THE THERMAL CIS-TRANS ISOMERIZATION OF CINNAMIC ACID CATALYZED BY IODINE

By

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The iodine-catalyzed thermal conversion of cis-cinnamic acid to trans-cinnamic acid.

In this investigation a study was made of the kinetics and the mechanism suggested by the kinetics of the iodine-catalyzed thermal conversion of cis-cinnamic acid to trans-cinnamic acid. Berthoud and Urech(1) studied the kinetics of the iodine-sensitized photo-chemical conversion of cis-cinnamic acid to trans-cinnamic acid and proposed a mechanism for it. They found that the reaction rate is given by

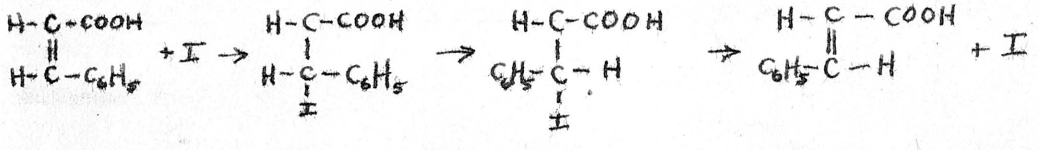
$$-\frac{dc}{dt} = kI_o^{\frac{1}{2}} (I_2)^{\frac{1}{2}}(C).$$

They suggested the following mechanism for the photochemical conversion:

$$I_2 + h\nu \rightarrow 2I$$
$$C + I \rightarrow CI$$
$$CI \rightarrow TI$$
$$TI \rightarrow T + I$$
$$2I \rightarrow I_2$$

where C and T denote cis-cinnamic acid and trans-cinnamic acid, resp.

Structurally, the conversion is represented as follows:



At this point I wish to acknowledge and express my appreciation for the suggestions and assistance of Dr. R. G. Dickinson under whom this investigation was conducted.

Experimental

PREPARATION OF MATERIALS

The cis-cinnamic acid was prepared by the hydrogen-reduction of phenylpropiolic acid by a method essentially due to Paal and Hartmann(2). The procedures for making phenylpropiolic acid, described in Volume XII of Organic Syntheses (Wiley and Sons), were used. Briefly, ethyl cinnamate was brominated and the ethyl α, β -dibromo-β- phenylpropionate obtained was refluxed with alcoholic potash in which reaction potassium phenylpropiolate was produced. On liberating the acid from its salt with dilute sulphuric acid, crude phenylpropiolic acid was obtained which was purified by recrystallization from carbon tetrachloride. The yields for these preparations reported in Organic Syntheses were obtained.

The colloidal palladium(3) used in the reduction of the phenylpropiolic acid was prepared by adding 2.5 gr. of palladium chloride, dissolved in 150 ml. of water containing just enough hydrochloric acid to dissolve the palladium chloride, to a 150 ml. solution of 1.5 gr. sodium protalbinate(4) and of a quantity of sodium hydroxide slightly more than that equivalent to the palladium chloride. The palladium chloride solution was added slowly with stirring so that the palladium hydroxide formed went into a colloidal state in the presence of the protalbinate ion which acts as a protective colloid. This solution was heated for two hours on a water bath at 60°C. during which time hydrogen was bubbled through it. The colloidal solution as such was used in the subsequent reduction of phenylpropiolic acid.

Since the method used in the preparation of the sodium protalbinate was a modification of the method by Paal(4), a detailed description of the preparation is given. 50 gr. of egg-albumen, added in small portions, was shaken with a solution of 7.5 gr. of sodium hydroxide in 250 ml. of water in a 500 ml. flask. The mixture was heated on a water bath for one hour until all but a small residue was dissolved. The solution was cooled and filtered. Dilute acetic acid was added to the solution in a large evaporating dish until precipitation of the protalbinic acid was complete. Care must be taken lest more acetic acid than is required for the precipitation is added because the protalbinic acid redissolves. After the mixture was allowed to stand for 10 hours so that the hydrogen sulphide was evolved, the mixture was centrifuged in 250 ml. bottles. The liquid was poured off and the protalbinic acid packed on the bottom of the bottles was stirred up with 250 ml. portions of water and centrifuged again. This process was repeated until the acid was free from salts. The protalbinic acid was dried by sucking air through it on a filter paper. About 30% yield was realized. In preparing the colloidal palladium solution, described above, 1.5 gr. protalbinic acid was added to 150 ml. of water and dissolved by the addition of sodium hydroxide.

