July, 1971] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 1901—1904 (1971) 1901

Kinetics and Equilibrium Positions of *cis-trans* Isomerization of 1,2-Bis(phenylthio)ethylene and Its Exchange with Benzenethiyl Radicals

Atsuyoshi Ohno, Tomo'o Saito, Akio Kudo, and Gen-ichi Tsuchihashi
Sagami Chemical Research Center, Ohnuma, Sagamihara-shi, Kanagawa

(Received December 7, 1970)

Kinetics of the *cis-trans* isomerization of 1,2-bis(phenylthio)ethylene induced by benzenethiyl radicals and the exchange of phenylthio group have been studied by using thiophenol-*phenyl*-^{14}C. Pseudo-first order rate constants for the isomerization and the exchange are $2.08\pm0.22\times10^{-5}$ sec^{-1} and $2.03\pm0.26\times10^{-5}$ sec^{-1} at 50°C, respectively. The *cis*/*trans* ratio of this olefin is 55—58/45—42 at the completion of the reaction, which differs from the value obtained from the reaction induced by iodine (48—49/51—52). The difference has been interpreted with the idea that the isomer composition in the *cis-trans* isomerization is determined by kinetic factors when the reaction is initiated by thiyl radicals.

Many studies have been carried out on the *cis-trans* isomerization of olefins. We know that there are generally two types of equilibria, thermal and photochemical. The thermodynamically more stable isomer is favored by thermal or catalytic isomerization, while the unstable isomer is favored by photochemical isomerization. In the course of our studies on the photocycloaddition of thiobenzophenone to propenylbenzene, we have found that *cis-trans* isomerization of the olefin takes place during the reaction, but the equilibrium compositions of the isomers are completely different from those of thermal and photochemical ones. Thus thermal equilibrium of propenylbenzene forms (at 27°C) 21.8% of *cis*- and 78.2% of *trans*-isomers,[1] while direct photo-irradiation to this olefin produces an equilibrium mixture of about 60—68% *cis*- and 40—32% *trans*-isomers.[2] On the other hand, when thiobenzophenone is present in the photo-irradiated system, the *cis*/*trans* ratio changes to 3.1/96.9, which is the same as that when thiyl radicals are employed for the catalysts of the thermal isomerization of the olefin (*cis*/*trans*=4.1/95.9 at 52.3°C[2])). Since it is known that photo-irradiation to thiobenzophenone yields its n,π^* triplet state and this species behaves like a thiyl-radical,[3,4] there is no doubt that thiyl radicals play a different role form that of other radical catalysts in *cis-trans* isomerizations of olefins.

These findings prompted us to study the *cis-trans* isomerizations of 1,2-bis(phenylthio)ethylene induced by benzenethiyl radicals and iodine, and the exchange reaction of this olefin with isotopically labeled benzenethiyl radicals.

Results

All experiments were carried out in *p*-xylene at 50.0±0.05°C. Isomerization of 1,2-bis(phenylthio)ethylene was initiated by benzenethiyl radicals derived from benzenethiol and azobisisobutyronitrile. The *cis-trans* ratios of the olefin at desired time intervals were determined by vpc and the equilibrium composition was found to be 55% and 45% for *cis*- and *trans*-olefins, respectively. Similar results were also obtained by isotope-labeling technique (*cis*/*trans*=57.6/42.4). Results are illustrated in Figs. 1 and 2. When 1,2-bis(phenylthio)ethylene was isomerized with the aid of iodine atoms, the composition of the olefin approached the asymptote of 48.5% *cis*- and 51.5% *trans*-isomers.

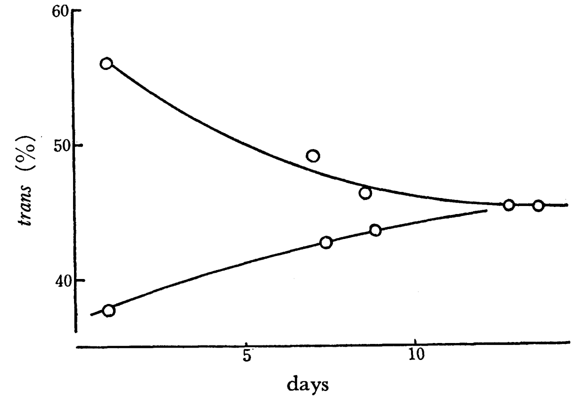

Fig. 1. Time-dependency of the isomer composition of 1,2-bis(phenylthio)ethylene catalyzed by benzenethiyl radicals and followed by vpc-method.

