

## CIS-TRANS PHOTOISOMERIZATION OF 4-NITROSTILBENES

Dietrich Schulte-Frohlinde and Helmut Görner

Institut für Strahlenchemie im Max-Planck-Institut für Kohlenforschung,  
Stiftstr. 34-36, D-4330 Mülheim a.d. Ruhr, Federal Republic of Germany

Abstract - Results on cis-trans photoisomerization of 4-nitrostilbenes obtained in recent years are summarized and discussed. Mechanisms for the direct trans  $\rightarrow$  cis and cis  $\rightarrow$  trans photoisomerization are presented. The trans  $\rightarrow$  cis isomerization occurs via a triplet state as intermediate whereas in the cis  $\rightarrow$  trans isomerization the main route bypasses the triplet state. The triplet state shows a configurational equilibrium between the planar trans ( $tr^3$ ) and more twisted forms ( $p^3$  or  $c^3$ ). The equilibrium is mainly on the trans side. The influence of substitution, temperature, viscosity, solvent, and addition of quenchers on quantum yields of isomerization, fluorescence studies, and spectroscopic as well as kinetic laser flash photolysis results support the above conclusions.

### INTRODUCTION

The cis-trans photoisomerization of stilbene and various substituted stilbenes has been studied thoroughly during the last years and several comprehensive articles have appeared (Ref. 1-5). The most interesting result of these studies was that the direct trans  $\rightarrow$  cis photoisomerization of unsubstituted stilbene occurs in singlet states (Ref. 1,6). Triplet states which are observed in rigid media (Ref. 7-11) are not populated in the course of this interconversion in fluid solvents. Photoisomerization via triplet states has been observed in the case of triplet sensitization (Ref. 12-17) and partly for heavy-atom substituted stilbenes, e.g. 4-bromostilbene (Ref. 2, 17).

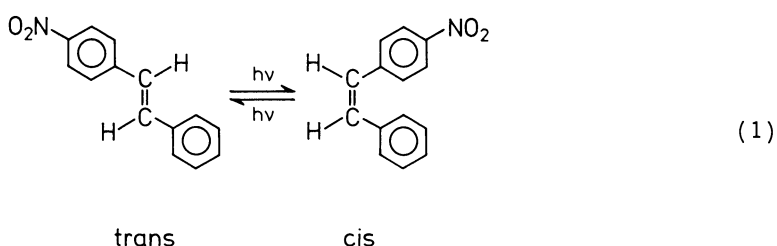
Recently the problem was raised whether or not for the stilbene molecule a configurational equilibrium exists in the excited singlet state which involves the planar trans ( $tr^1$ ) and the perpendicular ( $p^1$ ) states ( $tr^1 \rightleftharpoons p^1$ , Ref. 18,19). The  $p^1$  state is characterized by an angle of twist of  $90^\circ$  about the central double bond whereas  $tr^1$  has the planar trans configuration. The discussion of this problem is still in progress (Ref. 20, 21).

The present paper summarizes our knowledge of the direct cis-trans photoisomerization of 4-nitrostilbenes (Ref. 22-31). This class of compounds gives rise to triplet states on irradiation and it has been shown that these triplet states are intermediates in the direct trans  $\rightarrow$  cis and partly in the cis  $\rightarrow$  trans photoisomerization (Ref. 22,23,27). The problem of a configurational equilibrium in the triplet state arises and the results, summarized in the present paper indicate that indeed a  $tr^3 \rightleftharpoons p^3$  equilibrium exists. It is shown that the assumption of such an equilibrium explains the experimental results satisfactorily.

For thioindigo dyes (Ref. 32,33), phenyl-naphthylene-ethylenes (Ref. 34), and nitrostyrenes (Ref. 35,36) triplet states have been observed recently by flash photolysis. For the first two classes it has been shown that triplet states are intermediates in the cis-trans photoisomerization (Ref. 32-34,37).

### 1. Trans → Cis Photoisomerization of 4-Nitrostilbenes

Photoisomerization of stilbenes occurs via internal rotation about the C=C-double bond (eq. 1, Ref. 1,2). Inversion as a possible isomerization mechanism is suggested for the N=N-double bond, e.g. in azobenzenes (Ref. 38,39) and the C=N-double bond, e.g. in benzylideneanilines (Ref. 40) but not for stilbenes due to excessive energy requirements (Ref. 1).



The quantum yields for the direct trans → cis photoisomerization of various 4-nitrostilbenes in different solvents are listed in Table 1.

TABLE 1. Quantum yields of trans → cis ( $\phi_{t \rightarrow c}$ ) and cis → trans ( $\phi_{c \rightarrow t}$ ) photoisomerization, fluorescence ( $\phi_F$ ) of the trans isomer, and cyclization ( $\phi_{DHP}$ ) of the cis isomer for 4-nitrostilbenes at room temperature.

Compound	Solvent	$\phi_{t \rightarrow c}$ <sup>a</sup>	$\phi_{c \rightarrow t}$ <sup>a</sup>	$\phi_F$ <sup>b</sup>	$\phi_{DHP}$ <sup>c</sup>
4-Nitrostilbene	Benzene	0.50	0.34	$< 10^{-3}$	$7 \times 10^{-4}$ <sup>d</sup>
	Methanol	0.39	0.35		
4,4'-Dinitrostilbene	Benzene	0.47	0.30	$< 10^{-3}$	not measurable <sup>e</sup>
	Methanol	0.38	0.25		
4-Nitro-3'-methoxystilbene	Benzene	0.38	0.40		
	Methanol	0.28	0.40		
4-Nitro-4'-methoxystilbene	Cyclohexane	0.55	0.38		$\leq 10^{-4}$
	Benzene	0.53	0.37	$7 \times 10^{-3}$ <sup>f</sup>	
	Methanol	0.13	0.31	$1 \times 10^{-3}$	
	Dimethylformamide	0.05	0.41	$9 \times 10^{-2}$	

<sup>a</sup> Ref. 27,31,41,42; irradiation at 366 nm.

<sup>b</sup> Ref. 25; irradiation at 366 nm.

<sup>c</sup> Ref. 43; irradiation at 313 nm.

<sup>d</sup> In cyclohexane.

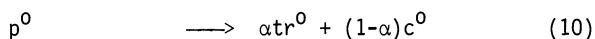
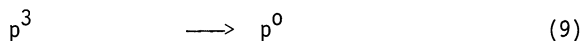
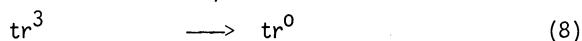
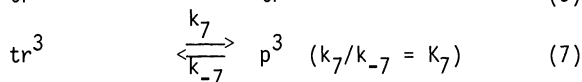
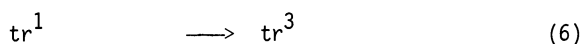
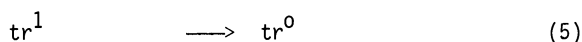
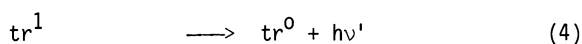
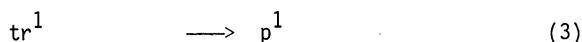
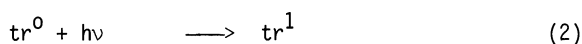
<sup>e</sup> In cyclohexane, Ref. 44.

