favorable to the ketal. Equal volumes of cyclohexanone and methanol give only a 28% conversion. From equal volumes at 25°, about 78% conversion was obtained. The conversion could be increased to 92% from a mixture of 23.1% by weight cyclohexanone, or to more than 95% from a mixture of 12.1% cyclohexanone.

By distillation, a sample of the ketal was obtained which had only a trace of ketone. It had a boiling point of 73.0° at 50 mm. and a refractive index n_D^{25}, of 1.4372. This compares reasonably well with the value $n_D^{17.5}$ of 1.4416 for a sample prepared from methyl orthosilicate.[5]

Acknowledgment. The authors wish to thank R. F. Lind, R. F. Hamilton, S. A. Schrader, and their associates for the distillation work, E. R. Hopke for the ultraviolet analyses, and R. B. Duvall, D. S. Early, and R. A. Nyquist for assisting with the infrared work after one of us (A.W.B.) had left Midland near the conclusion of this research.

MIDLAND, MICH.

[CONTRIBUTION FROM THE APPLIED SCIENCE DEPARTMENT, UNIVERSITY OF CINCINNATI]

Selenium-catalyzed Isomerization of *cis*-Stilbene

J. D. FITZPATRICK[1] AND MILTON ORCHIN

Received March 4, 1957

The isomerization of *cis* to *trans*-stilbene can be achieved by elemental selenium at 200–210°. The reaction is homogeneous and depends upon the formation and decomposition of a *pi* complex between selenium and the stilbene. The reaction is pseudo first order wih respect to *cis*-stilbene. The catalyst dependence appears to involve the concentration of selenium to the one-third power and suggests that, as in the case of the oleic-elaidic acid transformation, a dissociation of Se_6 to $3Se_2$ is involved.

In previous work in this laboratory[2] it was shown that the selenium-catalyzed interconversion of oleic (*cis*) and elaidic (*trans*) acids is a homogeneous reaction, the first step of which consists of the formation of a *pi* complex between the unsaturated fatty acid and selenium. The reversible formation and decomposition of the complex results in the isomerization. It was further shown that most other olefinic substrates complex reversibly with selenium at 200°. If the substrate contains a hydrogen atom on the carbon alpha to the double bond, the catalytic activity of the selenium slowly disappears, presumably by irreversible rearrangement of the *pi* complex to a new species (*sigma* complex) in which it is assumed that a carbon-selenium *sigma* bond is formed. In the present work, the isomerization of *cis*-stilbene was investigated not only because this is a classical substrate for *cis-trans* studies but also because the lack of an *alpha* hydrogen atom would preclude formation of the postulated sigma complex.

EXPERIMENTAL

Apparatus. The isomerization studies were performed in a short test tube fitted with a stirrer, a side-arm inlet for inert gas and a small bore, angled side arm for the insertion of a sampling tube. The test tube was placed in a salt bath heated by a mantle. Temperature control was maintained at ± 1° in the temperature range 190–210° by means of a Thermocap relay. Samples for analysis were removed by inserting an open-end, melting-point capillary tube through the side arm, allowing the liquid to fill the capillary to the desired level, and then withdrawing the tube and sample.

Materials. cis-Stilbene purchased from the Aldrich Chemical Co. was used as received since the ultraviolet spectrum showed it to be of good quality. Selenium powder, reagent grade, was purchased from the Fisher Scientific Co. and was used as received.

Analytical Procedure. The ultraviolet spectra of *cis* and *trans*-stilbene show significant differences[3] and a quantitative method based on ultraviolet absorption spectroscopy was therefore applied. After consideration of several possible methods of selecting and treating the data, the graphical absorbance ratio method[4] was employed. In this method a graph is used, which has as one coordinate, the ratio of observed absorbances at two wave lengths, one of which is an "isoabsorptive" point (the wave length at which both isomers have the same absorptivity). The other coordinate is the relative composition of the mixture and hence runs from 0 to 100% of one of the isomers. This method does not require a prior knowledge of the total concentration of the two components, a fact which is of advantage in the present work where very small liquid samples are involved. The method does however place great weight on the accurate selection of the isoabsorptive wave length. Because the graph is a straight line, the accuracy can be improved by drawing the best straight line through intermediate points of known composition as well as the intercepts. Fig. 1 shows an experimental plot of the ratio of the absorbance at the indicated wave length over the absorbance at the isoabsorptive point (λ 266 mμ) *vs.* the percent of *trans*-stilbene in the mixture. The best straight line was drawn through the points and the composition determined from these best values.

