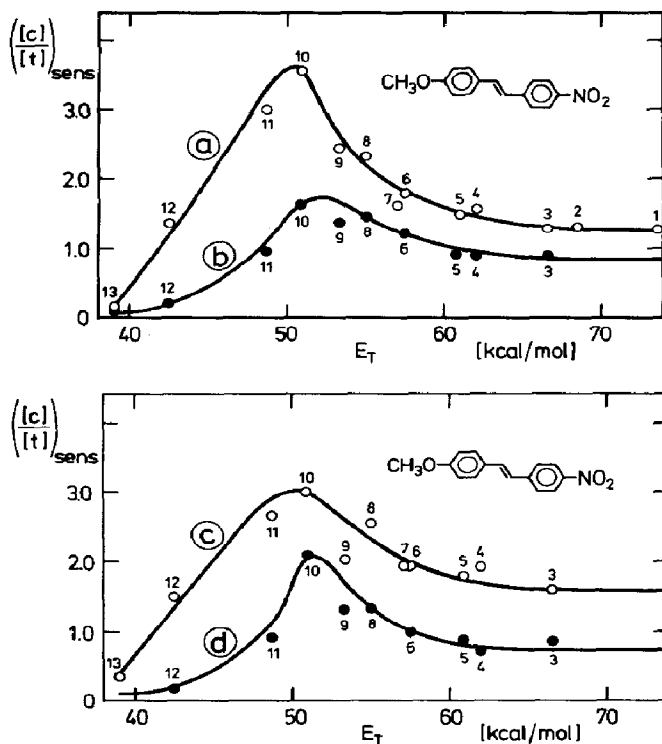
Fig. 1. *Cis/trans* ratio in the photostationary state as a function of the triplet energy of the sensitizer (Saltiel plot) for NMS. Curves a - d refer to oxygen-free solutions of benzene, methanol, cyclohexane and dimethylformamide, respectively. The following conditions were used ($t = 25$ °C):

No.	Sensitizer	Irradiation wavelength(s) (nm)		E_T (kcal mol^{-1})	Reference
1	Acetophenone	254	313	73.6	2, 6, 17
2	Benzophenone	254	313	68.5	2, 6, 17
3	Triphenylene	254	313	66.6	6, 17
4	Phenanthrene	254	313	62.0	2, 6, 17
5	Naphthalene	254	313	60.9	2, 17
6	1-Naphthonitrile	254		57.5	18
7	Chrysene	254		57.0	2, 17
8	Biacetyl	417		55.0	2, 17
9	Fluorenone	254	313	53.3	2, 6, 17
10	Benzil	254		50.9	2
11	Pyrene	254	313	48.7	2, 3, 17
12	Anthracene	254		42.5	2, 3, 17
13	Azulene	254		39	20

and dimethylformamide solutions of NMS. Starting from the high triplet energy side, on decreasing E_T the ratio $([c]/[t])_{sens}$ increases in all solvents to a maximum value and decreases again. The triplet energy at which the maximum ratio $([c]/[t])_{sens}$ is obtained is defined as E_T^0.

Using high triplet energy sensitizers the *trans* and the *cis* triplet states (tr^3 and c^3, respectively) are assumed to be populated at the same rate of energy transfer. When E_T is smaller than the energy of c^3 the percentage of the *cis* isomer is increased, since c^3 is higher in energy than tr^3 [9] and the amount of energy transfer to c^3 is reduced. However, when E_T becomes smaller than the energy of tr^3 ($E_T < E_T^0$), energy transfer to both triplet states is reduced and the percentage of *cis* isomer decreases. As a consequence of this inefficient energy transfer longer irradiation times are necessary to establish the photostationary state.

The values for $([c]/[t])^*_{sens}$, which refer to the photostationary *cis/trans* ratio extrapolated to $E_T \approx 70$ kcal mol^{-1}, are listed in Table 2. On increasing solvent polarity $([c]/[t])^*_{sens}$ decreases.

