Spectrophotometric Study of the Iodine-Complexes of cis- and trans-Stilbene

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Results of the experiments[1], carried out recently in this laboratory, on the iodine-catalyzed *cis-trans* isomerization of stilbene in *n*-hexane led to the suggestion that the molecular complex formed between iodine and stilbene may play an important role in the photochemical as well as in the thermal isomerization at low temperatures around room temperature. It seemed then desirable to investigate the equilibria in the formation of iodine-complexes of both *cis*- and *trans*-stilbene quantitatively, since only limited information was available about these equilibria and related thermodynamic quantities. The present paper reports a spectrophotometric study of these complexes. The equilibrium constants, the heats and the entropy changes for the formation of iodine-complexes of *cis*-stilbene in *n*-hexane and of *trans*-stilbene in *n*-hexane and in carbon tetrachloride have been determined.

Experimental

Materials.—*Iodine.*—The commercial reagent of special grade was used without any further purification.

cis-Stilbene. — The preparation described in "Organic Syntheses"[2] was followed. After several repetitions of vacuum distillation, the product (b. p. 114~119°C/3.5~4.0 mmHg) was stored in the dark under reduced pressure. The absorption curve was in good agreement with that previously reported[3].

trans-Stilbene.—The commercial reagent (m. p. 119~120°C) was used without any further purification. The absorption curve was again in good agreement with that previously reported[3].

n-Hexane.—The commercial reagent of chemically pure grade was treated with fuming sulfuric acid, concentrated sulfuric acid and an aqueous solution of potassium permanganate, successively. After drying over anhydrous calcium chloride, the product was fractionally distilled.

Carbon tetrachloride.—The commercial reagent was successively treated with potassium hydroxide and anhydrous calcium chloride and then fractionally distilled.

Methods.—The absorption spectra were measured with an EPB-U type Hitachi-spectrophotometer. A quartz cell with a glass stopper (10.0 mm. light path) was used for the measurement in all wavelength regions.

The temperature of the absorption cell was kept constant in a water-circulating thermostat equipped with windows, as described by Bell[4].

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[1] To be published in a later paper.

[2] R. E. Buckles and N. G. Wheeler, "Organic Syntheses", Vol. 33, John Wiley & Sons, New York (1953), p.88.

[3] G. P. Mueller and D. Pickens, *J. Am. Chem. Soc.*, **72**, 3626 (1950); M. Orchin et al., *J. Chem. Educ.*, **34**, 493 (1957).

[4] P. H. Bell, *Science*, **105**, 15 (1947).

All the operations were carried out in a dark place in order to avoid the occurrence of iodine-catalyzed *cis*-*trans* photoisomerization of stilbene.

Results and Discussion

Visible Absorption Bands of Iodine-Stilbene Complexes.—Iodine has an absorption maximum at 520 mμ in *n*-hexane, its absorbance over the range from 430 to 270 mμ being very weak. *cis*-Stilbene shows no absorbance in the range longer than 350 mμ in the same solvent. As *cis*-stilbene is added in increasing amounts to a dilute solution of iodine in *n*-hexane, the absorption peak at 520 mμ characteristic of the free iodine diminishes and is replaced by a new peak at 420 mμ as shown in Fig. 1. This new peak at 420 mμ may, therefore, be interpreted as a blue shift of iodine such as is frequently observed for iodine-complexes[5]. The charge-transfer band of the complex which may also be expected to appear in a still shorter wavelength region has not been studied in this work on account of difficulties due to the overlapping intense absorption of *cis*-stilbene.

Preliminary experiments in which the ratio of concentration of iodine to that of *cis*-stilbene was varied, keeping the sum of these constant, showed that the optical density at the absorption maximum was greatest in the equimolar mixture, indicating that the composition of the complex formed is 1 : 1. Isosbestic points such as those seen in Fig. 1 and less clearly in Fig. 2 have frequently been observed for 1 : 1 complexes.