To effect the reduction of phenylpropiolic acid, 20 ml. of the colloidal palladium solution was added to 20 ml. of sodium phenylpropiolate solution prepared by dissolving 5 gr. of phenylpropiolic acid in an equivalent amount of sodium hydroxide solution. The solution contained in a 200 ml. flask, was shaken as hydrogen, measured with a gas burette, was added. When the calculated amount of hydrogen necessary for the half-reduction of the phenylpropiolic acid had been added the reaction was interrupted. About 50 minutes was required for the process.

The solution was transferred to a beaker and somewhat more than the equivalent amount of cold dilute sulphuric acid was added slowly with stirring. The cis-cinnamic acid liberated from its salt separated as an oil which was extracted with ether. To separate the cis-cinnamic acid from the non-polar impurities produced in the reduction process the ether solution was shaken with sodium carbonate solution in a separatory funnel. To the aqueous layer cold dilute sulphuric acid was added and the cis-cinnamic acid liberated from its salt again separated as an oil which was extracted with ether.

The first preparation of crystalline cis-cinnamic acid was prepared by evaporating off the ether and by converting the oily cis-cinnamic acid to the crystalline aniline salt(5). The cis-cinnamic acid was liberated from its salt by adding cold dilute hydrochloric acid to the aniline salt suspended in a little water. The mixture was filtered and the cis-cinnamic acid was recrystallized from water. The melting-point of the cis-cinnamic did not correspond to any one of the three cis-cinnamic acids but extended over a range from 48° C. to 53°C. The yield for this preparation was low so in preparing a second quantity of cis-cinnamic acid the method was modified. In this case the oil of cis-cinnamic acid was frozen with solid carbon dioxide and then was allowed to melt. On repeating this process several times partial crystallization of the oil was effected. The cis-cinnamic acid was purified by two recrystallizations from hot water. From 10 gr. of phenylpropiolic acid 3.2 gr. of cis-cinnamic acid, which had been twice recrystallized from 100 ml. portions of water, was obtained. The melting point of this preparation was not sharp but extended from 58°C. to 65°C.

Some interesting observations were made in the crystallization of the oily cis-cinnamic acid. When the oil was dissolved in hot water to produce a saturated solution and the solution cooled, an emulsion of the oil in water was formed. However, the minute particles coalesced after some twenty minutes of stirring and settled to the bottom of the beaker. When a large quantity of crystalline cis-cinnamic acid was added to the emulsion, complete crystallization of the oil particles was effected.

An altogether different phenomenon was observed in the case where the oil was partially crystallized as a consequence of the freezing process described above. When warm water (45°C.) was added to the mixture of crystals and oil, the whole mass reverted to oil but on cooling the solution, saturated with the cis-cinnamic acid, an emulsion was formed from which complete crystallization of the acid followed.

The trans-cinnamic acid used was Eastman's which had been recrystallized from hot water.

Thiophene free benzene was used. The residue, from 20 ml. of benzene, dissolved in 100 ml. of water, changed the specific conductivity of the water from 1.0×10^{-6} mhos to 1.3×10^{-6} mhos.

The water used was commercial distilled water which had been redistilled from alkaline permanganate. The specific conductivity of the water at 25°C. was 1.0×10^{-6} mhos.

Iodine solutions were prepared from Merck's iodine.

ANALYTICAL METHOD

To determine the composition of a mixture of cis- and trans-cinnamic acids advantage was taken of the fact that cis-cinnanic acid is about four times as strong an acid as trans-cinnamic acid.

A graph of the specific conductivities at 25°C. of mixtures of the two acids varying from 100% cis-cinnamic acid to 100% trans-cinnamic acid was constructed from experimental data. These values were checked theoretically.

The specific conductivity of a mixture of cis- and trans-cinnamic acids was calculated as follows:

$\bar{L}$ = the specific conductance of a mixture of the two acids.

C_1= normal concentration of cis-cinnamic acid.

C_2= normal concentration of trans-cinnamic acid.

α_1= degree of ionization of cis-cinnamic acid.

α_2= degree of ionization of trans-cinnamic acid.

λ_1= equivalent conductance of cis-cinnamic acid at infinite dilution.

λ_2= equivalent conductance of trans-cinnamic acid at infinite dilution.