TABLE 2

Values for E_T^0, $([c]/[t])^*_{sens}$, triphenylene sensitized quantum yields and α' derived from sensitized photoisomerization measurements (Saltiel plots) for NMS in several oxygen-free solvents

Solvent	E_T^0 (kcal mol^{-1})	$([c]/[t])^*_{sens}$	$\phi^{sens}_{t \to c}$	$\phi^{sens}_{c \to t}$	α' [a]
Cyclohexane	49	1.6	0.35	0.55	0.38
Benzene	50	1.3	0.40	0.50	0.43
Methanol	52	0.9	0.47	0.42	0.53
Dimethylformamide	52	0.8	0.45	0.40	0.56

[a]Calculated using eqns. (10) - (11b).

The dependence of $([c]/[t])^*_{sens}$ on E_T was also measured in the case of two cyanostilbenes and several other 4-substituted nitrostilbenes. The Saltiel plots for benzene and methanol solutions of 4-nitrostilbene (NS) and of 4,4'-dinitrostilbene (DNS) and for cyclohexane and benzene solutions of 4-nitro-4'-dimethylaminostilbene (NDMAS) are shown in Figs. 2, 3 and 4. The values for $([c]/[t])^*_{sens}$ and for E_T^0 are listed in Table 3. For NS and DNS the
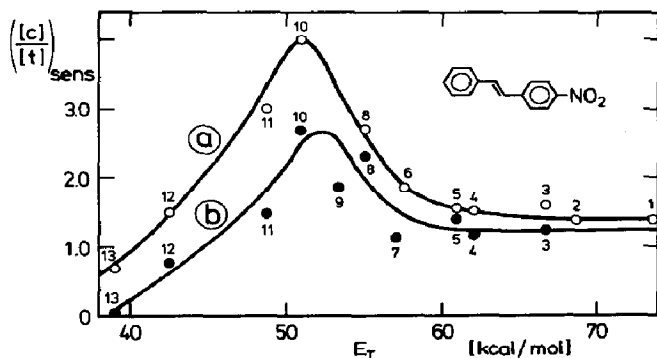

Fig. 2. Saltiel plots for (a) benzene and (b) methanol solutions of NS for the same experimental conditions as in Fig. 1.
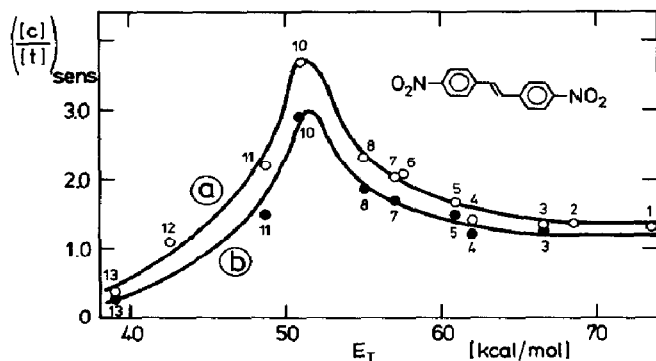
Fig. 3. Saltiel plots for (a) benzene and (b) methanol solutions of DNS for the same experimental conditions as in Fig. 1.
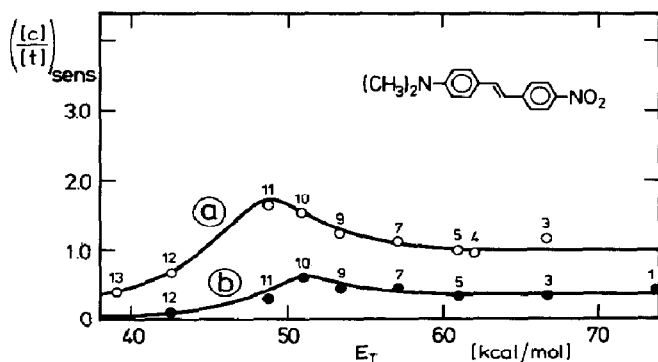

Fig. 4. Saltiel plots for (a) cyclohexane and (b) benzene solutions of NDMAS. Irradiation wavelength, 254 nm.

