

THE cis \rightarrow trans PHOTOISOMERIZATION OF AZOBENZENE: AN EXPERIMENTAL RE-EXAMINATION

NARCISSE SIAMPIRINGUE^a, GHISLAIN GUYOT^a, SANDRA MONTI^b and
PIETRO BORTOLUS^b

^aLaboratoire de Photochimie Moléculaire et Macromoléculaire, U.A. CNRS 433,
U.F.R. de Recherche Scientifique et Technique, Université de Clermont II, B.P. 45,
63170 Aubière (France)

^bIstituto di Fotochimica e Radiazioni di Alta Energia del Consiglio Nazionale delle
Ricerche, 40126 Bologna (Italy)

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Summary

The quantum yields ϕ_t for the cis \rightarrow trans photoisomerization of azobenzene have been redetermined in various solvents. As for the reverse process, there is a quantum yield dependence on the excitation wavelength.

Reasons for the discrepancy with previous reported values are briefly discussed.

1. Introduction

The photochemical trans \rightleftharpoons cis isomerization of azobenzene has been studied since 1954 [1]: in all the published papers a marked difference in the quantum yields by excitation in the π, π^* or in the n, π^* absorption bands has been reported for the trans \rightarrow cis process (ϕ_c) [1 - 8]. There is very good agreement in the literature values of ϕ_c by irradiation, in hydrocarbon solvents, in both bands and of ϕ_t , the quantum yield for the cis \rightarrow trans process, in the n, π^* band. However, the ϕ_t values in the π, π^* band appear to be more scattered so that the extent of the wavelength dependence in the photochemistry of the cis isomer is not conclusively established. In particular, the ϕ_t values in non-polar solvents obtained in our laboratories were 0.42 [5] and 0.27 [6]. A reliable assessment of the ϕ_t value in the π, π^* band is of interest for both the understanding of the photoreaction mechanism and the utilization of azobenzene as a chemical actinometer [8 - 10].

2. Results and discussion

For these reasons, we have reconsidered the problem and the results of new quantum yield determinations are reported in Table 1. The values

TABLE 1

Quantum yields for *cis* → *trans* photoisomerization of azobenzene in various solvents by excitation in the π, π^* band

<i>This work</i> ($\lambda_{exc} = 313 \text{ nm}$)		<i>Literature data</i>		
<i>Solvent</i>	ϕ_t	<i>Solvent</i>	ϕ_t	<i>Reference</i>
		Iso-octane	0.40	2
		Benzene	0.44	3
		Methylcyclohexane–isohexane (66.7 vol.%–33.3 vol.%)	0.40	4
Cyclohexane	0.40 ± 0.030	Cyclohexane	0.42	5
<i>n</i> -Hexane	0.44 ± 0.035	<i>n</i> -Hexane	0.27	6
		Ethanol	0.24	6
			0.31	7
Acetonitrile	0.35 ± 0.030	Acetonitrile	0.21	6
H ₂ O–ethanol (80 vol.%–20 vol.%)	0.40 ± 0.030	H ₂ O–ethanol (80 vol.%–20 vol.%)	0.15	6
Methanol	0.37 ± 0.025	Methanol	0.30	9
Tetrahydrofuran	0.40 ± 0.035			

obtained are about 0.4 in all the solvents examined and there is good agreement between the results obtained in our laboratories despite the different procedures used for the determination of ϕ (see Section 3). The values of ϕ_c in the π, π^* and the n, π^* bands and ϕ_t in the n, π^* band remeasured in *n*-hexane are the same as those already reported [5, 6]. A possible explanation of the above-mentioned discrepancy is related to the presence of a small amount (0.7%–3% according to the preparation procedure) of *trans* isomer in the *cis* isomer used for the irradiation. Given the large difference in the molar extinction coefficients of the two isomers ($\epsilon_t \approx 10\epsilon_c$) at the excitation wavelength, the fraction of light absorbed by the *trans* isomer must be taken into account for the kinetic treatment. Moreover, in these cases, the stirring during the irradiation is of crucial importance. In fact, the ϕ_t values in *n*-hexane, tetrahydrofuran and water–ethanol, reported in Table 1, drop to about 0.3 in non-stirred solutions.