From the mass action law, for each acid

$$\frac{(\overset{+}{H})(\overset{-}{A}_1)}{(HA_1)} = K_1 \quad ; \quad \frac{(C_1\alpha_1)^2}{(C_1 - C_1\alpha_1)} = K_1 \qquad (1)$$

$$\frac{(\overset{+}{H})(\overset{-}{A}_2)}{(HA_2)} = K_2 \quad ; \quad \frac{(C_2\alpha_2)^2}{(C_2 - C_2\alpha_2\ )} = K_2 \qquad (2)$$

HA_1 designates cis-cinnamic acid

HA_2 designates trans-cinnamic acid

K_1 is the ionization constant for cis-cinnamic acid

K_2 is the ionization constant for trans-cinnamic acid

From the mass action law for a mixture of the two acids

$$\frac{(C_1\alpha_1 + C_2\alpha_2)C_1\alpha_1}{(C_1 - C_1\alpha_1)} = K_1 \qquad (3)$$

$$\frac{(C_1\alpha_1 + C_2\alpha_2)C_2\alpha_2}{(C_2 - C_2\alpha_2)} = K_2 \qquad (4)$$

On dividing (3) by (4)

$$\frac{\alpha_1}{1-\alpha_1}\cdot\frac{1-\alpha_2}{\alpha_2} = \frac{K_1}{K_2}$$

whence

$$\alpha_1 = \frac{\frac{K_1}{K_2}\cdot\frac{\alpha_2}{(1-\alpha_2)}}{\left(1 + \frac{K_1}{K_2}\cdot\frac{\alpha_2}{(1-\alpha_2)}\right)} \qquad \text{or} \qquad \alpha_2 = \frac{\frac{K_2}{K_1}\cdot\frac{\alpha_1}{(1-\alpha_1)}}{\left(1 + \frac{K_2}{K_1}\cdot\frac{\alpha_1}{(1-\alpha_1)}\right)}$$

On substituting the above value of α_2 in (3)

$$\left\{C_1\alpha_1 + C_2\left[\frac{\frac{K_2}{K_1}\cdot\frac{\alpha_1}{(1-\alpha_1)}}{1 + \frac{K_2}{K_1}\cdot\frac{\alpha_1}{(1-\alpha_1)}}\right]\right\}\frac{\alpha_1}{1-\alpha_1} = K_1$$

Let $\frac{\alpha_1}{1-\alpha_1} = x$

$$\therefore \left\{C_1\left(\frac{x}{1+x}\right) + C_2\left[\frac{\frac{K_2}{K_1}\cdot x}{1 + \frac{K_2}{K_1}x}\right]\right\} x = K_1$$

whence

$$\left(\frac{K_2}{K_1}C_1 + \frac{K_2}{K_1}C_2\right)X^3 + \left(\frac{K_2}{K_1}C_2 + C_1 - K_2\right)X^2 - (K_1 + K_2)X - K_1 = 0 \qquad (5)$$

By a similar substitution of the above value of α_1 in equation (4), the equation

$$\left(\frac{K_1}{K_2}C_1 + \frac{K_1}{K_2}C_2\right)y^3 + \left(\frac{K_1}{K_2}C_1 + C_2 - K_1\right)y^2 - (K_1 + K_2)y - K_2 = 0 \qquad (6)$$

is obtained where y has been substituted for $\frac{\alpha_2}{1-\alpha_2}$

In solving equations (5) and (6) the following values have been used:

$$(C_1 + C_2) = 0.003$$

$$K_1 = 1.41 \times 10^{-4}$$

$$K_2 = 3.68 \times 10^{-5}$$

From the values of X and y obtained in solving equations (5) and (6) values for α_1 and α_2 are obtained, which, when substituted in the equation

$$\bar{L} = \frac{C_1\alpha_1\lambda_1}{1000} + \frac{C_2\alpha_2\lambda_2}{1000}$$ permit $\bar{L}$ to be found.

$$\lambda_1 = \lambda_2 = 378$$

In table I are shown the observed and calculated specific conductivities of mixtures of cis- and trans-cinnamic acids at 25°C. and at a total concentration of 0.003N. and the corresponding values of α_1 and α_2

TABLE I

PER CENT CIS-CINNAMIC ACID	α_1	α_2	$\bar{L}\times10^3$ (CALC.)	$\bar{L}\times10^3$ (OBS.)
100.0	0.1945		0.2206	0.2200
90.0	0.2006	0.05874	0.2114	0.2108
80.0	0.2083	0.06418	0.2035	0.2025
70.0	0.2157	0.06568	0.1935	0.1934
60.0	0.2248	0.07011	0.1848	0.1838
50.0	0.2343	0.07365	0.1746	0.1743
40.0	0.2453	0.07817	0.1645	0.1641
30.0	0.2574	0.08299	0.1537	0.1537
20.0	0.2725	0.08900	0.1424	0.1421
10.0	0.2893	0.09600	0.1308	0.1307
0.0		0.1048	0.1188	0.1188

No correction was made for the specific conductivity of the water because carbonic acid which is the chief impurity in the water is a weaker acid than the cinnamic acids.