TABLE 3

Values for E_T^0, $([c]/[t])_{sens}^*$ and α' derived from Saltiel plots for various nitrostilbenes and cyanostilbenes in oxygen-free solutions

Compound	Solvent	E_T^0	$([c]/[t])_{sens}^*$	α'[a]
NS	Benzene	51	1.4	0.42
NS	Methanol	52	1.2	0.45
DNS	Benzene	51	1.4	0.42
DNS	Methanol	51	1.2	0.45
NDMAS	Cyclohexane	49	1.0	0.50
NDMAS	Benzene	51	0.35	0.74
NDMAS	Methanol	—	≤0.05	≥0.95
CMS	Benzene	51	1.4	0.42
CDMAS	Benzene	—	1.3	0.43

[a]Calculated using eqns. (10) - (11b).

ratio of $([c]/[t])^*_{sens}$ is almost constant; however, for NDMAS $([c]/[t])^*_{sens}$ decreases from 1.0 to 0.35 when the solvent is changed from cyclohexane to benzene and to 0.05 or less when it is changed to methanol.

The mechanism for direct *cis–trans* photoisomerization of cyanostilbenes may be different from that of the corresponding nitrostilbenes although the cyano group has electron-attracting properties similar to those of the nitro group. For 4-cyano-4'-methoxystilbene (CMS) it has been concluded that a singlet mechanism is operative [16, 19]. However, under sensitized excitation conditions the same isomerization mechanism should hold for nitrostilbenes and cyanostilbenes. Values for $([c]/[t])^*_{sens}$ were therefore also derived for CMS and for 4'-cyano-4'-dimethylaminostilbene (CDMAS) (Table 3).

In order to calculate α' independent of assumptions about the energy transfer mechanism, quenching measurements were performed using naphthalene as sensitizer ($E_T = 60.9$ kcal mol^{-1}) and ferrocene (Q) as quencher ($E_T = 39$ kcal mol^{-1}) [20]. Two samples containing *trans* or *cis* isomers, a suitable concentration of ferrocene and a concentration of about 1×10^{-1} M naphthalene were irradiated simultaneously either at 254 nm or at 313 nm. Linear dependences of $([t]/[c])_{sens}$ on [Q] were observed for all nitrostilbenes used. Values for the slope s_{sens} and for the ratio r_{sens} of slope to intercept measured in various oxygen-free solutions of NMS, NS and DNS are listed in Table 4. Linear plots of $([t]/[c])_{sens}$ as a function of the ferrocene concentration are shown for methanol, benzene and cyclohexane solutions of NMS and for methanol solutions of DNS in Fig. 5.

TABLE 4

Comparison of values for α' obtained from the Saltiel plots (α'_1) with those obtained from ferrocene quenching measurements (α'_2)

Compound	Solvent	s_{sens}	r_{sens} (M^{-1})	r_1[a] (M^{-1})	α'_1[b]	α'_2[c]
NMS	Cyclohexane	440	790	300	0.38	0.38
NMS	Benzene	990	1600	790	0.49	0.43
NMS	Methanol	5000	5000	2700	0.54	0.53
NMS	Dimethylformamide	5300	4100	2100	0.51	0.56
NS	Benzene	520	810	320	0.40	0.42
NS	Methanol	1280	1600	650	0.41	0.45
DNS	Benzene	1140	1900	740	0.39	0.42
DNS	Methanol	1520	2270	1040	0.46	0.45

Values for the ratio of slope to intercept using direct (r_1) and sensitized ($r_{sens} = s_{sens}/i_{sens}$) excitation conditions.

[a] From ref. 22.
[b] Calculated using eqn. (16).
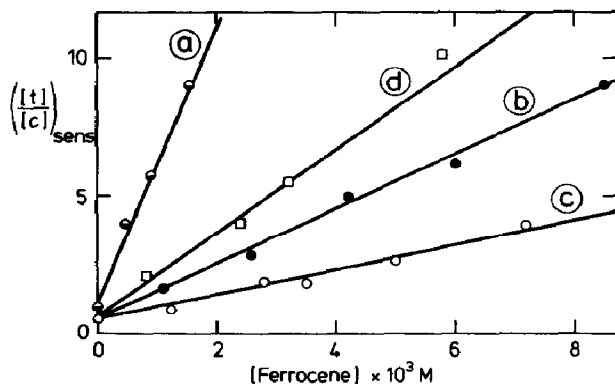[c] From Tables 2 and 3.