<sup>f</sup> In toluene.

Contribution of photochemical formation of 4a,4b-dihydrophenanthrenes (DHP) is low for 4-nitrostilbenes (Table 1) in contrast to other stilbene derivatives (Ref. 43-45). The quantum yields presented in Table 1 are smaller than  $10^{-3}$ . Other side reactions at low stilbene concentrations (Ref. 46) do not seem to have been reported in the literature.

For the direct trans  $\rightarrow$  cis photoisomerization of 4-nitrostilbenes the following reaction scheme has been proposed (Scheme 1, Ref. 27).

## Scheme 1



Reaction 2 represents absorption of light by the trans ground state ( $\text{tr}^0$ ). The formed excited singlet trans state ( $\text{tr}^1$ ) fluoresces (eq. 4), decays to  $\text{tr}^0$  (eq. 5) or to the lowest triplet trans state ( $\text{tr}^3$ , eq. 6). Formation of a twisted (perpendicular) excited singlet state ( $\text{p}^1$ ) from  $\text{tr}^1$  (reaction 3) either does not occur or occurs only to a small extent. The further reactions of  $\text{p}^1$  are shown in Scheme 2. The  $\text{tr}^3$  state is in thermal equilibrium with the twisted triplet state ( $\text{p}^3$ , eq. 7). Fluorescence (eq. 4) does not play a significant role (Table 1). The incidence of the radiationless transition  $\text{tr}^1 \rightarrow \text{tr}^0$  (eq. 5) is large only in polar solvents and with 4-nitrostilbenes carrying a methoxy-, amino-, or substituted amino group in the 4'-position (Ref. 28,31).

Deactivation of the triplet states in equilibrium at room temperature is observed from  $\text{p}^3$  (eq. 9) but not from  $\text{tr}^3$  (eq. 8). The former step is an intersystem crossing which leads to a perpendicular ground state ( $\text{p}^0$ ) which subsequently converts to trans and cis forms depending on the coefficient  $\alpha$  (eq. 10).

Scheme 1 has been found to be valid for 4-nitro-, 2,4-dinitro-, 4,4'-dinitro-, 4-nitro-3'-methoxy-, 4-nitro-4'-methoxy-, and 4-nitro-2',5'-dimethoxystilbene. 4-Nitro-4'-amino- and 4-nitro-4'-dimethylaminostilbene also photoisomerize via triplet states, the mechanism however has not yet been studied in detail.

Experimental evidence for Scheme 1 is based on quantum yield data in different solvents as a function of temperature, viscosity, and concentration of triplet quenchers, on corresponding spectroscopic laser flash photolysis studies, and on fluorescence data. In the following sections the experimental results and arguments leading to the above scheme are presented in detail.

## 2. Triplet State as Intermediate in the Trans $\rightarrow$ Cis Photoisomerization

In Fig. 1 the decrease of  $\phi_{t \rightarrow c}$  is shown as a function of ferrocene concentration (Ref. 23,27). This decrease is not due to quenching of a fluorescent state because fluorescence quenching contributes at much higher ferrocene concentrations (Fig. 1).

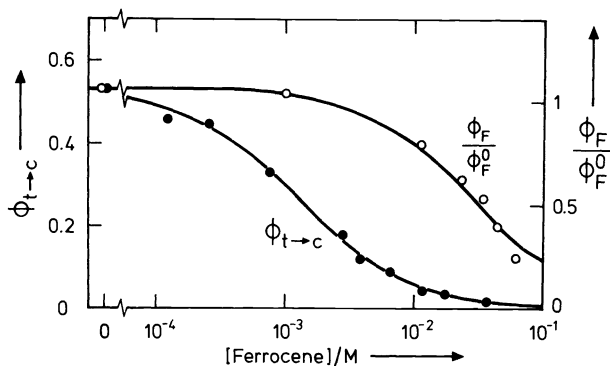


Fig. 1. Quantum yields of direct trans  $\rightarrow$  cis photoisomerization and of fluorescence as a function of ferrocene concentration for 4-nitro-4'-methoxystilbene in benzene at room temperature in the absence of oxygen; irradiation at 366 nm (Ref. 23,31).

Since there is no evidence for formation of a ground state complex by 4-nitro-4'-methoxystilbene and ferrocene or azulene it is concluded that ferrocene (or azulene) quenches an intermediate which is involved in the trans  $\rightarrow$  cis photoisomerization and which has a longer lifetime than the fluorescent state. These results suggest the intermediate to be a triplet state. Additional evidence is derived from the properties of the intermediate at low temperatures in rigid media and the comparison with the triplet state of stilbene (Ref. 7,8).

At high ferrocene concentrations  $\phi_{t \rightarrow c}$  tends to zero (Fig. 1). This indicates that ferrocene quenches the triplet state only to the trans form and shows that there is no trans  $\rightarrow$  cis isomerization pathway via excited singlet states in competition to the triplet route. Hence, in the trans  $\rightarrow$  cis photoisomerization every excited trans molecule which does not deactivate to  $tr^0$  via reactions 4 and 5 crosses to the triplet state. Quantum yield measurements under sensitized excitation conditions confirm this result (Ref. 28).

The postulated triplet state can be identified directly by spectroscopic laser flash photolysis. In Fig. 2 the absorption spectrum of the triplet state of 4-nitrostilbene is shown as an example. The triplet absorption maxima ( $\lambda_{max}$ ) and lifetimes of various nitrostilbenes in benzene at room temperature are listed in Table 2.

Since laser flash photolysis allows direct measurements of the lifetime ( $\tau = 1/k_0$ ) and rate constant for quenching reactions of the triplet state, it is possible to demonstrate kinetically that the triplet state is an intermediate in the trans  $\rightarrow$  cis photoisomerization. The ratio of trans  $\rightarrow$  cis quantum yields in the presence ( $\phi_{t \rightarrow c}$ ) and in the absence of quenchers

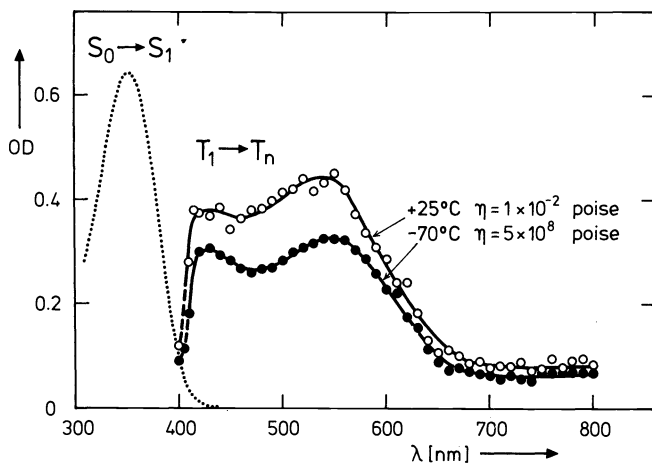


Fig. 2. Triplet absorption spectrum of trans-4-nitrostilbene in glycerol triacetate at room temperature (open circles) and at  $-70^{\circ}\text{C}$  (full circles) corresponding to viscosities of  $10^{-2}$  and  $5 \times 10^8$  poise, respectively, (Ref. 29) and absorption spectrum at room temperature (dotted line).