THE CONDUCTIVITY CELL

The cell constant was obtained by measuring the conductances of solutions OF KCl extending from 0.01N. TO 0.001N. at 25°C. The values for the specific conductivities of the KCl solutions used were obtained from data by Shedlovsky(6). The specific conductivity of the water used was 0.8 x 10^{-6} mhos.

TABLE II

Conc.of KCl	Specific conductivity of KCl plus that of the solvent	Resistance (ohms)	Cell constant
0.01N.	0.001414	114.1	0.1608
0.005N.	0.0007190	223.5	0.1607
0.002N.	0.0002924	548.1	0.1603
0.001N.	0.0001477	1083	0.1600

Since the resistance of the solutions of the cinnamic acids was around 1000 ohms, the cell constant used was 0.1600.

PRELIMINARY EXPERIMENTS

Conditions:

(a) All conductivites were measured at 25°C.

(b) The total concentration of the cinnamic acids whose conductivity was to be measured was 0.003N.

(c) The water used had a specific conductivity of 1.0×10^{-6} mhos.

(d) ALL SOLUTIONS WERE PREPARED AT 25°C.

1. 20 ml. of benzene were placed in a 250 ml. volumetric flask and the benzene was pumped off. 100 ml. of water was added to the flask and was shaken thoroughly. The specific conductivity of the water changed from 1.0×10^{-6} mhos. TO 1.3×10^{-6} MHOS.
2. The same was repeated for 20 ml. of benzene which was 2×0.001N. in I_2. Likewise the specific conductivity changed from 1.0×10^{-6} to 1.3×10^{-6} mhos.
3. In a third experiment 20 ml. of benzene, 2×0.003N. in I_2, were sealed off in an ampule which was then heated for four hours at 130°C. The contents were transferred to the volumetric flask and the benzene and iodine were pumped off. After the residue was shaken with 100 ml. of water, the conductivity of the water changed from 1.0×10^{-6} to 1.3×10^{-6} mhos.
4. 0.4438 gr. of cis-cinnamic acid were dissolved in 50 ml. of benzene AT 25°C. in a calibrated volumetric flask to give a 0.06N. solution. A 5 ml. portion was pipetted out and transferred to a volumetric flask to which 5 ml. of benzene, 2×0.003N. in I_2, were added.

The benzene and iodine were pumped off and the acid was dissolved in 100 ml. of water. The specific conductivity of the solution was 0.0002191 which checks fairly well with the specific conductivity of an aqueous solution of cis-cinnamic acid at a concentration of 0.003N.

Therefore, the procedure in handling the cis-cinnamic acid from the point where it's solution in benzene is prepared to the final analysis is satisfactory.

5. Before the thermal experiments with cis-cinnamic acid were made, the possibility of a trans-cis isomerization was considered. 0.4438 gr. of trans-cinnamic acid were dissolved in 50 ml. of benzene AT 25°C. and 5 ml. portions of it were pipetted out and transferred to ampoules approximately 15 ml. in volume. In order to check the precision with which the solution was prepared, the conductivity of the acid contained in 5 ml. of the benzene solution was measured as described above. To each of four ampoules, containing 5 ml. of the solution of the acid in benzene, was added 5 ml. of benzene, 2×0.003N. in I_2. The ampoules were sealed off and were heated for different lengths of time at 99.4°C. in a light tight vapor chamber. The contents were analysed as described previously. The results are summarized in table III.

TABLE III

Period of Heating (Hours)	Specific conductivity of the 0.003N. aqueous soln. of cinnamic acid	Composition (% trans-cinnamic acid)
0	0.0001196	99.1
5	0.0001199	98.9
10	0.0001203	98.5
47	0.0001192	99.4
91	0.0001195	99.1

THERMAL EXPERIMENTS ON CIS-CINNAMIC ACID

1. Starting with the addition of iodine solution to the cis-cinnamic acid solution all operations were carried out in the dark or in red light except in sealing off the ampules in a blue oxygen-gas flame. However, exposure to these light sources was avoided as much as possible.

2. The water used had a specific conductivity of 1.0×10^{-6} mhos.

3. All aqueous solutions of the cinnamic acids were 0.003N. and the conductivity measurements were made at 25°C.

4. After the contents of the ampules were transferred to the volumetric flask and the iodine and benzene were pumped off, the acids were redissolved in benzene if they were discolored with iodine, and the benzene pumped off again. This was repeated until the acids were perfectly white.