Fig. 5. *Trans/cis* ratio in the photostationary state under naphthalene-sensitized excitation conditions as a function of the ferrocene concentration for NMS and for DNS in oxygen-free solutions. The linear dependences for NMS were obtained in solutions of (a) methanol, (b) benzene and (c) cyclohexane, and (d) for DNS in methanol. Irradiation wavelengths, 254 nm or 313 nm; $t = 25$ °C.
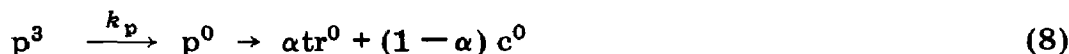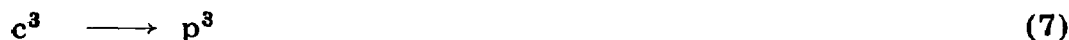
Treatment of the data

The following reaction scheme is used to account for the energy transfer from the sensitizer molecule (S) to *cis* and *trans* forms of cyanostilbenes or nitrostilbenes.

$$S \quad + \quad h\nu \quad \xrightarrow{k_a} \quad {}^1S^* \tag{1}$$

$$ {}^1S^* \quad \longrightarrow \quad {}^3S^* \tag{2a}$$

$$ {}^3S^* \quad \xrightarrow{k_b} \quad S \tag{2b}$$

$$ {}^3S^* \quad + \quad c^0 \quad \xrightarrow{k_{s \to c}} \quad S \quad + \quad c^3 \quad (\text{or } c^0) \tag{3}$$

$$ {}^3S^* \quad + \quad tr^0 \quad \xrightarrow{k_{s \to t}} \quad S \quad + \quad tr^3 \quad (\text{or } tr^0) \tag{4}$$

Here, ${}^1S^*$ and ${}^3S^*$ refer to the first excited singlet state and the lowest triplet state of the sensitizer. The same symbols and abbreviations for the isomerization mechanism and the nitrostilbene states involved are used as in a previous paper [11]. The rate constants $k_{s \to t}$ and $k_{s \to c}$ refer to the energy transfer from ${}^3S^*$ to the lowest *trans* and *cis* triplet states of nitrostilbene, respectively. In the case of unsubstituted stilbene energy wastage has been found to occur for several sensitizers [6] and may also reduce energy transfer to the $tr^3 \rightleftharpoons p^3$ (where p^3 is the twisted triplet state) equilibrium in the case of nitrostilbenes. Other deactivation steps from ${}^3S^*$ to S, including quenching of ${}^3S^*$ (*e.g.* by ferrocene), are summarized by k_b. Quenching of the sensitizer triplets does not affect the position of the photostationary state. For high triplet energy sensitizers the absence of back-energy transfer from stilbene triplets to the donor molecule is assumed.

After rapid formation of an equilibrium between the *trans* and twisted triplet states (tr^3 and p^3 respectively, reaction (5)), two deactivation steps to the corresponding ground states (tr^0 and p^0 respectively, reactions (6) and (8)) are incorporated in the scheme. The reason for assuming the equilibrium in the following reaction has been given elsewhere [21, 22]:

$$tr^3 \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} p^3 \qquad (K_5 = k_5/k_{-5}) \tag{5}$$

$$tr^3 \longrightarrow tr^0 \tag{6}$$

$$c^3 \longrightarrow p^3 \tag{7}$$

$$p^3 \xrightarrow{k_p} p^0 \to \alpha tr^0 + (1-\alpha)\, c^0 \tag{8}$$

The quantum yields for sensitized photoisomerization, $\phi_{t\to c}^{sens}$ and $\phi_{c\to t}^{sens}$, are defined by eqn. (9) [5]. Here I_{abs} (in quanta $s^{-1} \times cm^{-3}$) denotes the rate of light absorption by the sensitizer.

$$\frac{d[tr^0]}{dt} = \frac{I_{abs}}{k_b + k_{s\to t}[tr^0] + k_{s\to c}[c^0]} \left(-\phi_{t\to c}^{sens} k_{s\to t}[tr^0] + \phi_{c\to t}^{sens} k_{s\to c}[c^0]\right) \tag{9}$$