TABLE 2. Triplet absorption maxima and lifetime of various 4-nitrostilbenes in benzene in the absence of oxygen at room temperature (Ref. 22,27,31).

Compound	$\lambda_{\text{max}}$ , [nm] <sup>a</sup>	$\tau$ , [ns] <sup>a</sup>
4-Nitrostilbene	410, 535	65
2,4-Dinitrostilbene	430, 530	50
4,4'-Dinitrostilbene	500	95
4-Nitro-3'-methoxystilbene	410, 540	85
4-Nitro-4'-methoxystilbene	435, 600	150
4-Nitro-2',5'-dimethoxystilbene	450, 550, 790	200
4-Nitro-4'-aminostilbene	480, 680	300
4-Nitro-4'-dimethylaminostilbene	790	1000
3-Nitrostilbene	370	50
4-Cyano-4'-methoxystilbene	none	-

<sup>a</sup> Excitation at 347 and/or 353 nm.

( $\phi_{t \rightarrow c}^0$ ) plotted as a function of the ferrocene (or azulene) concentration ( $[Q]$ ) gives a straight line (Ref. 27). This indicates that only one intermediate along the trans  $\rightarrow$  cis route is quenched. The slope of this Stern-Volmer plot should represent the ratio of the rate con-

starts for the quenching reaction ( $k_Q$ ) and for decay of the triplet state in the absence of ferrocene ( $k_o$ , eq. 11).

$$\frac{\phi_{t \rightarrow c}^0}{\phi_{t \rightarrow c}} = 1 + \frac{k_Q}{k_o} [Q] \quad (11)$$

The ( $k_Q/k_o$ ) ratio measured by these two independent methods should be identical if the triplet state is an intermediate in the trans  $\rightarrow$  cis photoisomerization. Table 3 shows that ( $k_Q/k_o$ )-values obtained with both methods are in good agreement for various 4-nitrostilbenes and for different solvents. However, if singlet quenching were included in eq. 11 a larger discrepancy would arise between the values in the first two columns in Table 3.

It should be noted that no transient intermediate at room temperature (Table 2) and much smaller quenching constants corresponding to those from fluorescence quenching (Table 3) were found when the nitro group was replaced by a cyano group. This suggests a singlet route for trans  $\rightarrow$  cis photoisomerization in the case of 4-cyanostilbenes (Ref. 23-25).

TABLE 3. Comparison of ( $k_Q/k_o$ )-values obtained from trans  $\rightarrow$  cis quantum yields and from laser flash photolysis studies on the triplet state, and Stern-Volmer constants for fluorescence quenching ( $\tau_s k_Q$ ) for various 4-nitrostilbenes in the absence of oxygen, using ferrocene as quencher (Ref. 23,27,31).

Compound	Solvent	$\frac{k_Q}{k_o}$ <sup>a</sup>	$\frac{k_Q}{k_o}$ <sup>b</sup>	$k_o$ <sup>b</sup>	$k_Q$ <sup>b</sup>	$\tau_s k_Q$ <sup>c</sup>
		[M <sup>-1</sup> ]	[M <sup>-1</sup> ]	[10 <sup>-6</sup> s <sup>-1</sup> ]	[10 <sup>-9</sup> M <sup>-1</sup> s <sup>-1</sup> ]	[M <sup>-1</sup> ]
4-Nitrostilbene	Benzene	315	320	15	4.8	d
	Methanol	650	740	12	8.9	
4,4'-Dinitrostilbene	Benzene	740	830	11	9.1	d
	Methanol	1040	1250	8.0	10	
4-Nitro-4'-methoxystilbene	Cyclohexane	300	360	13	4.7	12
		(350) <sup>e</sup>	(340)		(4.4)	
	Benzene	790	820	6.7	5.5	30
	Methanol	2700	3300	3.0	9.9	30
	Dimethylformamide	2100	1600	2.7	4.3	$\leq 80$
4-Cyano-4'-methoxystilbene	Benzene	20	-	-	-	$\leq 30$

<sup>a</sup> From equation (11); irradiation at 366 nm. <sup>b</sup> From measurements of triplet decay by laser flash photolysis; excitation at 347 and/or 353 nm. <sup>c</sup>  $\tau_s$  is the lifetime of excited trans singlet state; irradiation at 366 nm. <sup>d</sup> Due to small values of  $\phi_F$ , no quenching measurements could be performed. <sup>e</sup> Values in parenthesis refer to azulene as quencher.

### 3. Population of the Triplet State and Mechanism of Cis $\rightarrow$ Trans Photoisomerization

In Scheme 1 the reaction which populates  $tr^3$  is  $tr^1 \rightarrow tr^3$  (eq. 6). Contribution of the reaction sequence:  $tr^1 \rightarrow p^1 \rightarrow p^3 \rightarrow tr^3$  is excluded on the basis of the effect of ferrocene (azulene) on the quantum yield of the cis  $\rightarrow$  trans photoisomerization ( $\phi_{c \rightarrow t}$ ) as described in the following.

Excitation of the cis form of 4-nitrostilbenes produces the same triplet state as obtained by excitation of the trans form, however, with a different yield (Ref. 27,31). In the case of the trans form the quantum yield of triplet formation in non-polar solvents is almost unity since deactivation via reactions 4 and 5 is small. This follows from a comparison of direct and triplet sensitized trans  $\rightarrow$  cis quantum yield measurements (Tables 1,4 and Ref. 27,28).  $\phi_{t \rightarrow c}$  tends to zero at high ferrocene concentrations since every triplet state is quenched to the trans form.

Increasing the ferrocene (azulene) concentrations using the cis form does not lead to unity for  $\phi_{c \rightarrow t}$  (Fig. 3). However, a yield of unity for  $\phi_{c \rightarrow t}$  should be observed if every excited cis isomer were converted to the triplet state. Since ferrocene (azulene) does not quench the excited singlet state of the cis form ( $c^1$ ) due to its short lifetime ( $c^1$  shows no fluorescence (Ref. 41)) but quenches every triplet state to  $tr^0$ , it is likely that the cis  $\rightarrow$  trans photoisomerization does not proceed via triplet states only. In competition with the triplet route there should be a singlet pathway. The most plausible mechanism for the cis  $\rightarrow$  trans photoisomerization is given in Scheme 2.