5. The experimental procedure is identical with that described under "Preliminary experiments".

6. The heating apparatus was a large test tube containing the constant boiling-point liquid. Inserted in a large rubber stopper which fitted in the mouth of the test tube were a calilibrated thermometer, a reflux condenser, and a brass tube in which the ampule was

placed. To insure thermal equilibrium between the vapor of the boiling liquid and the contents of the ampoule, the brass tube was filled with mineral oil. Water was used for the constant temperature "bath" for these reactions at 99.4°C. and methyl cellosolve for those between 122.2°C. and 122.9°C. The variation in temperature is due to two reasons; firstly, two different fractions of the methyl cellosolve were used, and secondly, the boiling temperature of the cellosolve varied from one experiment to the next but remained constant over the course of any one experiment.

7. Table IV is a summary of the results for which no correction was made for the benzene residue while table V contains these results with the applied benzene residue correction. From the temperature coefficient of the overall specific reaction rate constant the overall specific reaction rate constants for the reactions between 122.2°C. and 122.9°C. were converted to 122.5°C. and are tabulated in column VII of tables IV and V. In calculating the overall specific reaction rate constant, it was assumed that the cis-trans isomerization proceeds first order with respect to the cis-cinnamic acid concentration.

8. ALL SOLUTIONS WERE PREPARED AT 25°C.

TABLE IV

	MOLAR CONC. OF CIS CINNAMIC ACID	MOLAR CONCENTRATION OF IODINE	TEMP. (°C)	HEATING TIME (HOURS)	PER CENT TRANS-CINNAMIC ACID	$\frac{k}{2.303}$	$\frac{k_{122.5°C}}{2.303}$	$\frac{k_{122.5°C}/I_2^{1/2}}{2.303}$
				0	0.0			99.4°C
1	0.03	0.0015	99.4	24	12.4	0.00240		0.0620
2	0.03	0.0015	99.4	50	25.1	0.00251		0.0649
3	0.03	0.0015	99.4	100	42.8	0.00243		0.0628
4	0.09	0.024	99.4	24	40.1	0.00927		0.0598
5	0.03	0.0015	122.2	10	31.8	0.0166	0.0170	0.439
6	0.03	0.0015	122.2	35	74.3	0.0169	0.0173	0.447
7	0.03	0.0015	122.8	19	53.7	0.0176	0.0172	$0.44\overset{6}{4}$
8	0.03	0.003	122.9	15	56.0	0.0238	0.0231	0.422
9	0.03	0.006	122.2	11	56.2	0.0326	0.0334	0.431
10	0.03	0.012	122.9	5	43.7	0.499	0.0484	0.440
11	0.03	0.012	122.9	8	59.5	0.0491	0.0476	$0.43\overset{8}{3}$
12	0.03	0.024	122.6	6.5	63.2	0.0668	0.0663	0.428
13	0.09	0.0015	122.7	8	25.8	0.0166	0.0163	0.421
14	0.09	0.006	122.8	10	52.3	0.0321	0.0313	0.404
15	0.09	0.024	122.4	6.5	60.0	0.0612	0.0617	0.398
	I	II	III	IV	V	VI	VII	VIII

TABLE V

	MOLAR CONC. OF CIS-CINNAMIC ACID	MOLAR CONCENTRATION OF IODINE	TEMP. (°C)	HEATING TIME (HOURS)	PER CENT TRANS-CINNAMIC ACID	$\frac{k}{2.303}$	$\frac{k_{122.5°C}}{2.303}$	$\frac{k_{122.5°C}/I_2^{1/2}}{2.303}$
				0	0.0			99.4°C
1	0.03	0.0015	99.4	24	13.0	0.00251		0.0649
2	0.03	0.0015	99.4	50	25.7	0.00258		0.0667
3	0.03	0.0015	99.4	100	43.3	0.00246		0.0636
4	0.09	0.024	99.4	24	40.4	0.00937		0.0604
5	0.03	0.0015	122.2	10	32.3	0.0169	0.0173	0.447
6	0.03	0.0015	122.2	35	74.8	0.0171	0.0175	0.452
7	0.03	0.0015	122.8	19	54.1	0.0178	0.0174	0.450
8	0.03	0.003	122.9	15	56.5	0.0241	0.0234	0.427
9	0.03	0.006	122.2	11	56.6	0.0330	0.0338	0.436
10	0.03	0.012	122.9	5	44.0	0.0504	0.0488	$0.44\overset{6}{4}$
11	0.03	0.012	122.9	8	59.8	0.0495	0.0480	$0.43\overset{8}{6}$
12	0.03	0.024	122.6	6.5	63.8	0.0679	0.0674	0.435
13	0.09	0.0015	122.7	8	26.7	0.0169	0.0166	0.429
14	0.09	0.006	122.8	10	52.5	0.0323	0.0315	0.406
15	0.09	0.024	122.4	6.5	60.1	0.0614	0.0619	0.399
	I	II	III	IV	V	VI	VII	VIII

Experiment numbers 1,2,3,5, and 6, and the conductivity curve were obtained from the first preparation of cis-cinnamic acid and the rest were obtained from the second preparation. The agreement between the results obtained from the two preparations shows some indication there is no impurity in the cis-cinnamic acid which might affect the kinetics of the isomerization.