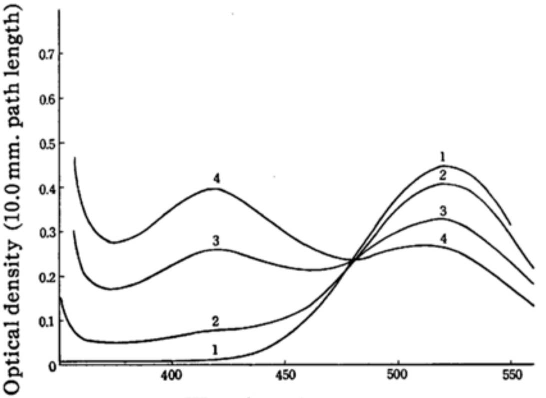

Fig. 1. Variation of the absorption band of iodine with increasing concentration of *cis*-stilbene: solvent, *n*-hexane; temperature, 24°C; concentration of I_2, 5.0×10^{-4} M; concentrations of *cis*-stilbene, 0, 2.0×10^{-2}, 1.0×10^{-1}, and 1.9×10^{-1} M for curves 1—4, respectively.

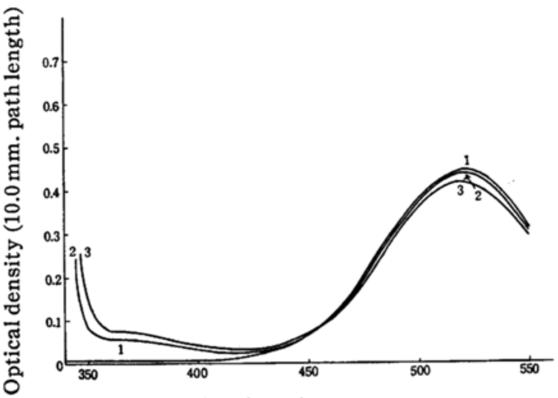

Fig. 2. Variation of the absorption band of iodine with increasing concentration of *trans*-stilbene: solvent, *n*-hexane; temperature, 24°C; concentration of I_2, 50×10^{-4} M; concentrations of *trans*-stilbene, 0, 5.0×10^{-2}, 9.5×10^{-2} M for curves 1—3, respectively.

Results obtained with *trans*-stilbene in the same solvent were, on the whole, similar to those with *cis*-stilbene. Here, however, the equilibrium constant for the complex formation has a lower value than for *cis*-stilbene as shown below. Consequently, the new maximum at 365 mμ which may again be taken as a blue shift of iodine is, as seen in Fig. 2, less sharp than that for *cis*-stilbene.

Andrews and Keefer[6a] reported an absorption maximum at 373 mμ, and a molar extinction coefficient of 7140 at this wavelength for the iodine-complex of *trans*-stilbene in carbon tetrachloride. In order to compare them with these results[6], measurements in carbon tetrachloride have been traced for the iodine-complex of *trans*-stilbene. The results obtained, together with those in *n*-hexane, are given in Table I where molar extinction coefficients determined as described below are included. As for the *trans*-stilbene complex in carbon tetrachloride, the values of $\lambda_{\max}$ obtained by the present author and by Andrews and Keefer agree with each other, but those of $\varepsilon_{\max}$ differ considerably from each other. Though the reason for the discrepancy in $\varepsilon_{\max}$ is not

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[5] H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949); C. Reid and R. S. Mulliken, ibid., **76**, 3869 (1954); S. Nagakura, ibid., **80**, 520 (1958); P. A. D. de Maine, *J. Chem. Phys.*, **26**, 1192 (1957).

[6] (a) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **74**, 4500 (1952); see also (b) R. Bhattacharya and S. Basu, *Trans. Faraday Soc.*, **54**, 1286 (1958).

clear yet*, Table I shows that all the values of ε_{max} found in this work for the iodine-stilbene complexes are nearly equal to each other and are of the same order of magnitude as those for free iodine. This is consistent with the interpretation that the observed absorption maxima are caused by the blue shifts of iodine since ε_{max} of the blue shift does not differ much from that of free iodine for many iodine-complexes, while far greater values, around 10000, have been reported for charge-transfer bands[5,7].