The determinations were made by removing samples from the reaction vessel by means of the capillary tube. The filled capillary was dropped into a volumetric flask without weighing and broken up by means of a glass rod. The flask was filled to the mark with spectral grade cyclohexane. Aliquots of this solution were taken for further dilution until absorbance readings were of a suitable magnitude. Readings

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[1] Present address, Emery Industries Inc., Cincinnati 2, Ohio.

[2] J. D. Fitzpatrick and M. Orchin, *J. Am. Chem. Soc.*, **79**, 4765 (1957).

[3] R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley and Sons, New York, 1951.

[4] R. C. Hirt, F. T. King, and R. G. Schmitt, *Anal. Chem.*, **26**, 1270 (1954).

were taken on a Beckman Model DU spectrophotometer at wave lengths of 310, 300, 290, and 285 mμ. From these readings the percentage *trans*-stilbene was determined by reference to the plot in Fig. 1. The variation between these four determinations was usually 1–2% and an average value was taken.

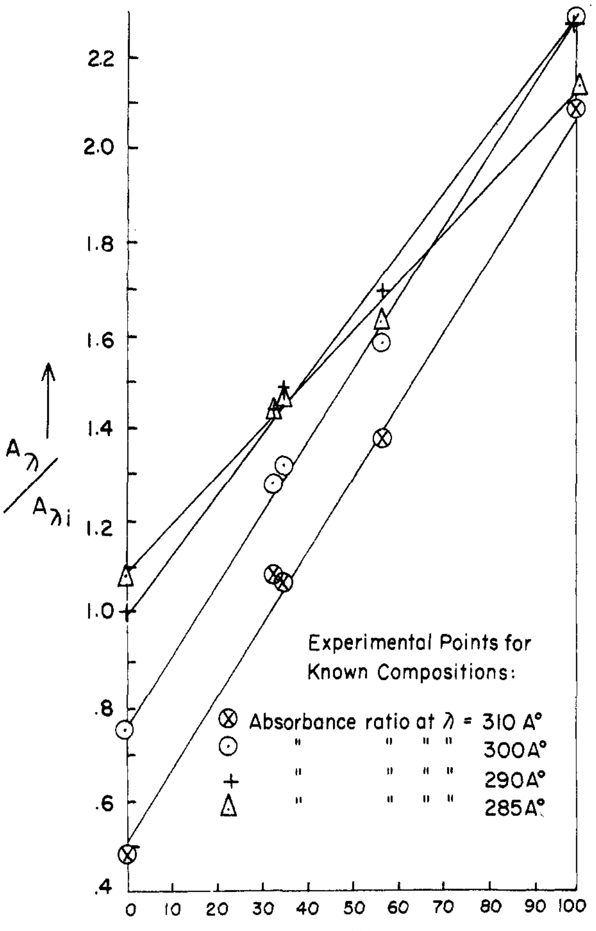

FIG. 1. ABSORBANCE RATIO *Vs.* PERCENT *trans*-STILBENE.

Isomerizations. All the isomerization experiments were carried out in essentially the same manner. A typical experiment will be described.

To the reaction vessel containing 8 g. of *cis*-stilbene at 210 ± 1° under a helium atmosphere, there was added a fragile glass boat containing 0.0240 g. of powdered selenium. The boat was dropped through the top of the apparatus after momentarily stopping the agitator while maintaining a helium atmosphere over the contents. Timing was begun at the moment the selenium sample was dropped into the reactor. The agitation was resumed as quickly as possible. Samples were removed at 10 min. intervals by inserting the melting point capillary tube.

The selenium goes into solution very rapidly. On cooling the solution, selenium precipitates again as the red modification. The solution process is reversible, continued heating and cooling do not change the behavior of the selenium.