INTERPRETATION OF THE RESULTS

Column 7 of tables IV and V proves that the assumption, that the rate of isomerization of cis-cinnamic acid is first order with respect to the concentration of cis-cinnamic acid when the concentration of the acid is the only variable, is correct. Column 8 of these tables shows that the rate is half-order with respect to the iodine concentration.

$$\therefore\ -\frac{dc}{dt} = k(C) = k'\sqrt{I_2}(C).$$

where C is the concentration of the cis-cinnamic acid

The decrease in k' with the larger concentration of cis-cinnamic acid and iodine might conceivably be due to the formation of α,β -diiodo- β - phenylpropionic acid.

The temperature coefficient of the specific reaction rate for 10°C. between 99.4°C. and 122.5°C. is calculated as follows; where X is the temperature coefficient for 10°C., 0.441 is k' at 122.5°C., and 0.0651 is k' at 99.4°C.

$$\frac{0.441}{0.0651} = X^{2.31}$$

whence $X = 2.29$

The kinetics of the isomerization can be explained on the basis of the following mechanism:

(1) $I_2 \rightarrow 2I$

(2) $C + I \rightarrow CI$

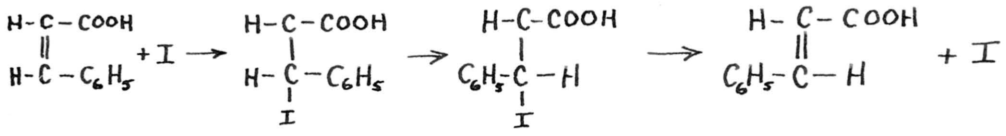
(3) $CI \rightarrow TI$

(4) $TI \rightarrow T + I$

(5) $2I \rightarrow I_2$

where C and T denote cis-cinnamic acid and trans-cinnamic acid, resp.

Reactions 2, 3, and 4 can be represented structurally as follows:



When the stationary state for the atomic iodine and the intermediate compounds is set up the following equations are valid:

$$\frac{dI}{dt} = k_1(I_2) - k_2(C)(I) + k_4(TI) - k_5(I)^2 = 0 \qquad (A)$$

$$\frac{d(CI)}{dt} = k_2(C)(I) - k_3(CI) = 0 \qquad (B)$$

$$\frac{d(TI)}{dt} = k_3(CI) - k_4(TI) = 0 \qquad (C)$$

On adding these three equations

$$k_1(I_2) - k_5(I)^2 = 0$$

$$\therefore\ I = \sqrt{\frac{k_1}{k_5}(I_2)} = \sqrt{K}\ (I_2)^{\frac{1}{2}}$$

where K is the equilibrium constant for the reaction

$$I_2 \rightleftarrows 2I$$

The rate at which the cis-cinnamic acid disappears is given by

$$-\frac{d(C)}{dt} = k_2(C)(I)$$

and by replacing (I) by $\sqrt{K}\,(I_2)^{\frac{1}{2}}$, the reaction rate expression is obtained, expressly,

$$-\frac{d(C)}{dt} = k_2\sqrt{K}\,(I_2)^{\frac{1}{2}}(C) = k'(I_2)^{\frac{1}{2}}(C) \qquad (D)$$

However, if reaction (2) is reversible, then

$$-\frac{d(C)}{dt} = k_2(C)(I) - k_2'(CI) \qquad (E)$$

WHERE k_2' IS THE SPECIFIC REACTION RATE CONSTANT FOR THE REVERSE REACTION.

and equation (B) becomes

$$\frac{d(CI)}{dt} = k_2(C)(I) - k_2'(CI) - k_3(CI) = 0$$

whence $(CI) = \dfrac{k_2(C)(I)}{(k_2' + k_3)}$

On substituting this value of (CI) in equation (E),

$$-\frac{dC}{dt} = k_2\left(\frac{k_3}{k_2' + k_3}\right)(C)(I) = k_2\left(\frac{k_3}{k_2' + k_3}\right)\sqrt{K}(I_2^{1/2})(C) \qquad (F)$$

For the photochemical reaction the mechanism is as follows:

(1) $I_2 + h\nu \rightarrow 2I$

(2) $C + I \rightarrow CI$

(3) $CI \rightarrow TI$

(4) $TI \rightarrow T + I$

(5) $2I \rightarrow I_2$

and as was done for the thermal reactions,

$$\frac{dI}{dt} = k_1 iI_0 I_2 - k_2(C)(I) + k_4(TI) - k_5(I)^2 = 0 \qquad (A')$$

$$\frac{d(CI)}{dt} = k_2(C)(I) - k_3(CI) = 0 \qquad (B')$$

$$\frac{d(TI)}{dt} = k_3(CI) - k_4(TI) = 0 \qquad (C')$$

whence, on adding (A'), (B'), and (C'),

$$k_1 iI_0 I_2 - k_5(I)^2 = 0$$

or $(I) = \sqrt{\frac{k_1 iI_0}{k_5}}\sqrt{I_2}$

For the photochemical reaction (2)

$$-\frac{d(C)}{dt} = k_2(C)(I)$$

On replacing (I) by $\sqrt{\frac{k_1 iI_0 I_2}{k_5}}$

$$-\frac{d(C)}{dt} = k_2\sqrt{\frac{k_1 iI_0}{k_5}}\sqrt{I_2}(C). \qquad (D)$$

By correlating the photochemical and thermal rates of the cis-trans- isomerization the energy of activation of reaction (5) and the heat of reaction of reaction $I_2 \rightleftarrows 2I$ can be obtained.

For the photochemical cis-trans- isomerization

$$\frac{(k_2/\sqrt{k_5})_{35°C.}}{(k_2/\sqrt{k_5})_{25°C.}} = \frac{0.17}{0.13} = 1.31^{(1)} \qquad \text{(cf. equation D)}$$

assuming that the reaction $I_2 + h\nu \rightarrow 2I$ has no temperature coefficient; and for the thermal cis-trans- isomerization

$$\frac{(k_2\sqrt{K})_{122.5°C.}}{(k_2\sqrt{K})_{99.4°C.}} = \frac{0.441}{0.0651} = 6.77 \qquad \text{(cf. equation D)}$$

Assume

(I) $$\frac{d(\ln k_2)}{dT} = \frac{Q_2}{RT^2} + \frac{1}{2T}$$

where Q_2 is the energy of activation of reaction (2) and is assumed to be constant with respect to temperature.

(II) $$\frac{d(\ln k_5)}{dT} = \frac{Q_5}{RT^2} + \frac{1}{2T}$$

where Q_5 is the energy of activation of reaction (5) and is assumed to be constant with respect to temperature.

(III) $$\frac{d(\ln K)}{dT} = \frac{\Delta H}{RT^2}$$

where H is the heat of reaction for the reaction I_2 2I and is assumed to be constant with respect to temperature.

On subtracting (II) from (I)

$$\frac{d\ln(k_2/\sqrt{k_5})}{dT} = \frac{1}{RT^2}(Q_2 - \frac{Q_5}{2}) + \frac{1}{4T}$$

and on integration

$$\ln\frac{(k_2/\sqrt{k_5})_{T_2}}{(k_2/\sqrt{k_5})_{T_1}} = \frac{(Q_2 - \frac{Q_5}{2})}{R}\left(\frac{T_2 - T_1}{T_1T_2}\right) + \frac{1}{4}\ln\frac{T_2}{T_1}$$

For T_1 = 298.1°A, and T_2 = 308.1°A

$$(Q_2 - \frac{Q_5}{2}) = \frac{2.303 \times 1.988 \times 298.1 \times 308.1}{10}\left(\log 1.31 - \frac{1}{4}\log\frac{308.1}{298.1}\right)$$

$$= 4,780 \text{ cal.}$$

On adding (II) and (III)

$$\frac{d\ln(k_2\sqrt{K})}{dT} = \frac{1}{RT^2}\left(Q_2 + \frac{\Delta H}{2}\right) + \frac{1}{2T}$$

and on integration

$$\ln\frac{(k_2\sqrt{K})_{T_4}}{(k_2\sqrt{K})_{T_3}} = \frac{1}{R}\left(Q_2 + \frac{\Delta H}{2}\right)\left(\frac{T_4 - T_3}{T_3T_4}\right) + \frac{1}{2}\ln\frac{T_4}{T_3}$$

For $T_3 = 372.5^\circ A$ and $T_4 = 395.6^\circ A$

$$\left(Q_2 + \frac{\Delta H}{2}\right) = \frac{2.303 \times 1.988 \times 372.5 \times 395.6}{23.1}\left(\log 6.77 - \frac{1}{2}\log\frac{395.6}{372.5}\right)$$

$$= 23{,}890 \text{ cal.}$$

Therefore, $Q_2 - \frac{Q_5}{2} = 4{,}780$ cal.

and $Q_2 + \frac{\Delta H}{2} = 23{,}890$ cal.