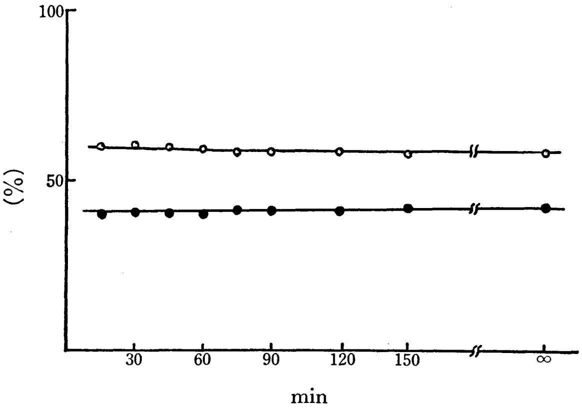

Fig. 2. Time-dependency of the labeled isomer composition of 1,2-bis(phenylthio)ethylene catalyzed by thiyl radicals and followed by isotope-labeling technique.
○: *cis*-isomer ●; *trans*-isomer

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[1] J. E. Kilpatrick, C. W. Beckett, E. J. Prosen, K. S. Pitzer, and F. D. Rossini, *J. Res. Natal. Bur. Stand.*, **42**, 225 (1949).

[2] A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *Tetrahedron Lett.*, 643 (1969).

[3] A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *J. Amer. Chem. Soc.*, **91**, 5038(1969).

[4] E. S. Huyser and R. M. Kellogg, *J. Org. Chem.*, **30**, 2867 (1965).

TABLE 1. KINETICS OF ISOMERIZATION AND EXCHANGE OF 1,2-BIS(PHENYLTHIO)ETHYLENE

Starting isomer	*cis*	*trans*	*cis*	*trans*	*cis*
Olefin, g/50 m*l*	1.2286	1.2333	1.2286	1.2321	1.2327
AIBN, mg/50 m*l*	8.135	8.213	8.213	8.242	8.000
Thiophenol-^{14}C, mg/50 m*l*	311.45	311.70	311.70	310.90	310.90
No. of points plotted	8	8	8	10	9
Total activity,a) 10^{-6} dpm/10 m*l*	1.982	2.017	1.971	2.010	1.988

	% Activity in olefinb)									
Recovered isomer / Reaction time, min	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*	*trans*	*cis*
15	0.80	1.26	0.51	0.80	0.85	0.97	1.17	2.40	0.48	0.66
30	1.37	2.06	1.04	1.53	1.14	1.82	1.77	2.84	0.75	1.32
45	2.03	2.79	1.83	2.62	1.57	2.31	2.68	4.03	1.96	2.77
60	2.56	3.67	2.20	3.23	1.49	2.21	2.81	3.96	2.42	3.56
75	3.04	4.62	3.42	4.42	2.15	2.97	3.57	4.98	2.32	3.41
90	3.77	5.31	3.48	4.78	2.93	4.00	3.93	5.95	3.15	4.57
120	4.75	6.52	4.09	5.57	3.20	4.79	5.53	7.87	4.00	5.68
150	5.58	7.71	5.70	7.52	4.10	5.58	6.80	8.94	4.84	6.83
∞c)	33.38	47.83	35.85	43.99	33.45	46.40	35.32	43.34	34.31	47.24
Composition, %	41.12	58.88	43.84	56.16	41.73	58.27	44.90	55.10	41.62	58.38
k_i or k_e,d) 10^5 sec^{-1}	1.99	1.87	1.85	2.00	2.34	2.36	2.34	2.36	1.71	1.73

a) The total activity of the reaction mixture.

b) Percentage of the activity of an olefin to the total activity of the reaction mixture.

c) 15 days.

d) k_i for the recovered *trans*-olefin and k_e for the recovered *cis*-olefin, when the starting isomer is the *cis*-olefin, and *vice versa.*

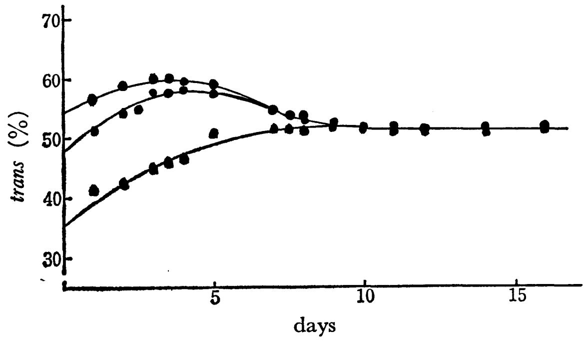

Fig. 3. Time-dependency of the isomer composition of 1,2-bis(phenylthio)ethylene catalyzed by iodine atoms and followed by vpc-method.

