β-스티릴나프탈렌의 방사화학적 시스-트란스 이성질화 반응*

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Radiochemical cis-trans Isomerizaton of β-Styrylnaphthalene

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요 약. β-스티릴나프타렌의 방사화학적 이성질화 반응을 G 값과 방사정류상태를 측정하여 연구하였다. 여기서 얻은 결과와 광화학적 이성질화 반응의 연구결과를 비교함으로써 이 올레핀의 벤젠 용액을 γ-선으로 쪼여주면 들뜬 단일상태와 삼중상태가 다 이성질화 반응에 참여함을 알았다.

ABSTRACT. Radiation-induced *cis-trans* isomerization of β-styrylnaphthalene is studied by determination of *G* values and the radiostationary states. The results are compared with data obtained in direct and sensitized photoisomerization of the compound. Both the excited singlet and triplet states are involved in the isomerization of β-styrylnaphthalene in the radiolysis of benzene solution.

INTRODUCTION

The high-energy irradiation of aromatic compounds in benzene solution has been studied extensively. The aromatic compounds are relatively stable toward degradation by ionizing ^{60}Co γ-rays due to the availability of high electronic excited states having little probability of dissociation.
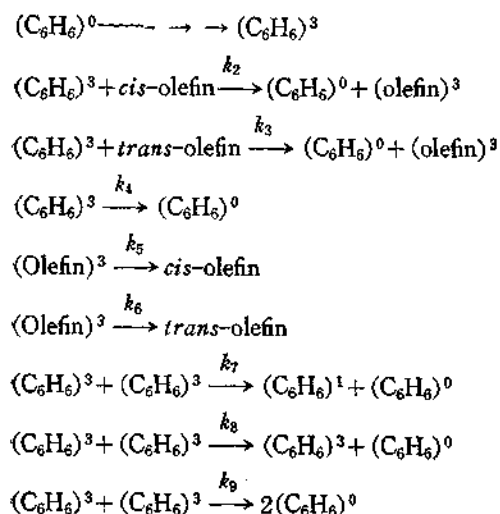
Sensitized *cis-trans* isomerization of simple alkenes and stilbenes has been used to estimate the *G*-value (molecular yield/100 eV absorbed) for benzene triplets[1~5]. $G_{triplet}$ values of 4.2 ~5.4 in benzene were reported by these measurements. Radiochemical *cis-trans* isomerization of stilbene and substituted stilbenes in benzene solution was investigated in our laboratory[6]. It was concluded from the comparison of the radiostationary states and photostationary states established with high energy sensitizers that the radiation-induced isomerization involves formation and decay of excited triplet states of stilbenes. It was believed from the studies of *G* values of triplets that a large fraction of the energy delivered to the system ultimately appears

in the scavenging solutes as triplet excitation and the key step of kinetics is transfer of triplet excitation from solvent to solute. The proposed mechanism is as follows:

$$(C_6H_6)^0 \text{------} \to \to (C_6H_6)^3$$

$$(C_6H_6)^3 + cis\text{-olefin} \xrightarrow{k_2} (C_6H_6)^0 + (\text{olefin})^3$$

$$(C_6H_6)^3 + trans\text{-olefin} \xrightarrow{k_3} (C_6H_6)^0 + (\text{olefin})^3$$

$$(C_6H_6)^3 \xrightarrow{k_4} (C_6H_6)^0$$

$$(\text{Olefin})^3 \xrightarrow{k_5} cis\text{-olefin}$$

$$(\text{Olefin})^3 \xrightarrow{k_6} trans\text{-olefin}$$

$$(C_6H_6)^3 + (C_6H_6)^3 \xrightarrow{k_7} (C_6H_6)^1 + (C_6H_6)^0$$

$$(C_6H_6)^3 + (C_6H_6)^3 \xrightarrow{k_8} (C_6H_6)^3 + (C_6H_6)^0$$

$$(C_6H_6)^3 + (C_6H_6)^3 \xrightarrow{k_9} 2(C_6H_6)^0$$

EXPERIMENTAL

Materials. Both cis- and trans-β-styrylnaphthalene were synthesized as reported[7]. Analytical grade benzene (Mallinckrodt) was purified over sulfuric acid.

Radiolysis. Solutions (2 ml) of β-styrylnaphthalene in benzene were prepared, degassed, and irradiated in sealed Pyrex 13×10 mm tubes. Irradiations were carried out in a ^{60}Co cavity source. Dosimetry (Fricke, $G=15.5$) was carried out in similar Pyrex tubes, open to air. The dose rate (corrected for absorption by the organic solvent and solute) was approximately 2.7×10^{19} eV·g^{-1}·hr^{-1}. Conversions in the cis-trans isomeric systems were carried to 4~20% of completion. Stationary states were usually obtained after irradiating dilute solutions(0.2~0.04 M) until a total dose of $6 \sim 17 \times 10^{21}$ eV had been absorbed. Analyses were performed by vapor phase chromatography. A Loenco Model 70 dual flame gas chromatograph with 5% SE-30 silicon grease on Chromosorb W or 5% silicon gum rubber on Chromosorb W columns is used.