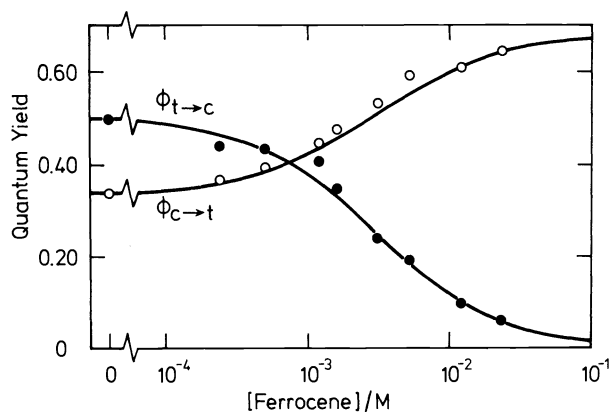
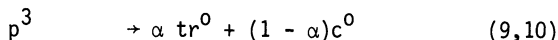
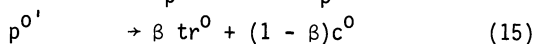
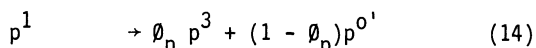


Fig. 3. Quantum yields of direct trans  $\rightarrow$  cis and cis  $\rightarrow$  trans photoisomerization as a function of ferrocene concentration for 4-nitrostilbene in benzene at room temperature in the absence of oxygen; irradiation at 366 nm (Ref. 27,31).

## Scheme 2

Mechanism of direct cis  $\rightarrow$  trans photoisomerization of 4-nitrostilbenes

Equation 12 represents absorption of light. The excited cis singlet state ( $c^1$ ) converts to the twisted excited singlet state ( $p^1$ , eq. 13). The deactivation pathways  $c^1 \rightarrow c^0$  and  $c^1 \rightarrow c^3$  are omitted from Scheme 2 although they may contribute. However, the first reaction ( $c^1 \rightarrow c^0$ ) cannot be the main deactivation step of  $c^1$  since  $\phi_{c \rightarrow t}$  is substantial (Table 1) and  $\beta$  is expected not to be much lower than  $\alpha$  which is  $\sim 0.4$  (Ref. 28). The second reaction ( $c^1 \rightarrow c^3$ ) is neglected since  $\phi_{c \rightarrow t}$  does not reach unity at high ferrocene concentrations (Fig. 3) and intersystem crossing is not likely due to the short lifetime of  $c^1$ . The state  $p^1$  either decays to  $p^3$  with the quantum yield  $\phi_p$  or to  $p^{0'}$  (eq. 14). The twisted ground state  $p^{0'}$  may have a somewhat different distribution of thermal excitation energy than  $p^0$  which is populated from  $p^3$ . The  $p^{0'}$  state converts to trans and cis ground states with a probability of  $\beta$  and  $(1-\beta)$ , respectively. The  $p^3$  state which is in equilibrium with  $tr^3$  decays according to eqs. 9 and 10. The role of the DHP<sup>••</sup> is open to speculation.<sup>†</sup>) The reaction steps of Schemes 1 and 2 and the reversible formation of 4a,4b-dihydrophenanthrene are presented in Fig. 4.

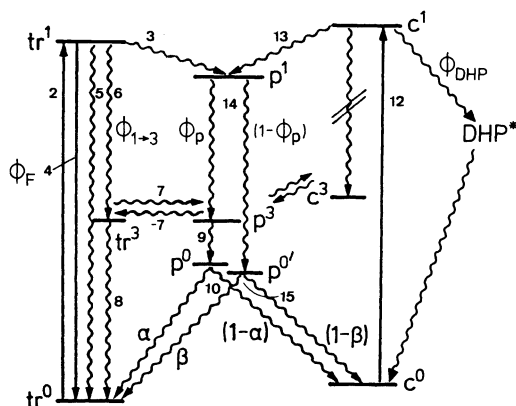


Fig. 4. Diagram representing the main reaction steps participating in the photochemical cis  $\rightleftharpoons$  trans isomerization of 4-nitrostilbenes.

Since  $p^1$  is a singlet state the internal rotation of  $c^1$  from  $\sim 180^\circ$  to  $90^\circ$  occurs in the excited singlet state. Deactivation of  $p^1$  is a fast process since  $p^1$  is a singlet state as is  $p^{0'}$  and the energy difference between  $p^1$  and  $p^{0'}$  is probably much smaller than that between  $tr^1$  and  $tr^0$  or  $c^1$  and  $c^0$ . Nevertheless since intersystem crossing competes in the deactivation

<sup>†</sup>) J. Saltiel suggests the step  $c^1 \rightarrow DHP^{••} \rightarrow p^3$  instead or in addition to  $c^1 \rightarrow p^1 \rightarrow p^3$  (private communication).



tion of  $p^1$  its lifetime is probably longer than that of  $c^1$ . Ferrocene even in high concentrations has therefore no chance to affect this process.

The yield of  $p^3$  formed from  $c^1$  has been found to be 0.3 for 4-nitro-4'-methoxystilbene in cyclohexane (Ref. 27). This means that 70% of  $p^1$  converts directly to  $p^{0'}$  and only 30% decays to the triplet state assuming that the quantum yield for the internal rotation  $c^1 \rightarrow p^1$  is unity. From these results it follows that the larger part of  $p^1$  decays to  $tr^0$  and  $c^0$  with a fast rate bypassing the triplet state. Since  $\phi_{t \rightarrow c}$  tends to zero at high ferrocene concentrations the pathway  $tr^1 \rightarrow p^1 \rightarrow p^{0'}$  and the population of the triplet state via  $tr^1 \rightarrow p^1 \rightarrow p^3 \rightarrow tr^3$  is of minor importance. Reaction 3 in Scheme 1 therefore does not play a role. The different behaviour of  $c^1$  and  $tr^1$  concerning their internal rotation to  $p^1$  may be explained by the steric hindrance which is present in  $c^1$  and absent in  $tr^1$ .

#### 4. Configuration and Internal Rotation of the Triplet State

In order to elucidate further details of the photoisomerization, the configuration of the observed triplet and possible internal rotation in the triplet state has to be established. Three triplet configurations may be distinguished: the planar trans ( $tr^3$ ), the twisted (perpendicular,  $p^3$ ) and the cis ( $c^3$ ) configuration. The latter is probably sterically hindered similar to the cis ground state. The following arguments have been advanced in favour of the observed triplet intermediate being predominantly in the planar  $tr^3$  configuration (Ref. 29,30):

- The triplet absorption spectra of trans-4-nitrostilbenes in fluid media at room temperature and in rigid media are very similar (Fig. 2 and Ref. 29). Since in rigid media  $\phi_{t \rightarrow c}$  tends to zero it has been suggested that the configuration of the trans-4-nitrostilbenes is not changed by excitation and by the subsequent relaxation processes. It follows that the triplet intermediate which is observed in fluid solutions should also have mainly the planar configuration ( $tr^3$ ) provided that  $tr^3$  and  $p^3$  have different absorption spectra.

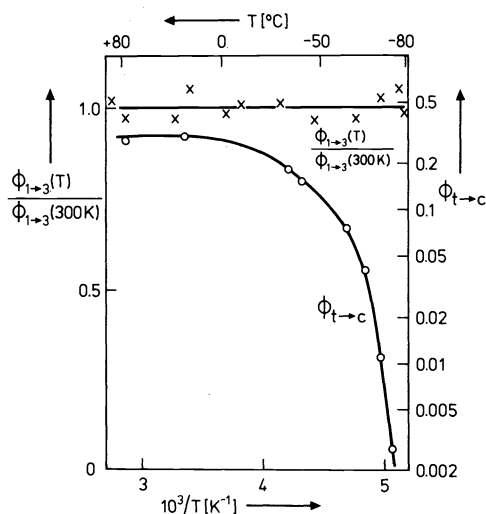


Fig. 5. Quantum yield of trans  $\rightarrow$  cis photoisomerization (irradiation at 366 nm) and relative triplet quantum yields ( $\phi_{1 \rightarrow 3}(T)/\phi_{1 \rightarrow 3}(300\text{ K})$ , excitation at 353 nm) of trans-4-nitro-4'-methoxystilbene in glycerol triacetate (GT) as a function of temperature (Ref. 29).