RESULTS AND DISCUSSION

The results of rate studies at 210° with three different selenium concentrations and at 200° with one selenium concentration are shown in Table I. The effect of selenium concentration on the rate was studied at 210°, since at higher temperatures thermal isomerization becomes important and at lower temperatures the rate becomes too slow. At 210° in the absence of catalyst, 2 to 3% *trans*-stilbene was formed after 1 hr. of heating. No correction was made for this thermal conversion. At 180°C. there appears to be little solubility of selenium in *cis*-stilbene. The experiment at 200°C. was performed in order to obtain data for the calculation of the activation energy.

Since the isomerization of *cis*-stilbene to *trans*-stilbene is a reversible reaction with the equilibrium point at 93% *trans* isomer,[5] the equation applying to a simple first order reaction where the selenium concentration is constant is:

$$\log (93 - \%\ trans\text{-stilbene}) = \frac{-k't}{2.303} + \log 93$$

This is the equation of a straight line, the slope of which gives the value of k′ the pseudo first order rate constant. When the data of Table I are plotted according to the above equation, satisfactory straight lines were obtained even though there is some spread in the data owing to the limits of the analytical procedure and the deficiencies of temperature control in all experiments. Calculations show that a 2% error in analysis would produce about a 10% change in rate constant. Accordingly, our results must be considered only semi-quantitative. Fig. 2 shows plots of these data at 210°. The values for the rate constants calculated from the slopes of these lines and the results from the 200° experiment are shown at the bottom of Table I.

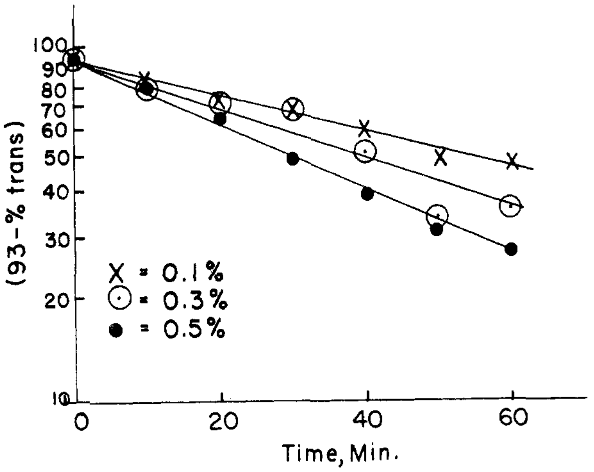

FIG. 2. SEMI-LOG PLOT FOR ISOMERIZATION OF *cis*-STILBENE AT 210° C.

For any given selenium concentration the following rate equation applies:

$$\frac{-d\,[cis\text{-S}]}{dt} = k'_1[cis\text{-S}] - k'_2\,[trans\text{-S}]$$

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[5] G. B. Kistiakowsky and W. R. Smith, *J. Am. Chem. Soc.*, 56, 638 (1934).

TABLE I
RESULTS OF RATE STUDIES WITH *cis*-STILBENE

	Percentage *Trans*-Stilbene			
	200°C.	210°C.		
Time,		Per Cent Selenium		
Min.	0.30	0.10	0.30	0.50
10		11	15	15
20		21	23	29
30	15	26	25	44
40		35	41	54
50		45	59	61
60	31			66
90	42			
120	53			
150	57			
		Rate Constants (k′, min.$^{-1}$)		
	0.006	0.111	0.015	0.020

where k_1' and k_2' include the concentration of selenium. The true rate equation is therefore:

$$\frac{-d\,[\textit{cis}\text{-S}]}{dt} = k_1[\textit{cis}\text{-S}]\,[\mathrm{Se_x}]^{1/n} - k_2\,[\textit{trans}\text{-S}]\,[\mathrm{Se_x}]^{1/n}$$

where $[\mathrm{Se_x}]$ is the selenium concentration and n is some integer. It is apparent from these equations that

$$k_1' + k_2' = (k_1 + k_2)\,[\mathrm{Se_x}]^{1/n} \text{ or}$$

$$k' = k\,[\mathrm{Se_x}]^{1/n}, \text{ where } k' = k_1' + k_2' \text{ and } k = k_1 + k_2$$