Equilibrium Constants.—Equilibrium constants for the iodine-stilbene complexes were determined, as usual, by a series of experiments in which the concentration of the donor component was varied, keeping that of iodine constant. As the latter concentration was relatively low in this work, the following equation[8,9] was applied to the optical densities obtained at respective absorption maxima.

$$1/(\varepsilon_A-\varepsilon_F)=1/(\varepsilon_C-\varepsilon_F)(1/K_C)(1/C_D)+1/(\varepsilon_C-\varepsilon_F) \qquad (1)$$

n this equation ε_F and ε_C are, respectively, the molar extinction coefficients for free iodine and the complex in the mixture, and $\varepsilon_A=d/[(I_2)l]$, where d is the measured optical density of the solution containing the complex, (I_2) is the total concentration of iodine (free and complexed) and l is the path length of the absorption cell (1 cm.); C_D is actually the concentration of donor left free in the mixture but can be equated to its total concentration when an amount much greater than that of iodine is employed, as was the case in the present work; K_C is the equilibrium constant for the formation of the 1:1 complex.

Figs. 3 and 4 show that the linear relation required by Eq. 1 between $1/(\varepsilon_A-\varepsilon_F)$ and $1/C_D$ holds for *cis*- as well as for *trans*-stilbene in *n*-hexane, indicating that the compositions of these complexes are equally 1:1, as already inferred for *cis*-stilbene. Silmilar results were obtained with *trans*-stilbene in carbon tetrachloride. Values of ε_C calculated from intercepts of these straight lines have already been

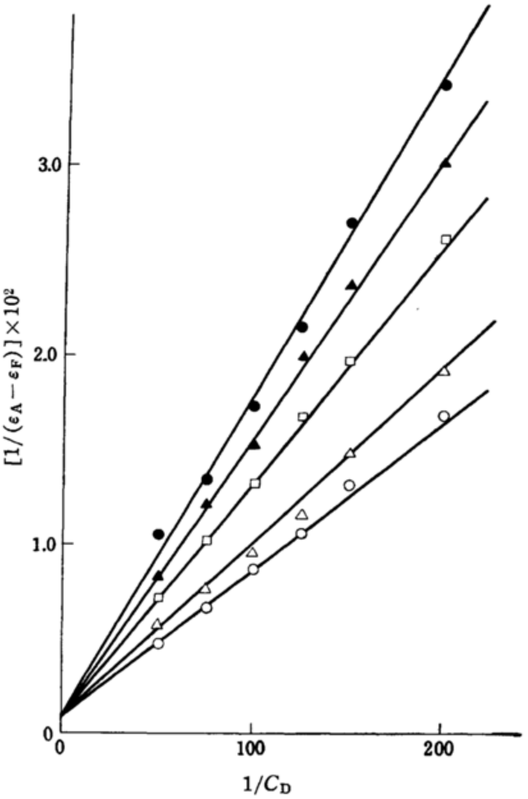

Fig. 3. $1/(\varepsilon_A-\varepsilon_F)$—$1/C_D$ diagram for the *cis*-stilbene—iodine system in *n*-hexane. —●— 30°C, —▲— 25°C, —□— 20°C, —△— 15°C, —○— 10°C.

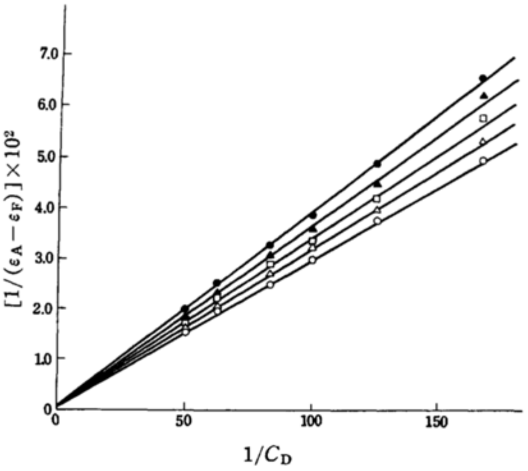

Fig. 4. $1/(\varepsilon_A-\varepsilon_F)$—$1/C_D$ diagram for the *trans*-stilbene-iodine system in *n*-hexane. —●— 30°C, —▲— 25°C, —□— 20°C, —△— 15°C, —○— 10°C.

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* Andrews and Keefer determined ε_{max} from the intercept of a Benesi-Hildebrand plot at 25°C using the optical densities corrected for free iodine. Their extrapolation at a single temperature is liable to produce a considerable error; however, it is not clear whether this is the sole reason for the large discrepancy in question. In the present work, as seen in Figs. 3 and 4, extrapolations at five different tempertures gave a constant intercept, making the value of ε_{max} thus determined much more reliable.