- b) In the high viscosity range  $\phi_{t \rightarrow c}$  decreases strongly with decreasing temperature (Figs. 5, 8, and Ref. 3, 47). At the lowest temperatures (i.e. highest viscosities) employed, no trans  $\rightarrow$  cis isomerization was detectable under our conditions. As shown in Fig. 6 the lifetime of the triplet state at these temperatures becomes independent of temperature and viscosity. This indicates that no change of configuration occurs during and after excitation of the trans isomer. On the other hand, the quantum yield of formation of the triplet state from the trans isomer ( $\phi_{1 \rightarrow 3}$ ) is independent of temperature and viscosity (Fig. 5). This suggests that the observed triplet state should have the planar ( $tr^3$ ) configuration.
- c) Above a certain temperature  $T_V$ , the lifetime of the triplet state depends only on temperature and  $\log \tau^{-1}$  versus  $T^{-1}$  is linear (Figs. 6 and 7). Below  $T_V$   $\log \tau^{-1}$  versus  $T^{-1}$  also gives a straight line, however, with another slope.  $T_V$  is defined as the temperature at which point the straight lines intersect (Figs. 6 and 7).

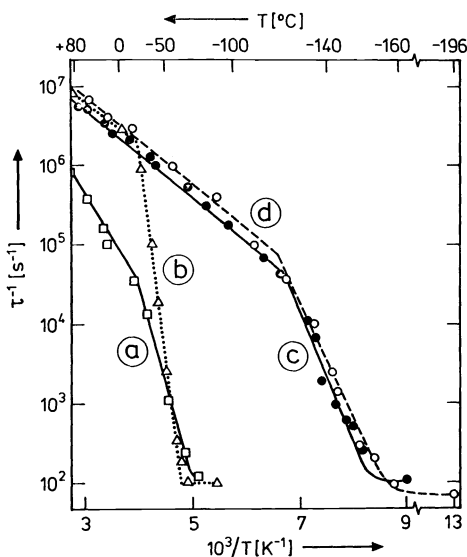


Fig. 6. Rate constants for decay of triplet state of 4-nitro-4'-methoxystilbene as a function of temperature in different solvents in the absence of oxygen: a) glycerol, b) glycerol triacetate (GT), c) E-M (a mixture of ethanol and methanol; 4:1) and d) EPA (diethyl ether, isopentane, and ethanol; 5:5:2; Ref. 30).  $T_V$  and  $T_0$  specify the upper and lower temperatures at the break in the plot of  $\log \tau^{-1}$  versus  $T^{-1}$ , respectively.

Comparing  $T_V$ -values for glycerol or glycerol triacetate (GT) as solvent with that for EPA or mixtures of ethanol and methanol (E-M) clearly shows that the reduction in the rate constants below  $T_V$  is determined by the effect of viscosity (Figs. 6 and 7). The temperatures at  $T_V$  are considerably different in these two classes of solvents, however, the viscosities are approximately the same, e.g. viscosities of  $1 \cdot 10^2$  poise at 150 K in EPA and at 250 K in GT (Ref. 47-49).

The strong influence of viscosity on the lifetime of the triplet state below  $T_V$  indicates that a change in configuration is involved in the decay process. In the case of triplet decay of 4-nitroanisole, 4-nitroaniline and 4-nitrobiphenyl which are compounds without an olefinic C=C-double bond only small or no effects of viscosity on transient lifetimes are observed (Fig. 7 and Ref. 30). These results suggest that twisting about the C=C-double bond in the triplet state participates in the triplet decay process.

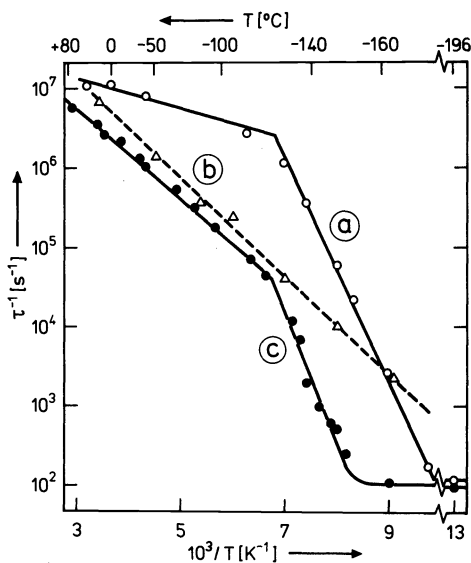


Fig. 7. Rate constants for decay of triplet states as a function of temperature in E-M in the absence of oxygen: a) 4-nitrostilbene, b) 4-nitroanisole and c) 4-nitro-4'-methoxystilbene (Ref. 30,31).

The most plausible explanation is that the configuration of the triplet state is predominantly  $tr^3$  which decays via  $p^3 \rightarrow p^0$  to  $tr^0$  and  $c^0$  (see section 5). The effect of viscosity is a decrease of the rate of interconversion  $tr^3 \rightarrow p^3$ . Laser flash photolysis results support this conclusion. On exciting the cis isomer the same triplet state as that from the trans isomer is observed immediately after the laser pulse ( $\sim 20$  ns) even slightly below  $T_V$ , i.e. formation of the triplet state is faster than decay. If the configuration of the observed triplet state would be  $p^3$  the effect of viscosity is difficult to explain since no configurational change is necessary for decay.

It has therefore been concluded that the triplet state has predominantly the  $tr^3$  configuration and that  $tr^3$  is able to convert into the  $p^3$  and possibly into the  $c^3$  configurations and back again during its lifetime. This leads to the suggestion of a  $tr^3 \rightleftharpoons p^3 (\rightleftharpoons c^3)$  equilibrium. Additional arguments are derived from results of isomerization quantum yields and triplet photoisomerization as follows.

The fraction of the triplet state decaying to the trans ground state ( $\alpha'$ , Ref. 50) ranges from 0.4 to 0.6 (Table 4). Similar values have been found for unsubstituted stilbene and 4-bromostilbene (Ref. 2,13). The configuration of the triplet state at the moment of intersystem crossing is, therefore, either  $p^3$  or almost 50%  $tr^3$  and 50%  $c^3$ . In both cases the triplet intermediate must be able to interconvert from the  $tr^3$  to the  $p^3$  configuration. This conclusion is confirmed by triplet sensitization experiments which show that population of  $tr^3$  via energy transfer to  $tr^0$  leads to  $c^0$  with a quantum yield of  $\sim 0.5$  (Table 4).