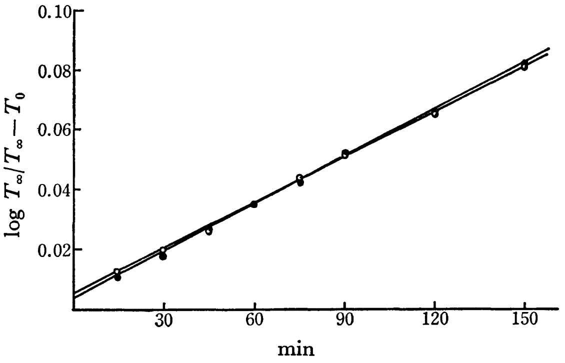

Fig. 4. The pseudo-first order rate plots for the isomerization and the exchange of 1,2-bis(phenylthio)ethylene (The first run of Table 1).

○: *cis*-isomer ●: *trans*-isomer

However, in this case, the composition does not change smoothly, and has a maximum point as shown in Fig. 3.

Pseudo-first order kinetics of the isomerization and exchange were followed by using benzenethiyl-*phenyl*-^{14}C radicals,[5] and rate constants k_i and k_e were found to be $2.08 \pm 0.22 \times 10^{-5}$ sec^{-1} and $2.03 \pm 0.26 \times 10^{-5}$ sec^{-1}, respectively.[6] The rate constants were calculated by the least-squares method using the data in Table 1. An example of the pseudo-first order rate plots is shown in Fig. 4.

Substantial amounts of diphenyl disulfide were formed during the reactions, but the yield was larger in the reaction with iodine than with benzenethiyl radicals. About 10% of 1,2-bis(phenylthio)ethane was also obtained from the reaction with iodine.

Discussion

As has been observed with propenylbenzene, benzenethiyl radical shifts the equilibrium composition of 1,2-bis(phenylthio)ethylene from that given by iodine. The latter constant is thought to be thermodynamically controlled.[7]

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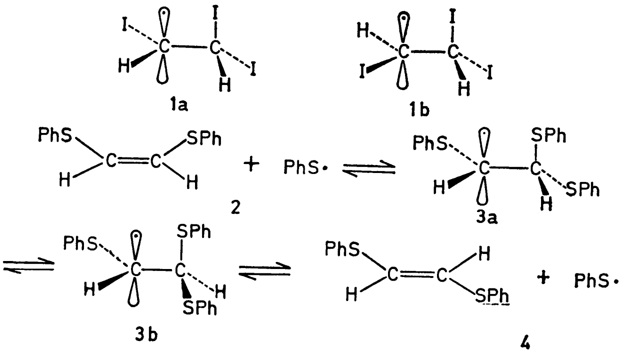
[5] Since the rate of isomerization must be followed during the very early stage of the reaction in order to avoid complexity caused by the other isomer produced, the vpc-method is inadequate as it includes comparison of very small and very large peak areas which inevitably leads to large errors.

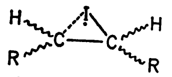
[6] The *true* rate constants for the isomerization k'_i and the exchange k'_e should be calculated by $k'_i = \alpha k_1$ and $k'_e = \alpha k_0$ $(1 \leq \alpha \leq 2)$. The value of α changes according to relative rates of the rotation of the central carbon-carbon bond in the intermediate radicals **3**, and the elimination of benzenethiyl radical from it. However, since both rate constants have the same factor, we will employ the observed rate constants k_i and k_e for discussions.

[7] For example, E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., New York, N. Y. (1962). pp. 337—346.

The kinetics of the *cis-trans* isomerization of diiodoethylene and its exchange with iodine have been studied extensively by Noyes and his co-workers.[8] The rate constants for the isomerization and the exchange with this system are, on an average, $1.5\times10^{-3}\,\mathrm{sec}^{-1}$ and $1.4\times10^{-1}\,\mathrm{sec}^{-1}$, respectively, at 144°C. Thus, the exchange is one hundred times faster than the isomerization in this system. On the other hand, the kinetics with the system of 1,2-bis(phenylthio)ethylene and benzenethiyl radicals has revealed that the isomerization and the exchange proceed at the same rate. This is the main difference in the behavior of iodine and thiyl radicals.