For high triplet energy sensitizers it is assumed that the rates of exothermic energy transfer $k_{s\to t}$ and $k_{s\to c}$ are equal. Thus $([c]/[t])_{sens}^*$ in eqn. (10) is obtained by setting the left-hand side of eqn. (9) to zero:

$$\left(\frac{[c]}{[t]}\right)_{sens}^* = \frac{\phi_{t\to c}^{sens}}{\phi_{c\to t}^{sens}} \tag{10}$$

According to the proposed scheme [11] the quantum yields for isomerization under sensitized conditions are given by the following simple formulae:

$$\phi_{t\to c}^{sens} = \phi_{ISC}^s (1-\phi_t')(1-\alpha') \tag{11a}$$

$$\phi_{c\to t}^{sens} = \phi_{ISC}^s (1-\phi_c')\alpha' \tag{11b}$$

ϕ_{ISC}^s is the intersystem crossing (ISC) quantum yield of the sensitizer, ϕ_c' and ϕ_t' are the yields for energy wastage during the quenching processes (eqns. (3) and (4)) and α' is given by

$$\alpha' = \frac{\alpha + A_0}{1 + A_0} \tag{12}$$

where $A_0 = k_6/(K_5 k_p)$ defines competition of deactivation steps (6) and (8) in the absence of quenchers. From eqns. (10) - (12) it follows that α, the fraction of p^3 decaying to tr^0 via the twisted ground state p^0, cannot be calculated from $([c]/[t])_{sens}^*$ without knowledge of A_0. Therefore α has been replaced by α', the fraction of molecules in the $tr^3 \rightleftharpoons p^3$ triplet equilibrium decaying to tr^0. The values of α' calculated from $([c]/[t])_{sens}^*$ are listed in Tables 2 and 3.

A second method for determination of α' was employed using ferrocene (Q) as quencher. It has been established by direct photoisomerization measurements [10, 11, 23] that ferrocene quenches the tr^3 state of substituted 4-nitrostilbene efficiently. Therefore quenching step (13) is also incorporated in the scheme:

$$tr^3 + Q \xrightarrow{k_Q} tr^0 + Q \qquad (Q \text{ or } Q^3) \tag{13}$$
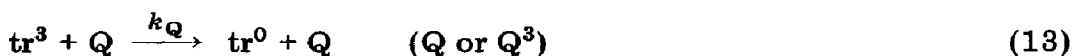
The *trans/cis* ratio in the photostationary state (in the absence of back-energy transfer from the stilbene to the sensitizer) which is obtained from eqns. (5) - (9) and eqn. (13) is given by

$$\left(\frac{[t]}{[c]}\right)_{sens} = \frac{k_{s\to c}}{k_{s\to t}} \frac{1 - \phi_c'}{1 - \phi_t'} \frac{\alpha}{1 - \alpha} \left(1 + \frac{A_0}{\alpha}\right) \left(1 + \frac{K_Q}{\alpha + A_0} [Q]\right) \tag{14}$$

where $K_Q = k_Q/(K_5 k_p)$ defines the decay (eqn. (8)) and the quenching by ferrocene (eqn. (13)) of the $tr^3 \rightleftharpoons p^3$ equilibrium in the absence of oxygen. The ratio $([t]/[c])_{sens}$ is linearly dependent on the ferrocene concentration (eqn. (14)).

The factor α' was calculated by comparing results from ferrocene quenching measurements which were obtained by sensitized isomerization with those obtained by direct photoisomerization. For NMS, NS and DNS it has been shown in the case of direct photoisomerization that the ratio of the *trans–cis* quantum yields $\phi_{t\to c}^0/\phi_{t\to c}$ in the absence and presence of ferrocene is linearly dependent on [Q] [11, 22]. The ratio r_1 of slope to intercept from the Stern–Volmer plot is given by

$$r_1 = \frac{K_Q}{1 + A_0} \tag{15}$$

α' is simply given by eqn. (16), where r_{sens} is the ratio of slope to intercept of eqn. (14),

$$\alpha' = \frac{r_1}{r_{sens}} \tag{16}$$

Values for α' determined by the two different methods are in reasonable agreement (Table 4). It should be noted that r_{sens} is independent of the yields of energy wastage (ϕ_t' and ϕ_c') and also of the rates of energy transfer. This agreement suggests that the assumption about equally fast energy transfer from high energy sensitizer to the triplet states of NMS, NS and DNS is valid ($k_{s\to t} = k_{s\to c}$). For triphenylene sensitized photoisomerization of NMS it is concluded that energy wastage does not occur since the sum $\phi_{t\to c}^{sens} + \phi_{c\to t}^{sens}$ is almost 0.9 (Table 2) and equals the ISC quantum yield of triphenylene [17].