TABLE 4. Quantum yields for triplet sensitized trans  $\rightarrow$  cis ( $\phi_{t \rightarrow c}^{sens}$ ) and cis  $\rightarrow$  trans ( $\phi_{c \rightarrow t}^{sens}$ ) isomerization and  $\alpha'$  for three 4-nitrostilbenes in different solvents at room temperature in the absence of oxygen (Ref. 28).

Compound	Solvent	$\phi_{t \rightarrow c}^{sens}$	$\phi_{c \rightarrow t}^{sens}$	$\alpha'$
4-Nitrostilbene	Benzene	-	-	0.42
	Methanol	-	-	0.45
4,4'-Dinitrostilbene	Benzene	-	-	0.42
	Methanol	-	-	0.45
4-Nitro-4'-methoxystilbene	Cyclohexane	0.55	0.35	0.38
	Benzene	0.50	0.40	0.43
	Methanol	0.42	0.47	0.53
	Dimethyl-formamide	0.40	0.45	0.56

Triplet sensitization of the cis form with a quantum yield of  $\sim 0.4$  (Table 4) indicates that  $c^3 \rightarrow p^3$  is possible. Furthermore, direct excitation of  $c^0$  leads to the same triplet state as excitation of  $tr^0$  which shows that the interconversion  $p^3 \rightarrow tr^3$  occurs since the triplet state has predominantly the  $tr^3$  configuration. The possibility that  $p^3$  is obtained by absorption of two quanta via  $c^0 + h\nu \rightarrow c^1 \rightarrow tr^0$ ;  $tr^0 + h\nu \rightarrow tr^1 \rightarrow tr^3 \rightarrow p^3$  is excluded on the basis of intensity-dependent laser flash photolysis measurements (Ref. 31). The first excited cis singlet state ( $c^1$ ) does not interconvert to  $tr^1$  since  $tr^1$  shows fluorescence in contrast to  $c^1$  (Ref. 41). The configurational equilibrium  $tr^3 \rightleftharpoons p^3$  should therefore exist.

It is not known whether or not the interconversion  $p^3 \rightleftharpoons c^3$  plays a role in the equilibrium since the form of the potential energy curve is not known. The spectroscopically determined energy of  $c^3$  is considerably higher than that of  $tr^3$  ( $\Delta E \sim 7$  kcal/mol, Ref. 51). However, the spectroscopically determined energy may be larger than the energy of  $c^3$  in its potential energy minimum.

### 5. Decay of the Triplet State

The most probable route for decay of the triplet states is reaction  $p^3 \rightarrow p^0$  (eq. 9). This has been deduced from the fact that in reaction  $tr^3 \rightarrow tr^0$  (eq. 8) a much larger amount of electronic energy has to be converted into vibronic energy than in reaction  $p^3 \rightarrow p^0$  (eq. 9, Ref. 30). In the case of 4-nitro-4'-methoxystilbene the energy difference  $E(tr^3) - E(tr^0)$  is 46.5 kcal/mol whereas  $E(p^3) - E(p^0)$  is only 5-10 kcal/mol (Ref. 26,51). In other words the Franck-Condon factors strongly favour reaction 9 over reaction 8.

Since the triplet state is predominantly in the trans configuration the rate determining step for decay could be either  $tr^3 \rightarrow p^3$  ( $k_9 \gg k_{-7}$ ) or  $p^3 \rightarrow p^0$  ( $k_7, k_{-7} \gg k_9$ ). In the latter case there exists a fast thermal  $tr^3 \rightleftharpoons p^3$  equilibrium. It turns out, as is shown further on in detail, that from room temperature down to  $T_V$  the reaction  $p^3 \rightarrow p^0$  is rate determining and below  $T_V$  the reaction  $tr^3 \rightarrow p^3$  becomes important.

From the rate constant of decay above  $T_V$  a pre-exponential factor of the Arrhenius equation of  $\sim 10^8 \text{ s}^{-1}$  has been obtained (Ref. 30 and Table 6). This is in agreement with intersystem crossing ( $p^3 \rightarrow p^0$ ) as the rate determining step whereas reaction  $tr^3 \rightarrow p^3$  should show a pre-exponential factor of normal magnitude ( $\sim 10^{12} \text{ s}^{-1}$ ) because no change of electronic states and a small positive change in entropy are involved. A second argument for  $p^3 \rightarrow p^0$  as the rate determining step emerges from quenching measurements with ferrocene as presented below.

The effect of ferrocene on photostationary trans/cis ratios under direct and sensitized excitation conditions should yield the same slope to intercept ratio if  $tr^3 \rightarrow p^3$  were rate determining ( $k_9 \gg k_{-7}$ ). The experimental results presented in Table 5 exclude this case since slope/intercept ratios ( $r$ ) are larger for the sensitized ( $r_3$ ) than for the direct ( $r_2$ ) photoisomerization. It should be noted that a comparison of quenching data for direct and sensitized photoisomerizations has already been made for unsubstituted stilbene and bromostilbenes (Ref. 2,14,17) and for thioindigo dyes (Ref. 32).

These arguments together with those of section 4 show that above  $T_V$ ,  $p^3 \rightarrow p^0$  is rate determining and that a thermal  $tr^3 \rightleftharpoons p^3$  equilibrium exists. A lower limit for the rate of establishment of this equilibrium has been obtained from kinetic studies. Laser flash measurements at room temperature show a clean first order decay of the triplet intermediate beginning immediately after the laser pulse (20 ns) and no change of the triplet absorption spectrum with time (Ref. 22,27,30). Since this is valid for excitation of cis and trans isomer the  $tr^3 \rightleftharpoons p^3$  equilibrium is established within the duration of the laser pulse (20 ns) which is shorter than the lifetime of the triplet state (Table 2).

A consequence of the fast establishment of the  $tr^3 \rightleftharpoons p^3$  equilibrium and the position of this equilibrium on the trans side for the 4-nitrostilbenes is that the free energy must be lower for the  $tr^3$  state than for the  $p^3$  state.

TABLE 5. Comparison between slope/intercept ratios obtained under direct and sensitized excitation conditions in the absence of oxygen at room temperature, using ferrocene as quencher.

Compound	Solvent	$r_1^a$ [M <sup>-1</sup> ]	$r_2^b$ [M <sup>-1</sup> ]	$r_3^c$ [M <sup>-1</sup> ]
4-Nitrostilbene	Benzene	315	630	810
	Methanol	650	1150	1600
4,4'-Dinitrostilbene	Benzene	740	1850	1900
	Methanol	1040	2080	2270
4-Nitro-4'-methoxystilbene	Cyclohexane	300	470	790
	Benzene	790	1100	1600
	Methanol	2700	3800	5000
	Dimethylformamide	2100	2050	4100

<sup>a</sup> Slope/intercept obtained from Stern-Volmer plot;  $r_1 = k_Q/k_0$  (eq. 11).

<sup>b</sup> Slope/intercept from photostationary trans/cis ratios using direct excitation at 366 nm; kinetic evaluation of Schemes 1 and 2 gives  $r_2 = k_Q/(\gamma k_0)$  (Ref. 27, 31). The factor  $\gamma$  ( $\alpha \leq \gamma \leq 1$ ) defines branching from  $p^1$  to  $p^3$  and  $p^0$ , assuming the  $tr^3 \rightleftharpoons p^3$  equilibrium and reaction 9 as the rate determining step ( $\phi_p < 1$ , Ref. 27).