RESULTS and DISCUSSION

The cis-trans isomerization reaction was carried out with β-styrylnaphthalene in benzene solution to low conversions (4~21%) and the G values were corrected for the back reactions[6]. The symbol G's are defined as follows:

G_T=initial yield of substrate excited states,

$G_{c,t}$=initial yield of trans from pure cis, and

$G_{t,c}$=initial yield of cis from pure trans isomer.

The results are shown in Table 1.

Radiostationary states were also established by irradiating both cis- and trans-β-styrylnaphthalene solutions with various concentration in benzene for long periods of time and the results are shown in Table 2.

The triplet energy of benzene is high enough (84.4 kcal/mol) to transfer the triplet excitation to cis- and trans-β-styrylnaphthalene with diffusion controlled rate. A small amount of side products were observed. These are probably biphenyl, partially reduced biphenyl, hydrogen, and fulvene formed from bimolecular and unimolecular reactions of electronically excited state within spurs in benzene radiolysis. The cyclization and cyclodehydrogenation of β-styrylnaphthalene were also abserved but to small extent. The formation of these side products from β-styrylnaphthalene was far more efficient when the cis isomer was irradiated indicating that the side products are formed from the cis isomer as abserved in the photochemistry of the oiefin when direct irradiation of UV light was applied. The small difference between $(c/t)_{r.s.s.}$ ratio obtained when the cis and trans isomers were used as starting materials may be attributed to these side reactions.

As shown in Table 3, there is good agreement between radiostationary state (r.s.s.) and photostationary state (p.s.s.) established with benzene as a sensitizer. However, there is

Table 1. G values of β-styrylnaphthalene in benzene.

Starting material	Conc. of solute (mol/l)	% Conversion	$G_{t \to c}$ or $G_{c \to t}$	G_T	Dose rate
trans-β-Styrylnaphthalene	2.626×10^2	21.50 ± 0.79	1.58	3.58	a
trans-β-Styrylnaphthalene	2.631×10^{-2}	9.54 ± 0.38	1.63	3.70	b
trans-β-Styrylnaphthalene	3.938×10^{-2}	17.27 ± 0.37	1.76	4.00	a
trans-β-Styrylnaphthalene	3.947×10^{-2}	7.13 ± 0.24	1.77	4.02	b
trans-β-Styrylnaphthalene	5.250×10^{-2}	14.68 ± 0.54	1.92	4.36	a
trans-β-Styrylnaphthalene	5.263×10^{-2}	5.76 ± 0.12	1.87	4.25	b
trans-β-Styrylnaphthalene	1.178×10^{-1}	4.06 ± 0.09	2.21	5.01	c
cis-β-Styrylnaphthalene	3.539×10^{-2}	13.59 ± 0.25	2.40	4.17	c

a: Dose (benzene) $= 6.977 \times 10^{19}$eV/ml/hr, tubes containing 2 ml of solutions were irradiated for 4 hours,
b: Same dose rate were used for 1 1/2 hours,　　c: Dose $= 27.272 \times 10^{19}$ eV/2 ml benzene/2 hours. All values are means of three measurements.

Table 2. Radiostationary states of β-styrylnaphthalene in benzene.

Starting Compound	Conc. of starting compound (mol/l)	% *Cis* at stationary states	$(cis/trans)_{r.s.s.}$	Dose
trans-β-Styrylnaphthalene	1.764×10^{-2}	44.68	0.81	b
trans-β-Styrylnaphthalene	1.764×10^{-2}	44.30	0.80	c
trans-β-Styrylnaphthalene	2.625×10^{-2}	44.04	0.70	a
trans-β-Styrylnaphthalene	3.527×10^{-2}	45.53	0.84	b
trans-β-Styrylnaphthalene	3.527×10^{-2}	44.57	0.81	c
trans-β-Styrylnaphthalene	5.291×10^{-2}	44.90	0.82	b
cis-β-Styrylnaphthalene	1.698×10^{-2}	43.27	0.76	b
cis-β-Styrylnaphthalene	1.698×10^{-2}	43.68	0.77	c
cis-β-Styrylnaphthalene	2.588×10^{-2}	43.68	0.77	c
cis-β-Styrylnaphthalene	2.588×10^{-2}	45.81	0.85	b
cis-β-Styrylnaphthalene	3.539×10^{-2}	43.92	0.78	c
cis-β-Styrylnaphthalene	3.539×10^{-2}	42.45	0.74	d
			average $0.80 + 0.03$	

Dose: $a = 6.80 \times 10^{21}$eV,　$b = 6.62 \times 10^{21}$eV,　$c = 1.66 \times 10^{22}$eV and $d = 6.022 \times 10^{21}$eV.

Table 3. Comparison of radiostationary and photostationary states of β-styrylnaphthalene.