Discussion

It has been shown earlier for NMS that the quantum yield for direct *trans→cis* photoisomerization ($\phi_{t\rightarrow c}$) decreases strongly with increasing solvent polarity [12 - 14]. The reason for this effect could be due to an increase of α' or to a decrease of the population of the triplet state from the excited singlet *trans* state.

The factor α' increases with increasing polarity from 0.38 in cyclo-hexane to 0.56 in dimethylformamide (Table 2). Therefore the fraction of decay from the triplet equilibrium to the *trans* ground state is greater in polar solvents than in non-polar solvents. For NDMAS this effect is even more significant since α' increases from 0.50 in cyclohexane to 0.74 in benzene and to at least 0.95 in methanol solutions (Table 3). For NS and DNS, which are compounds without electron donating substituents, only a small change in α' is obtained in benzene as compared with methanol (Table 3).

The shift of α', however, is not large enough to explain completely the decrease of $\phi_{t\rightarrow c}$. For NMS, $\phi_{t\rightarrow c}$ decreases at room temperature by a factor of 10 when the solvent is changed from benzene to dimethylformamide [13] whereas α' changes only by a factor of 1.5. For NDMAS, $\phi_{t\rightarrow c}$ decreases by a factor of at least 10 when cyclohexane is replaced by benzene [13] (or toluene [14]) and α' changes by only a factor of 1.5. The reduction of $\phi_{t\rightarrow c}$ and hence of the quantum yields for the transition $tr^1 \rightarrow tr^3$ ($\phi_{1\rightarrow 3}$) is possible if the quantum yields of fluorescence (ϕ_f) or of internal conversion increase. Since for NMS, NS and DNS the transition $tr^1 \rightarrow p^1$ does not occur [11, 22], the quantum yield of internal conversion from tr^1 to tr^0 is given by $(1 - \phi_f - \phi_{1\rightarrow 3})$.

The ϕ_f of *trans* NMS is too small to account for the reduction of $\phi_{t\rightarrow c}$ in polar solvents since ϕ_f is less than 0.003 in methanol, 0.003 in ethanol and 0.09 in dimethylformamide at room temperature [17]. Since there is a reduction of the magnitude of $\phi_{1\rightarrow 3}$ it is concluded that a transition from an excited singlet *trans* state to the *trans* ground state (bypassing the lowest triplet state) should occur for NMS in polar solvents. It is interesting to note that for the case of thioindigo dyes non-radiative decay from the excited singlet states to the ground states has also been suggested [24].

Since the cyano compound CMS does not show a solvent dependence of $\phi_{t\rightarrow c}$ [19] and therefore no enhanced internal conversion in polar solvents, it is obvious that the $(n\pi)^*$ states in the nitro compound NMS are responsible for the increase of internal conversion. The mechanism of this internal conversion is unknown. A chemical reaction with a quantum yield greater than 0.01 leading to products has not been observed for NMS in polar and in non-polar solvents under conditions of direct photoisomerization [22].

It has been shown previously for NMS in cyclohexane solutions [11] that β (the fraction of p^1 decaying to tr^0) and ϕ_p (the ISC quantum yield for the transition $p^1 \rightarrow p^3$) can be derived by direct photoisomerization measure-

ments with the assumption that $\phi_{1\to3}$ is unity. From α' of 0.38 (Table 2), $\phi_{1\to3}$ is calculated to be 0.89 which is in reasonable agreement with this assumption. By combining results from direct and sensitized photoisomerization measurements the parameters α', β, $\phi_{1\to3}$ and ϕ_p which represent branching routes in the isomerization pathways can be calculated. This will be published shortly for NMS, NS and DNS in various solvents [22].

Acknowledgments

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