<sup>c</sup> Slope/intercept from photostationary trans/cis ratios using naphthalene-sensitized excitation; kinetic evaluation of Schemes 1 and 2 gives  $r_3 = k_Q/(\alpha k_0)$  (Ref. 28).

Decay of  $tr^3$  and  $p^3$  states may be treated kinetically in analogy to decay of  $tr^1$  and  $p^1$  states of unsubstituted stilbene which has already been carried out by several authors (Ref. 18,19). Two decay rate constants ( $\lambda_1, \lambda_2$ ) result from eq. 16. In the case of an experimentally observed first order decay, one of the two rate constants is large and only the smaller one is observed.

$$\lambda_{1,2} = \frac{1}{2} \{ (k_8 + k_7 + k_9 + k_{-7}) \mp [(k_9 + k_{-7} - k_8 - k_7)^2 + 4k_7k_{-7}]^{1/2} \} \quad (16)$$

At room temperature the triplet equilibrium is established before the decay becomes significant. Thus condition 17 holds

$$k_7, k_{-7} \gg k_8, k_9 \quad (17)$$

Using  $K_7 = k_7/k_{-7}$ , eq. 16, and condition 17 the triplet lifetime is expressed by eq. 18

$$\tau = \frac{1 + K_7}{k_8 + k_9 K_7} \quad (18)$$

A simplification of eq. 18 is described in the following section.

## 6. Influence of Temperature on Triplet Lifetime and Isomerization Quantum Yields

Equation 18 may account for the linear dependences of  $\log \tau^{-1}$  versus  $T^{-1}$  since for the case that conditions  $K_7 < 1$  and  $k_8 < k_9 K_7$  are valid eq. 18 simplifies to eq. 19.

$$k_0 = \tau^{-1} \approx k_9 K_7 \quad (19)$$

The first condition is in agreement with the  $tr^3 \rightleftharpoons p^3$  equilibrium being on the  $tr^3$  side. The second condition is fulfilled in non-polar solvents because the sum of  $\phi_{t \rightarrow c}$  and  $\phi_{c \rightarrow t}$  is close to unity. This means that reaction 8 cannot play a significant role. Triplet sensitization measurements show that the condition  $k_8 < k_9 K_7$  holds also in polar solvents since the observed decrease of  $\phi_{t \rightarrow c}$  for 4-nitro-4'-methoxystilbene in polar solvents (Table 1) is due to excited singlet state behaviour (increased contribution of the radiationless deactivation  $tr^1 \rightarrow tr^0$ ) and not to an increased contribution of reaction 8 (Ref. 28).

The measured activation energies ( $E_a(\tau)$ ) for decay of the triplet state in different solvents above  $T_V$  are listed in Table 6. The origin of the activation energy  $E_a(\tau)$  should be due to  $k_9$  and/or the energy difference between  $tr^3$  and  $p^3$  (if eq. 19 is valid). The activation energy  $E_a(\tau)$  is not the result of an activation barrier between  $tr^3$  and  $p^3$ . As mentioned above the A-factors presented in Table 6 reflect the small probability for the intersystem crossing step  $p^3 \rightarrow p^0$ .

TABLE 6. Activation energies obtained from  $\phi_{t \rightarrow c}/\phi_{c \rightarrow t}$  ( $E_a(\phi)$ ) and from triplet lifetime ( $E_a(\tau)$ ) measurements and the pre-exponential factor (Ref. 30,31).

Compound	Solvent	$E_a(\phi)$ [kcal/mol]	$E'_a(\phi)^a$	$E_a(\tau)$ [kcal/mol]	$E'_a(\tau)^b$	A <sup>c</sup> [s <sup>-1</sup> × 10 <sup>-6</sup> ]
4-Nitrostilbene	GT	0.1	≥ 8	1.0	27	120
	EPA	≤ 0.1	4	0.9	7.7	70
	E-M	≤ 0.1	6	0.7	6.7	40
4,4'-Dinitrostilbene	GT	≤ 0.1	11	1.4	22	120
	E-M	≤ 0.1	5	1.5	7.2	80
4-Nitro-4'-methoxystilbene	Methylcyclohexane	0.1	-	0.35	-	20
	Toluene	0.2	-	1.6	-	110
	GT	0.6	17	2.4	24	230
	EPA	0.6	2.9	2.7	6.7	500
	E-M	0.3	3.3	2.6	7.7	200

<sup>a</sup>  $E_a(\phi)$  refers to  $T > T_u$  and  $E'_a(\phi)$  refers to  $T < T_u$  (Fig. 8).

<sup>b</sup>  $E_a(\tau)$  refers to  $T > T_v$  and  $E'_a(\tau)$  refers to  $T_o < T < T_v$  (Fig. 6).

<sup>c</sup> A refers to  $T > T_v$ .

The activation energy below  $T_v$  ( $E_a'(\tau)$ ) is much higher due to the viscosity dependent barrier against the twisting process  $tr^3 \rightarrow p^3$  (Table 6 and Ref. 30). It should be noted that the influence of viscosity on relaxation process in the excited singlet state of unsubstituted stilbene has been discussed by several authors (Ref. 6,47,52).

Above  $T_u$  according to Schemes 1 and 2 the ratio of isomerization quantum yields is given by eq. 20.

$$\frac{\phi_{t \rightarrow c}}{\phi_{c \rightarrow t}} = \frac{\phi_{1 \rightarrow 3} (1 - \alpha')}{\beta + \phi_p (\alpha' - \beta)} \quad (20)$$

The constant  $\beta$  is the fraction of  $p^0$  decaying to  $tr^0$  (eq. 15) and  $\alpha'$  (Ref. 50) is the fraction of  $tr^3 \rightleftharpoons p^3$  decaying to  $tr^0$ ;  $\phi_{1 \rightarrow 3}$  and  $\phi_p$  denote the quantum yields for the  $tr^1 \rightarrow tr^3$  and  $p^1 \rightarrow p^3$  intersystem crossing processes, respectively. The value of  $\beta$  can be obtained from quenching measurements if the quantum yield for  $c^1 \rightarrow p^1$  is known (Ref. 27). For several nitrostilbenes Fischer et al. (Ref. 3,47) have already shown that  $\phi_{c \rightarrow t}$  is essentially temperature independent. It follows that  $\alpha'$ ,  $\beta$ , and  $\phi_p$  are probably also temperature independent since  $\phi_{c \rightarrow t}$  depends on these parameters.

For 4-nitro-, 4,4'-dinitro- and 4-nitro-4'-methoxystilbene in non-polar solvents pathway 8 does not contribute substantially at room temperature ( $k_8 \ll k_9 k_5$ ) since the sum of  $\phi_{c \rightarrow t}$  and  $\phi_{t \rightarrow c}$  is  $\sim 0.9$  (Table 1) and  $\phi_{1 \rightarrow 3}$  is close to unity. Provided that  $\alpha'$ ,  $\beta$  and  $\phi_p$  are temperature independent and  $\phi_{1 \rightarrow 3} = 1$ , it follows from eq. 20 that no temperature dependence of  $\phi_{t \rightarrow c}/\phi_{c \rightarrow t}$  should result. The experimentally determined  $E_a(\phi)$ -values (Fig. 8) are indeed very small, e.g.  $\leq 0.1$  kcal/mol for 4-nitro- and 4,4'-dinitrostilbene (Table 6).

