Concentration Dependent Photodimerization of Azobenzenes in Solution

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Cis-trans photoisomerization of azobenzenes in higher concentrations proceeds through a bimolecular reaction process, probably involving the dimer biradical intermediates, in competition with a unimolecular isomerization process, which is the predominant reaction in lower concentrations.

As one of the best known photochromic molecules used in optical molecular switches, azobenzene (**AB**) has attracted considerable interest. Many investigations into the mechanism of *cis-trans* photoisomerization and its applications have been reported since the 1950's.[1] However, attempts to apply the photoisomerization process in solid, polymer matrix, and polymer chains have often encountered the problem of poor formation of the *cis* isomer (*c*-**AB**), which has previously been explained in terms of the smaller free volume in solid and polymers compared to that in solution; namely, it has been thought likely that the *trans*-to-*cis* photoisomerization is greatly suppressed in the smaller spaces.[2] Furthermore, it has been reported that on irradiation in cyclohexane using 313-nm light the *cis/trans* (*c/t*) isomer ratio of **AB** in the photostationary state (PSS) reached ca. 80/20 in a concentration of 1×10^{-3} M (M = mol/dm^3) and was independent of the initial concentration of **AB**.[3] In our most recent study of the photoisomerization of **AB** in zeolite cavities,[4] we have noticed incidentally that irradiation of 1×10^{-2} M **AB** in cyclohexane using 313-nm light gives the isomers at a ratio of *c/t* = ca. 55/45 in PSS, which is a markedly different ratio from that in the lower concentrations reported previously.[3] Even in the case of aromatic alkenes there have so far been few examples of the concentration having an effect on the photoisomerization.[5] Therefore, we reinvestigated the concentration dependence of the *c/t* ratio of **AB** in PSS. In this paper, on the basis of the effect of initial concentration, excitation wavelength, substituent, and solvent on the *cis-trans* photoisomerization of **AB**, we propose a novel photoisomerization mechanism in higher concentrations. This mechanism consists of a bimolecular photoisomerization process favoring the formation of the *trans* isomer (*t*-**AB**), which competes with a *cis-trans* unimolecular isomerization process dependent on the ratio between the molar absorption coefficients (ε) of *c*- and *t*-**AB** ($\varepsilon_{c\text{-AB}}$ and $\varepsilon_{t\text{-AB}}$, respectively) as well as on that between the quantum yields of isomerization for *t*-**AB** to *c*-**AB** ($\Phi_{t\text{-}c}$) and *c*-**AB** to *t*-**AB** ($\Phi_{c\text{-}t}$) according to the excitation wavelength used.

When an aerated cyclohexane solution of 2×10^{-4} – 1×10^{-3} M **AB** was irradiated through a Hoya U-340 glass filter (313-nm band pass; $\varepsilon_{c\text{-AB}}$ and $\varepsilon_{t\text{-AB}}$ are 1160 and 21100 at 313 nm, respectively) using a 400-W high-pressure mercury lamp at room temperature, the *c/t* ratio in PSS was determined to be ca. 80/20 by analyzing the irradiated solutions at 40 °C using a JASCO Finepack SIL column (inner diameter, 4.6 mm; length, 25 cm), 271-nm light as monitoring light (isosbestic point of the isomers), and a mixed solvent of hexane/ethyl acetate = 90/10 as an eluent. In contrast, irradiation of 2.5×10^{-3} and 1×10^{-2} M **AB** yielded a very low quantity of *c*-**AB** (ca. 60% and 50%, respectively) in PSS as shown in Figure 1. The concentration dependent *c/t* ratio in PSS was also observed in 1,1,2-trichloro-1,2,2-trifluoroethane (CCl_2FCClF_2), but the ratio in benzene (PhH) was almost constant at ca. 80/20 regardless of the initial concentration, as can be seen in Figure 1 and Table 1. In order to explain these findings, we propose here, as shown in Scheme 1, that the photoisomerization of **AB** in higher concentrations proceeds through the excimers and exciplex of **AB**, followed by the production of a dimer singlet biradical intermediate (**1**). This finally collapses into *t*-**AB**, which is more stable than *c*-**AB**. Fluorescence emission from excited singlet state **AB** and from the excimers and exciplex was not observed under our conditions probably because the lifetime in the singlet excite state is too short. In fact, the fluorescence lifetime of *t*-**AB** has been determined to be ca. 25 ps.[7] However, it should be noted that on excitation of **AB** in cyclohexane by 254-nm light from a 160-W low-pressure mercury lamp, the *c/t* ratio in PSS was found to be almost independent of the initial concentration (*c/t* = ca. 15/85 in 1×10^{-2} M and 10/90 in 2×10^{-4} M). This is because a unimolecular photoisomerization process on using 254-nm light also favors the formation of *t*-**AB** over that of *c*-**AB** probably because the ratio of $\varepsilon_{c\text{-AB}}/\varepsilon_{t\text{-AB}}$ is 8300/2200 at the wavelength.[6] It should be noted that, as indicated above, the initial concentration has no effect on the *c/t* ratio in PSS in PhH on using 313-nm light. This is probably because the formation of the excimers and exciplex was disturbed by π-interaction between benzene molecules and the benzene rings of **AB**.

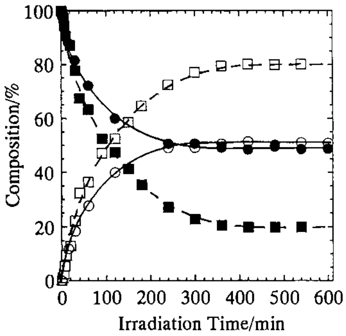

Figure 1. Irradiation of 1×10^{-2} M *t*-**AB** using 313-nm light in (a) cyclohexane (●, *t*-**AB**; ○, *c*-**AB**) and (b) benzene (■, *t*-**AB**; □, *c*-**AB**).