A greater exchange rate than that of isomerization in the case of diiodoethylene has been interpreted in terms of restricted rotation around the carbon-carbon bond[9] in the common intermediates, **1**.[7] If **3** had the life-time of the same order of magnitude as **1**, we should conclude that the energy barrier of the rotation in **3** must be lower than that in **1** in order to interpret the same rate of exchange and isomerization. This is, however, highly unlikely, since the volume of a phenylthio group is supposed to be large enough to form a barrier comparable to that of **1**. If one assumes the structure **5** only for the intermediate of the reaction



(R = I, PhS)
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with iodine, the exchange should not be as fast as the isomerization considering the microscopic reversibility of the reaction. Consequently, we believe that the intermediates **3** have a life-time long enough to rotate the carbon-carbon bond freely, or that they are fairly stable and can be regarded as only one species instead of two distinct radicals. In other words, **3a** and **3b** are conformational but not configurational isomers. Thus, 1,2-bis(phenylthio)ethylene has a different equilibrium composition, when treated with benzenethiyl radicals, from that expected from thermodynamics, which can be seen from the reaction diagram schematically shown in Fig. 5. Since the intermediate **3** is energetically more stable than systems of **2** and **4**, thermodynamic stabilities of olefin isomers no longer control the equilibrium composition, but free energies of activation of reactions **3**→**2** and **3**→**4** determine the amounts of isomers at the equilibrium state:

$$\frac{[\mathbf{2}]}{[\mathbf{4}]} = \frac{[cis\text{-olefin}]}{[trans\text{-olefin}]} = \exp\left(\frac{\Delta F_2^{\ddagger} - F_1^{\ddagger}}{RT}\right)$$

This explanation includes one ambiguous assumption that *cis*- and *trans*-olefins are produced only from conformations **3a** and **3b**, respectively. This possibility is discussed in terms of the angle of the rotation around the carbon-carbon bond at the transition state.[8]

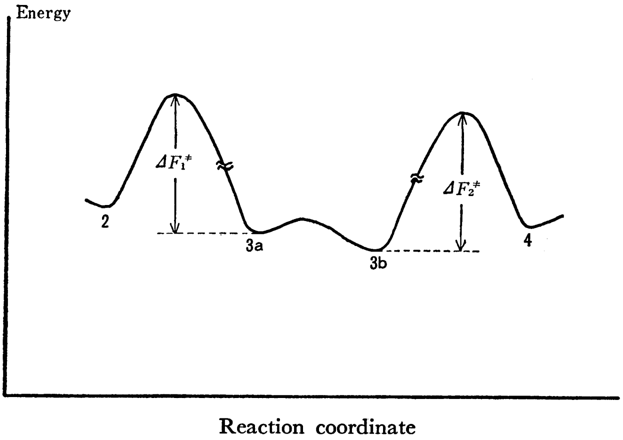

Fig. 5. Schematic energy diagram for reactions of 1,2-bis-(phenylthio)ethylene with benzenethiyl radicals.

The diagram in Fig. 5 can be explained by the fact that the addition of methanethiyl radical to ethylene is an exothermic reaction with $\Delta H = -14$ kcal/mol, while that of iodine atom to ethylene is an endothermic one with 7 kcal/mol.[10]

It should be noted that the third reaction, the formation of diphenyl disulfide by the combination of benzenethiyl radicals, takes place from **2** and **4** competitively during the isomerizations and exchanges, or leakage from the systems **2** and **4** occurs concurrently and the whole system is in dynamic equilibrium. In this connection, the term "equilibrium" composition may be inadequate, but it could be said that *the final compositions of isomers are determined by kinetic factors when the cis-trans isomerization of an olefin is catalyzed by thiyl radicals.*

It has been mentioned that the composition of isomers of 1,2-bis(phenylthio)ethylene does not approach the asymptote smoothly when the isomerization is catalyzed by iodine (Fig. 3). This indicates that the *true* or thermodynamic equilibrium composition should possess a larger proportion of the *trans*-isomer (smaller proportion of the *cis*-isomer) than that observed here. Since benzenethiyl radicals are produced, as can be seen by the formation of a large amount of diphenyl disulfide during the reaction, they also act as catalysts and the observed composition of isomers changes as the reaction proceeds. This may be an additional proof for the different catalytic behavior of a thiyl radical and an iodine atom in *cis-trans* isomerizations of olefins.