Radiostationary states in benzene, % *cis*	Photostationary states, % *cis*			
	Direct Isomerization		Sensitized Isomerization	
	366.0 nm in benzene	253.7 nm in *n*-Hexane	Benzophenone	benzene
44.20	41.23	40.47	56.41	45.17

a significant difference between r.s.s and p.s.s. when benzophenone, the most used triplet sen- sitizer, is used as a sensitizer. Also, the p.s.s. established with direct irradiation at 366 and

253. 7 nm are very close to r.s.s. observed in benzene solution. The singlet reactions are defi-nitely involved in photosensitized isomerization with benzene as a sensitizer. The important reasons are: 1) the benzene singlet is long-lived and effective to transfer its singlet energy to substrates 2) the singlet energy of benzene is much higher than that of β-styrylnaphthalene 3) the triplet yield of benzene never reaches unity, the highest value reported being $<$0.8. Thus singlet energy transfer from benzene to the olefin should be significant in benzene sensitized photoisomerization of the olefin. The formation of singlet excited states during the radiolysis of benzene has been known for some time and is the basis of liquid scintillation counting[9]. The G value for excited singlet states formed in the radiolysis of tetramethyloxetanone in benzene-biphenyl solution was determined to be 3.4±0.3 in our laboratory[10]. The singlet contribution in radiation-induced isomerization of β-styrylnaphthalene in benzene is therefore expected.

The similarity of r.s.s. and p.s.s. with direct irradiation indicates that the singlet mechanism is significant in determining the r.s.s. even though the amount of side products observed in radiolysis is much smaller than that observed in photoreactions.

The radiostationary cis/trans ratio in benzene should be determined by the ratio of triplet decay, k_5/k_6, if the triplet mechanism postulated for stilbenes is applied. The decay ratio of β-t-styrylnaphthalene was 1.29 when benzophenone was used as a sensitizer.

$$(c/t)_{r.s.s.} = k_5/k_6$$

The observed r.s.s. cis/trans ratio in benzene solution is 0.80±0.03 which is quite different from benzophenone sensitized p.s.s. The r.s.s. can also be expressed by following equation.

$$(c/t)_{r.s.s.} = \frac{G_{t \to c}}{G_{c \to t}}$$

and

$$(\% \ cis)_{r.s.s.} = \frac{G_{t \to c}}{G_{t \to c} + G_{c \to t}}$$

The calculated value of cis/trans ratio at r.s.s. is 0.73 when 3.6×10^{-2} M solution of β-styrylnaphthalene is used. The agreement is good compared to benzophenone sensitized photo-reactions. There is also excellent agreement between the observed (44.2%) and the calculated value (42.4%) of $(\%cis)_{r.s.s.}$. These observations strongly indicate that radiation-induced isomerization of β-styrylnaphthalene involves both singlet and triplet mechanism. This is not surprising because of the reasons mentioned earlier. Furthermore, benzene $G_{singlet}$ value is relatively high and the excited singlets of β-styrylnaphthalene do not decay exculsively by the triplet manifold.

G_T values are plotted against the logarithm of the β-styrylnaphthalene concentration in Fig. 1. These G_T values were determined by applying
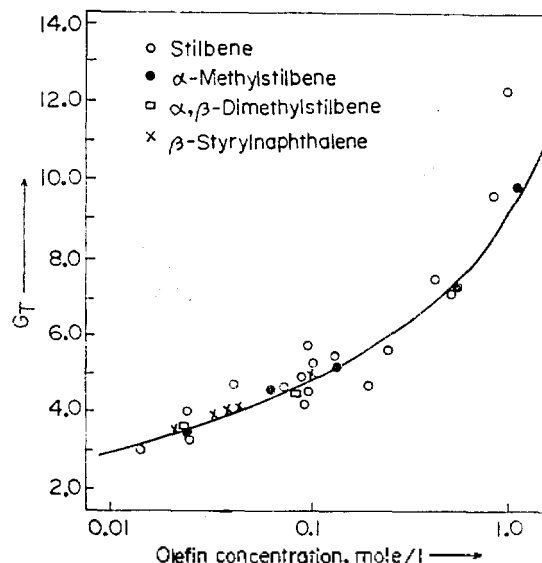

Fig. 1. G Values for β-Styrylnaphthalene.

the stationary state measurements. This provides the measure of the electronically excited β-styrylnaphthalene molecules and consequently the scavenged benzene excited molecules in radiolysis of benzene solution. As shown in the figure, G_T values of β-styrylnaphthalene agree excellently with those of stilbenes and substituted stilbenes. This was expected since all acceptors are expected to quench the excited benzene molecules with equal efficiency. The singlet contribution observed here may also be the reason for the anomalous behavior observed in stilbene radiolysis. This argument is further justified since the direct photoisomerization of stilbene is now believed to undergo via excited singlet state rather than the triplet manifold[11].

ACKNOWLEGEMENT

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