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KINETICALLY CONTROLLED EQUILIBRIUM IN CIS-TRANS ISOMERIZATION OF PROPENYLBENZENE

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The interconversion of the cis and trans isomers of olefins has been known to chemists almost ever since the discovery of geometrical isomerism and has been extensively studied, still remaining some ambiguous points(1). Nowadays, we know that (generally) there are two types of equilibria between isomers; thermal and photochemical. In common, the thermal or catalytic isomerization tends to predominate the thermodynamically more stable isomer over the other, while the unstable isomer is favored by photochemical isomerization.

In this paper, we will report that cis-trans isomerization of propenylbenzene forms quite unique spectrum when the isomerization is catalyzed by photoexcited thiobenzophenone or by thiyl radicals.

When a mixture of cis- or trans-propenylbenzene and thiobenzophenone was irradiated with 5890Å light from a sodium lamp under an atmosphere of carbon dioxide, 2,2,3-triphenyl-4-methylthietane was formed in 63% yield and, at the same time, the recovered olefin was found to be isomerized(2). The results on the isomerization of propenylbenzene are listed in Table I, from which the cis/trans composition at the equilibrium state is determined as 3.1/96.9. Since propenylbenzene is transparent at 5890Å but thiobenzophenone is excited to its n,π^* triplet state by the light of this wavelength(3,4), it is evident that the isomerization of propenylbenzene is sensitized by thiobenzophenone. However, almost the same cis/trans composition can be obtained at the equilibrium state of thermal isomerization: when a mixture of propenylbenzene, benzenethiol or butanethiol, and azobisisobutyronitrile was allowed to stand in a thermostat of 50° under an atmosphere of argon, the isomerization of the olefin leads the

Table I

Thiyl Radical	Temp, °C	%cis/%trans in Olefin[a] Initial	Final	Composition at Equilibrium[b] %cis	%trans
$^3(Ph_2CS)_{n,\pi^*}$	25	0.5/99.5	2.2/97.8	3.1 ± 0.7	96.9 ∓ 0.7
$^3(Ph_2CS)_{n,\pi^*}$	25	25.7/74.3	3.0/97.0		
$^3(Ph_2CS)_{n,\pi^*}$	25	98.7/ 1.3	4.2/95.8		
PhS·	52.3	0.6/99.4	3.6/96.4	4.1 ± 0.4	95.9 ∓ 0.4
PhS·	52.3	97.3/ 2.7	4.8/95.2		
n-BuS·	52.3	0.6/99.4	4.1/95.9		
n-BuS·	52.3	97.3/ 2.7	3.8/96.2		

a. Analyzed by vpc. The estimated error is ±0.5%. b. Mean of final compositions.

Table II

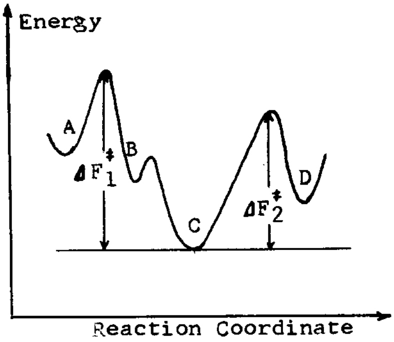
Time,hr	%cis/%trans in Olefin[a]	Time,hr	%cis/%trans in Olefin[a]
0	97.1/ 2.9	0	5.6/94.4
16	78.6/21.4	16	25.5/74.5
31	69.1/30.9	30	34.0/66.0
42	68.3/31.7	42	39.9/60.1
		150	58.2/41.8
		200	60.4/39.6

a. Analyzed by vpc. The estimated error is ±0.5%.

composition of isomers to 4.1% *cis* and 95.9% *trans* at the equilibrium state as shown in Table I.

On the other hand, the thermodynamic equilibrium composition of both isomers can be calculated, by using the equilibrium constants of formation ($\log K_{cis} = -37.874$, $\log K_{trans} = -37.320$)(5), as 21.8% *cis* and 78.2% *trans* at 27°. As commonly expected, the photochemical isomerization makes the *cis*-isomer larger component than the *trans*-isomer. The results of the irradiation of propenylbenzene with 3660Å light from a high-pressure mercury lamp with a Pyrex filter are listed in Table II.

Thus, the isomerization of propenylbenzene caused by thiyl radicals(6) has the equilibrium constant differing completely from those of thermal and photo-



A: cis-olefin + RS·
B: cis-type intermediate
C: trans-type intermediate
D: trans-olefin + RS·

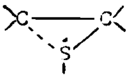
Fig. 1

chemical isomerizations. The presence of the third equilibrium constant may be interpreted in terms of fairly stable addition intermediate(s) which is in equilibrium with both isomers of propenylbenzene. As schematically shown in Fig.1, if one of intermediates, say C, is energetically more stable than systems of reactants and products, A and D, thermodynamic stabilities of both isomers no longer control the equilibrium composition but free energies of activation of the reactions C ⟶ A and C ⟶ D determine the amounts of isomers at the equilibrium state:

$$\frac{[A]}{[D]} = \exp\left(\frac{\Delta F_2^{\ddagger} - \Delta F_1^{\ddagger}}{RT}\right)$$

, where [A]/[D] is equal to [cis-olefin]/[trans-olefin] because the concentration of the thiyl radical cancels.

The addition of methanethiyl radical to ethylene is an exothermic reaction with ΔH = -14kcal/mole(7), which makes a sharp contrast to the addition of iodine atom to ethylene (ΔH = 7kcal/mole)(8). Coupled with our previous proposal on stabilization of a radical center by the participation of β-sulfur, likely representation being I(4), this supports the idea of fairly stable intermediate.



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Mention should be added on the fact that the trans-isomer is unexpectably preponderant in kinetically controlled equilibration than in thermodynamically controlled one. The reaction C ⟶ A involves the elimination of thiyl radical and the rotation of central C—C bond and since the former is nearly the same energetic process with the reaction C ⟶ D, the difference in free energies of activation, $\Delta\Delta F^{\ddagger} = \Delta F_2^{\ddagger} - \Delta F_1^{\ddagger} = -1.87 \sim -1.98$ kcal/mole, mainly depends on the free-energy difference between B and C. Although the exact value of the difference is not available, we can estimate it to be larger than that of formations of *cis*- and *trans*-propenylbenzenes (ΔF^{o} = 0.76kcal/mole at 27^{o})(5).

References

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