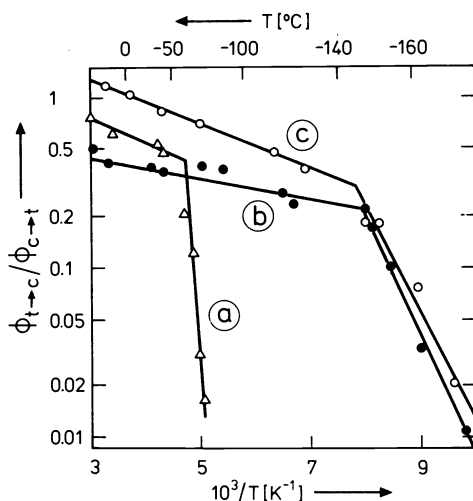


Fig. 8.  $\phi_{t \rightarrow c}/\phi_{c \rightarrow t}$  as a function of temperature for 4-nitro-4'-methoxystilbene in the absence of oxygen in a) GT, b) E-M, and c) EPA; irradiation at 366 nm (Ref. 30).  $T_u$  specifies the temperature at the break in the plot of  $\phi_{t \rightarrow c}/\phi_{c \rightarrow t}$  versus  $T^{-1}$ .



The slightly larger activation energies for 4-nitro-4'-methoxystilbene found in polar solvents above  $T_U$  (Table 6) are due to the radiationless transition  $tr^1 \rightarrow tr^0$  (Ref. 30), i.e. excited singlet state behaviour. The enhancement of the contribution of this radiationless transition is responsible for the decrease of  $\phi_{t \rightarrow c}$  in polar solvents (Table 1). Below  $T_U$  much higher activation energies ( $E_a'(\phi)$ ) are obtained than above  $T_U$  (Table 6). They result from a viscosity dependent barrier for the  $tr^3 \rightarrow p^3$  interconversion (Ref. 30).

### 7. Comparison of $T_V$ and $T_U$

The temperature  $T_V$  which marks the onset of the influence of viscosity on triplet lifetime may have been expected to be identical with  $T_U$ , the temperature which marks the onset of the influence of viscosity on  $\phi_{t \rightarrow c}/\phi_{c \rightarrow t}$  (Fig. 8). However, this is not the case (Table 7).

TABLE 7. Comparison of  $T_U$ ,  $T_V$ , and  $T_O$ .

Compound	Solvent	$T_U^a$ [K]	$T_V^b$ [K]	$T_O^b$ [K]
4-Nitrostilbene	GT	214	249	209
	EPA	118	149	108
	E-M	117	149	108
4,4'-Dinitrostilbene	GT	218	252	204
	E-M	123	143	109
4-Nitro-4'-methoxystilbene	GT	212	250	208
	EPA	128	150	115
	E-M	126	147	120

For definition of  $T_U$ ,  $T_V$  and  $T_O$  see legends of Figs. 6 and 8.

<sup>a</sup> From  $\phi_{t \rightarrow c}/\phi_{c \rightarrow t}$  measurements (Ref. 30,31). <sup>b</sup> From triplet lifetime measurements (Ref. 30,31).

For all 4-nitrostilbenes studied  $T_V$  is greater than  $T_U$  (Table 7), i.e. the triplet lifetime is already influenced by the viscosity at temperatures where the quantum yields of isomerization are still viscosity independent. This result is reasonably explained in the following way: The strong increase of the triplet lifetime below  $T_V$  with decreasing temperature is due to the hindrance of the  $tr^3 \rightarrow p^3$  twisting process by the increasing viscosity. This means that establishment of the equilibrium is hindered and  $p^3 \rightarrow p^0$  becomes faster than  $p^3 \rightarrow tr^3$ . In this case  $tr^3 \rightarrow p^3$  begins to be the rate determining step (see also section 4). Nevertheless, deactivation still occurs via  $p^3 \rightarrow p^0$  only. Therefore below  $T_V$  but above  $T_U$  viscosity only influences the lifetime but not  $\phi_{t \rightarrow c}/\phi_{c \rightarrow t}$ . Below  $T_U$  however  $\phi_{t \rightarrow c}/\phi_{c \rightarrow t}$  decreases with increasing viscosity. This could be the result of a deactivation at angles of twist smaller than  $90^\circ$  leading to an increase of  $\alpha'$ . It should be added that  $\phi_{c \rightarrow t}$  is almost temperature and viscosity independent up to relatively high viscosities (Ref. 3,29). Therefore the increase of  $\phi_{t \rightarrow c}/\phi_{c \rightarrow t}$  mainly reflects changes in  $\phi_{t \rightarrow c}$ .

The above result is not in agreement with the assumption that decay occurs with equal rates from  $tr^3$  and  $c^3$  in the presence of a rapidly established  $tr^3 \rightleftharpoons c^3$  equilibrium. If this were the case it is difficult to see how viscosity should affect the triplet lifetime when deactivation to  $tr^0$  has the same rate as deactivation to  $c^0$ .

At the highest viscosities attainable (corresponding to temperatures below  $T_0$ ) decay from  $tr^3$  occurs without twisting about the central double bond. This is indicated by the disappearance of an influence of viscosity and temperature on triplet lifetime as shown in Figs. 6 and 7. In the temperature range below  $T_0$   $\theta_{t \rightarrow c}$  is practically zero and it is therefore concluded that  $\tau$  is given by  $k_0^{-1}$  (Fig. 6,7 and Ref. 30) in agreement with previous suggestions (Ref. 11).

#### 8. Final remarks

The mechanism presented here provides an explanation of the experimental results discussed. The influence of solvent properties on quantum yields of fluorescence and photoisomerization and on triplet lifetime is discussed in detail elsewhere (Ref. 25,30,31). Results of quenching experiments with oxygen are not included in this review since they have been misleading in the past. Oxygen quenches the triplet state of 4-nitrostilbenes (Ref. 22,23,27) and of unsubstituted stilbene (Ref. 2,15,16) at room temperature without changing photo-stationary trans/cis ratios. This was used as a strong argument to suggest that the configuration of the triplet state is  $p^3$ . However, the number of weighty new arguments presented recently now provides evidence that the triplet configuration of the 4-nitrostilbenes is mainly  $tr^3$ . This raises the question as to the mechanism of quenching by oxygen. At least two possibilities may be discussed: the first one is based on a suggestion by Saltiel that oxygen may quench  $p^3$  to  $p^0$  by a spin exchange mechanism faster than  $tr^3$  to  $tr^0$  (Ref. 2,16). A second possibility would be a chemical quenching step involving a complex (suggestion by Saltiel) or a biradical as intermediate followed by dissociation of the intermediate to cis and trans stilbene. Turro (Ref. 53) has pointed out that it is difficult to predict the results of such a chemical reaction. Further work is needed to clarify this point.

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