7) L. E. Orgel, *Quart. Revs.*, 8, 422 (1954).

8) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, 77, 4202 (1955).

9) J. A. A. Ketelaar et al., *Rec. trav. chim.*, 71, 1104 (1952).

TABLE I. ABSORPTION MAXIMA AND MOLAR EXTINCTION COEFFICIENTS FOR IODINE AND IODINE-STILBENE COMPLEXES

Absorbing species	Solvent	λ_{max} mμ	ε_{max}
I_2	*n*-Hexane	520	8.40×10^2
I_2	Carbon tetrachloride	520	1.20×10^3
I_2—*cis*-Stilbene	*n*-Hexane	420	1.32×10^3
I_2—*trans*-Stilbene	*n*-Hexane	365	1.38×10^3
I_2—*trans*-Stilbene	Carbon tetrachloride	374	1.48×10^3

TABLE II. EQUILIBRIUM CONSTANTS FOR IODINE-STILBENE COMPLEXES

Complex	Solvent	K_C				
		10°C	15°C	20°C	25°C	30°C
I_2—*cis*-Stilbene	*n*-Hexane	9.74	8.35	6.13	5.10	4.42
I_2—*trans*-Stilbene	*n*-Hexane	2.42	2.22	2.10	1.97	1.82
I_2—*trans*-Stilbene	Carbon tetrachloride	—	1.68	1.53	1.45	1.36

TABLE III. THERMODYNAMIC CONSTANTS FOR COMPLEX FORMATION AT 25°C

Complex	Solvent	$-\Delta H$ kcal./mol.	$-\Delta F$ kcal./mol.	$-\Delta S$ e. u./mol.
I_2—*cis*-Stilbene	*n*-Hexane	7.54	0.965	22.1
I_2—*trans*-Stilbene	*n*-Hexane	2.54	0.402	7.18
I_2—*trans*-Stilbene	Carbon tetrachloride	2.40	0.220	7.32

given in Table I as ε_{max}'s and those of K_C obtained from the slopes are listed in Table II.

Heats and Entropy Changes.—Fig. 5 shows plots of log K_C against the reciprocal temperature for the three systems investigated. The heats of the complex formation obtained from these plots are given in Table III, together with free energy and entropy changes calculated at 25°C. As seen in the table, the change of solvent from *n*-hexane to carbon tetrachloride produces only slight changes, as would usually be expected, while there exist significant differences between the values for *cis*- and *trans*-stilbene. Apparently, *cis*-stilbene forms a more stable and rigid complex with iodine than *trans*-stilbene. A plausible explanation for such a difference may be given as follows. Since the molecule of stilbene is planar in the *trans*-form and also nearly planar in the *cis*-form[10], iodine will attach to either form of stilbene on either side of its molecular plane to form a molecular complex.

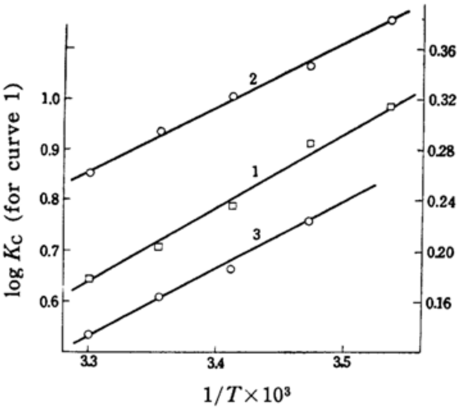

Fig. 5. Plots of log K_C vs. $1/T$:
1, I_2+*cis*-stilbene in *n*-hexane;
2, I_2+*trans*-stilbene in *n*-hexane;
3, I_2+*trans*-stilbene in carbon tetrachloride.

trans-Stilbene has, however, two phenyl groups projected almost in the opposite direction, while *cis*-stilbene has a bent and therefore much more compact structure. Hence the complex of *cis*-stilbene may have a more rigid structure than that of *trans*-stilbene, and, at the same time, the former complex may be more stable owing primarily to a greater van der Waals attraction.

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[10] G. N. Lewis, T. T. Magel and D. Lipkin, *J. Am. Chem. Soc.*, **62**, 2973 (1940).