The value $\phi_t \approx 0.4$ seems to be the most probable for irradiation in the π, π^* band in non-polar solvents: this value is lower than that pertinent to the irradiation in the n, π^* band, which is about 0.55. The different reactivities of the S_1 and S_2 states of azobenzene have found two interpretations [7, 11, 12]. The reported data do not allow a decision in favour of one or the other of these two hypotheses, but confirm a difference in the behaviour of the S_1 and S_2 states of *cis*-azobenzene.

3. Experimental details

trans-Azobenzene was a zone-refined product from Aldrich. Cyclohexane and *n*-hexane were RS grade from Carlo Erba; methanol and aceto-

nitrile were Uvasol from Merck; all were used as received. Tetrahydrofuran (Carlo Erba, RP grade) was refluxed over KOH pellets and then distilled.

The irradiations were carried out at room temperature (20 ± 2 °C); ferrioxalate actinometry was used [13].

In the Clermont-Ferrand laboratory, the ϕ_t values were calculated by irradiating cis-trans mixtures enriched in cis (about 97% cis), obtained by irradiation of the trans isomer with light of wavelength 344 - 348 nm, according to the solvent [14]. The irradiations were carried out in a cell 1 cm thick using a high pressure Osram HBO 200 W mercury lamp coupled with a Bausch and Lomb monochromator or a high pressure Osram 1600 W xenon lamp coupled with a Schoeffel monochromator (in both systems the bandpass was 10 nm). The solutions were vigorously stirred. The concentrations used were in the range (2×10^{-5}) - (5×10^{-4}) M. The isomerization progress was followed at 313 nm on the same cell subjected to the irradiation; a Cary 118 C spectrophotometer was used. ϕ_t was determined by two different methods: from the tangent at the origin of the isomerization and by the method originally proposed by Mauser [15] for the linearization of the kinetic curves and used by Gauglitz and Hubig [8, 9]. The slope of the straight line obtained gives the pseudo-quantum yield Q :

$$Q = 10^3(\phi_c \epsilon_t + \phi_t \epsilon_c)$$

where ϵ_t and ϵ_c are the molar extinction coefficients of the two isomers at the irradiation wavelength and ϕ_c and ϕ_t the quantum yields of the two processes. This value, combined with the photostationary state composition $[\text{cis}_\infty]/[\text{trans}_\infty]$ leads to the evaluation of ϕ_t

$$\phi_t = \frac{10^{-3}Q}{\epsilon_c(1 + [\text{cis}_\infty]/[\text{trans}_\infty])}$$

The mixture utilized for the irradiation at 313 nm was also irradiated at the cis-trans isosbestic point (267 - 270 nm, according to the solvent) to avoid the problem of differences in monochromaticity between the spectrophotometer (bandpass, 0.7 nm) used for the determination of ϵ and the irradiating system (bandpass, 10 nm); the ϕ_t values obtained at the two irradiation wavelengths are in good agreement.

In Bologna, ϕ_t values were calculated by irradiating solutions of the cis isomer purified by column chromatography, as reported in ref. 6; the product contains about 0.7% of trans isomer. The concentration of the irradiated solutions was 2.5×10^{-4} M. The solutions, irradiated in a cell 2 cm thick, absorb about 95% of the incident light. The progress of the photo-reaction was followed by UV spectrophotometry in the region 310 - 340 nm directly on the irradiated solutions transferred in a cell 1 cm thick. The conversion percentage was, in all cases, equal to or less than 2%. The irradiation system consisted of a 200 W HBO high pressure mercury lamp coupled with a high intensity Balzers monochromator blazed at 300 nm, and slits 1 mm in width.

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