Using *trans*-4-methoxyazobenzene (*t*-MeO**AB**), we further examined the effect of the initial concentration on photoisomerization. The *cis* (*c*-MeO**AB**) and *trans* isomers were analyzed under conditions similar to those described above for **AB** (monitoring light, 300 nm; eluent, hexane/ethyl acetate =

Scheme 1.

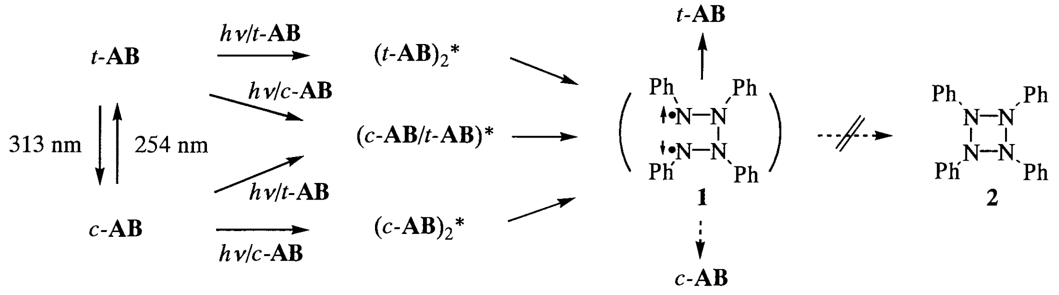

Table 1. *Cis/trans* isomer ratios of azobenzenes in the photostationary state (PSS) obtained by excitation using 254-, 313-, and 366-nm light in aerated cyclohexane (C_6H_{12}), benzene (PhH), and 1,1,2-trichloro-1,2,2-trifluoroethane (CCl_2FCClF_2)

	Concentration /M	*cis/trans* in PSS			
		254 nm[a]	313 nm for **AB** and 366 nm for MeO**AB**[b]		
		C_6H_{12}	C_6H_{12}	PhH	CCl_2FCClF_2
AB	2×10^{-4}	10/90	80/20	80/20	80/20
	1×10^{-2}	15/85	50/50	80/20	50/50
MeO**AB**	2×10^{-4}	20/80[c]	85/15	95/5	90/10
	1×10^{-2}	15/85[c]	–[d]	–[d]	–[d]

[a] Irradiated using 254-nm light. [b] Irradiated using 313-nm light for **AB** and 366-nm light for MeO**AB**. [c] $\varepsilon_{c\text{-MeOAB}}/\varepsilon_{t\text{-MeOAB}}$ = 9250/4720 at 254 nm.
[d] Not determined because of the formation of unknown dimer products.

80/20). The photoisomerization of 2×10^{-4} M *t*-MeO**AB** in aerated cyclohexane through Hoya U-360 and UV-36 glass filters (366-nm band pass; $\varepsilon_{c\text{-MeOAB}}/\varepsilon_{t\text{-MeOAB}}$ = ~0/12700) using a high pressure mercury lamp at room temperature yielded the *cis* isomer more selectively (*c/t* = ca. 85/15) as in the case of **AB** in lower concentrations using 313-nm light. However, when a 1×10^{-2} M *t*-MeO**AB** cyclohexane solution was employed, the formation of two other products was observed by HPLC analysis. The unknown products decomposed selectively to *t*-MeO**AB** on heating, on addition of MeOH, and on irradiation using 254-nm light. When CCl_2FCClF_2 and PhH, which are poor hydrogen donors, were used as solvents instead of cyclohexane, the production of the unknown products was considerably suppressed in the concentration of 1×10^{-2} M. The products could not be isolated by means of column chromatography for NMR measurement and readily decomposed to a mixture of *c*-and *t*-MeO**AB** during separation. However, their molecular weights were determined to be *m/z* = 213–215 using a Hitachi M-1200AP liquid chromatograph mass spectrometer. This corresponds to the molecular weight of the monomers; hence, the observed *m/z* corresponds to $M^+/2$ of the products and the one or two protonated fragments.

In the case of aromatic alkenes like stilbenes with a carbon-carbon double bond, irradiation of the higher concentration causes [2 + 2] cycloaddition to give cyclobutane dimers.[8] Thus, the photoisomerization of stilbenes is usually carried out in low concentrations, in which dimer products are not produced. Therefore, it seems probable, as proposed in Scheme 1, that for **AB** the corresponding tetraazacyclobutane dimers **2** are too unstable to be produced; accordingly, in higher concentrations irradiation of **AB** causes isomerization through dimer biradical **1,** which selectively collapses into *t*-**AB**, competing with a *cis-trans* unimolecular photoisomerization process dependent on the ratios of $\varepsilon_{t\text{-AB}}/\varepsilon_{c\text{-AB}}$ and $\Phi_{t\text{-}c}/\Phi_{c\text{-}t}$. However, the introduction of a methoxy group into one of the two benzene rings of **AB** would stabilize dimer biradical intermediate **1** due to resonance, and cause the formation of relatively stable dimer products by hydrogen abstraction from cyclohexane.

Finally, we suggest that the inefficient photoisomerization of azobenzenes observed in solid, polymer matrix, and polymer chains might be due to the production of the *trans* isomers through the bimolecular photo-isomerization process in an environment similar to solution in higher concentrations.

Further study is in progress to identify the dimer products obtained in the case of *t*-MeO**AB** and to gain deeper insights into the effect of initial concentration on *c/t* ratio in PSS using aromatic alkenes and other azobenzenes.

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