Further Comments on Propenyl Benzene. In our

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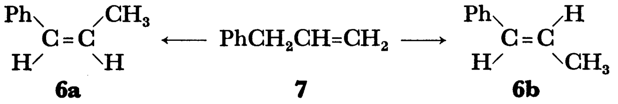
[8] R. M. Noyes, R. G. Dickinson, and V. Schomaker, *J. Amer. Chem. Soc.*, **67**, 1319 (1945).

[9] A. Berthoud and C. Urech, *J. Chem. Phys.*, **27**, 291 (1930).

[10] C. Walling, "Free Radicals in Solution." John Wiley & Sons, Inc., New York, N. Y. (1957), pp. 341 and 314.

proposal given above and previously,[2] we claim that the *cis-trans* isomerization of an olefin does not give a true or thermodynamically proposed equilibrium constant, when it includes a very stable intermediate and both isomers cannot equilibrate directly. Thus, it is reasonable to expect that such kind of phenomena could be observed from systems other than thiyl radical-catalyzed reactions.[11]

When allylbenzene is treated with potassium *tret*-butoxide in dimethylsulfoxide at 25°C, propenylbenzen with *trans*/*cis* ratio of 44.4 is formed.[12] However, if the reaction is



carried out starting form allylbenzene with potassium *tert*-butoxide in *tert*-butyl alcohol at 25°C, the *trans*/*cis* ratio in propenylbenzene changes to 12.9. Kinetically controlled equilibrium clearly exists in the latter case, since under the conditions the reactions **6a** to **7** and **6b** to **7** do not take place.

Another example can be seen in the isomerization of **7** to **6** catalyzed by palladium(II) chloride. Here again the reverse reactions are very slow and the final *trans*/*cis* ratio of 19.0 in **6** is controlled kinetically.[13]

These observations support our assumption that the isomer ratio in *cis-trans* isomerization of propenylbenzene induced by thiyl radicals are kinetically controlled.[2]

Experimental

Materials. The isomers of 1,2-bis(phenylthio)ethylenes were prepared after Parham and Herberling[14]; mp 31.5—32.0°C (lit,[14] 32.0—32.5°C) for the *cis*-isomer and 63.5—64°C (lit,[14] 64°C) for the *trans*-isomer. Azobisisobutyronitrile was purified by recrystallizations and used at the longest within 3 days. Thiophenol-*phenyl*-^{14}C was prepared from benzene-^{14}C and chlorosulfuric acid[15] followed by reduction with Zn-H_2SO_4[16] and purified as described previously[17]. The same procedure was employed for the purification of non-radioactive thiophenol. Iodine was purified by sublimations and used immediately. The solvent, *p*-xylene, was once distilled and carefully redistilled over sodium chips. All materials were stored at −18°C under an atomosphere of nitrogen and purities were confirmed by vpc prior to use.

Procedures. Reaction mixtures were prepared in a vacuum-dry box under an atomosphere of nitrogen or argon. An example for the experiment with vpc-method is as follows: 1 m*l* solutions of 0.10 M olefin, 0.056 M thiophenol, and 9.7×10^{-4} M of azobisisobutyronitrile each were combined and diluted to 5 m*l*. Aliquots of 50 μl were sealed in capillaries and immersed in a thermostat of 50.0±0.05°C. At desired intervals, compositions of aliquots were detected by vpc on a Hitachi K-53 (FID) with a column of XE-60 at 200°C. Peak areas of olefins were calculated by the half-height-width method and *cis*/*trans* ratios were calculated with the aid of a calibrating curve.

In experiments with thiophenol-*phenyl*-^{14}C, 22 m*l* solutions each prepared as described above were placed in ampuls and vacuum-sealed. After being immersed in the thermostat and picked up, two portions of 10 m*l* solutions were pipetted from the aliquot. To each solution, 700 mg of *cis*- and *trans*-1,2-bis(phenylthio)ethylene were added, respectively. The mixtures were washed immediately once with 20 m*l* of 10% aq-Na_2CO_3 and three times with 100 m*l* of water. After evaporation of the solvent, *cis*- and *trans*-olefins thus obtained were recrystallized from ethanol, vacuum dried, and subjected to activity-measurements on a Beckmann LS-250 Liquid Scintillation Counter. Activities were corrected with the aid of calibrating curves for each isomer. The total activity of the reaction mixture was obtained by pipetting 20 μl of solution from the aliquot after the reaction and subjecting to the activity countings.

The procedure for reactions with iodine was the same as described above except for the use of iodine in place of thiophenol.

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[11] We thank Dr. W. J. Muizebely of The Katholieke Universiteit, Netherlands for suggestions in his letter of August 25, 1969.

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