Taking the log of both sides of the above equation gives

$$\log k' = \frac{1}{n}\log\,[\mathrm{Se_x}] + \log k$$

from which it follows that a plot of log k′, the pseudo first order rate constants of Table I, *vs.* log $[\mathrm{Se_x}]$ is a straight line whose slope is 1/n. Fig. 3 shows such a plot. The value of n calculated from the slope of the straight line is 2.9. It must be considered more than fortuitous that the selenium dependence previously found in isomerization experiments with oleic and elaidic acids was also close to one third. It appears quite likely that a dissociation of selenium such as $\mathrm{Se_6} \rightleftharpoons 3\,\mathrm{Se_2}$ is involved. The $^1/_3$ order dependence of rate of isomerization on total selenium concentration is derived from the following argument. The equilibrium: $\mathrm{Se_6} \rightleftharpoons 3\,\mathrm{Se_2}$, almost certainly favors the $\mathrm{Se_6}$ species and it is assumed that $[\mathrm{Se_6}] \gg [\mathrm{Se_2}]$. Accordingly, $[\mathrm{Se_6}]$ is directly related to the initial concentration of selenium, $[\mathrm{Se_x}]$. From the above equilibrium

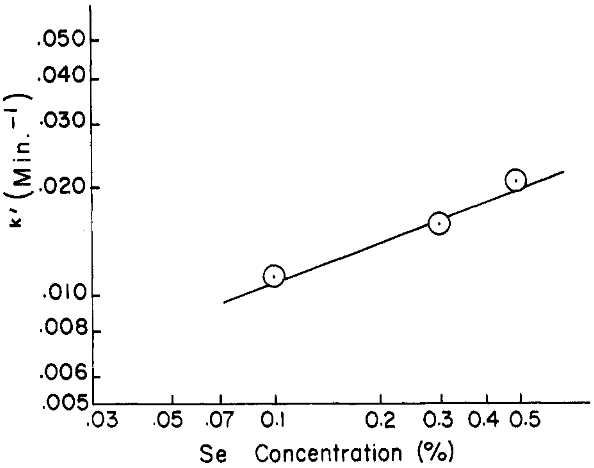

FIG. 3. LOG-LOG PLOT OF k′ AGAINST SELENIUM CONCENTRATION, 210°C.

$$[\mathrm{Se_2}] = [\mathrm{Se_6}]^{1/3}K^{1/3} \text{ and}$$

$$[\mathrm{Se_2}] = [\mathrm{Se_x}]^{1/3}K^{1/3}$$

Appropriate substitution into the rate equation then gives the $^1/_3$ order dependence on initial selenium concentration. One may accordingly write a mechanism for the isomerization involving the following equations:

$$\mathrm{Se_6} \xrightleftharpoons{\text{fast}} 3\mathrm{Se_2}$$

$$\begin{tikzcd}
\textit{cis}\text{-Stilbene} + \mathrm{Se_2} \arrow[r, shift left] & \textit{cis}\text{-Stilbene.}\mathrm{Se_2}\ (\textit{pi}) \arrow[l, shift left, "\text{(fast)}"] \arrow[d, shift left, "\text{(slow)}"] \\
\textit{trans}\text{-Stilbene} + \mathrm{Se_2} \arrow[r, shift left] & \textit{trans}\text{-Stilbene.}\mathrm{Se_2}\ (\textit{pi}) \arrow[l, shift left, "\text{(fast)}"] \arrow[u, shift left]
\end{tikzcd}$$

The dissociation of selenium and the establishment of the equilibrium concentration of complexed selenium must be fast. The rate-determining isomerization of one *pi* complex to the other continues until complete equilibrium is established.

An Arrhenius calculation of the rate constants with 0.3 percent selenium at 200 and 210° give an activation energy of 38 Kcal.

Acknowledgment. The authors wish to thank the Emery Co., Inc. for a generous fellowship which made this study possible. The authors are grateful to Moshe Ish-Shalom for assistance with the experimental work and for valuable suggestions.

CINCINNATI 21, OHIO