If Q_5 is assumed to be zero (the validity of this assumption is shown in the following paragraph)

then $Q_2 = 4{,}780$ cal.

and $\Delta H = 38{,}220$ cal.

The spectroscopic value for ΔH at $0^\circ A$ is 35,200 cal.

If $Q_5 = 0$, with every collision of iodine atoms a molecule of iodine is produced:

$$2I \longrightarrow I_2$$

According to the kinetic theory, the number of collisions of iodine atoms at $0^\circ C$. expressed in mols per litre per second is $10^{25.2922}\,(I)^2\,\sigma^2\sqrt{\frac{273.1}{126.92}}$, where σ is the collision diameter of iodine atoms.

The rate at which iodine atoms combine to form iodine molecules is $-\frac{d(I)}{dt} = C'(I)^2$, where C' is the specific reaction rate constant when the concentrations are in mols per litre and the time is in seconds.

$$\therefore \; -\frac{d(I)}{dt} = C'(I)^2 = 10^{25.2922} \, (I)^2 \, \sigma^2 \sqrt{\frac{273.1}{126.92}}$$

$$\text{or} \qquad C' = 10^{25.2922} \, \sigma^2 \sqrt{\frac{273.1}{126.92}}$$

According to van Vleck's(7) potential curves of the iodine molecule σ can be assigned the value 5×10^{-8} cms.

$$\therefore \; C' = 10^{25.2922} \times (5 \times 10^{-8})^2 \sqrt{\frac{273.1}{126.92}} = 7.2 \times 10^{10}$$

Rabinowitz and Wood(8) found experimentally that $C' = 10.3 \times 10^{10}$ ($= 1.73 \times 10^{-10}$ when the concentrations are in molecules per cubic centimeter) for the reaction $2I \rightarrow I_2$ in hexane. It is assumed that the solvent molecules have no serious influence on the rate of collision of the iodine atoms. At least, the reaction rate for $2I \rightarrow I_2$ is of the same order of magnitude in hexane and in carbon tetrachloride in which solutions the experiments were performed by Rabinowitz and Wood. The probably value of Q_5 is zero and the possible value is not greater than several hundred calories.

According to the kinetic theory, the number of collisions at temperature T, expressed in mols per cubic centimeter per second, between unlike molecules is

$$\frac{Z}{N} = 10^{28.4427} C_1 C_2 \, \sigma_{12}^2 \sqrt{T \frac{M_1 + M_2}{M_1 M_2}}$$

where the concentrations C_1 and C_2 are expressed in mols per cubic centimeter, σ_{12} the collision diameter, is expressed in centimeters, and M_1 and M_2 are the masses expressed in ordinary molecular weights. In applying this formula to reaction (2),

$$Cis + I \rightarrow Cis\ I,$$

the rate $k''(I_2)^{\frac{1}{2}}Cis$, expressed in mols per cubic centimeter per second, is equal to $S\frac{Z}{N}e^{-\frac{Q_2}{RT}}$ where S is an "orientation and steric factor".

$$\therefore\ k''(I_2)^{\frac{1}{2}}Cis = S \times 10^{28.4427}(I)\ (cis)\sigma_{12}^2\sqrt{T\frac{M_I+M_{cis}}{M_IM_{cis}}}\cdot e^{-\frac{Q_2}{RT}}$$

Since $\frac{(I^2)}{(I_2)} = K$

$$S\sigma_{12}^2 = \frac{k''}{\sqrt{K}\times 10^{28.4427}\sqrt{T\frac{M_I+M_{cis}}{M_IM_{cis}}}\cdot e^{-\frac{Q_2}{RT}}}$$

When the rate is expressed in mols per litre per hour, the specific reaction rate constant $k' = 0.441$ at 122.5°C. When the rate is expressed in mols per cubic centimeter per second, the specific reaction rate constant $k'' = 0.00387$.

$\sqrt{K}$ is obtained from the value of ΔF^0 for the REACTION $I_2(g) \rightarrow 2I(g)$. For the purpose of this calculation ΔF^0 at 25°C. is used. It is assumed that the free energy change is the same in benzene.

$$\Delta F_{25^\circ C.} = -RT\ln K = 26,310 \text{ cal.}$$

$$\therefore K \text{ (at } 25^\circ C.) = 2.98 \times 10^{-15}$$

K (at 122.5°C.) is obtained from the van't Hoff equation, $\ln\frac{K_2}{K_1} = \frac{\Delta H}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$

$$\therefore \log \frac{K_{122.5^\circ C.}}{K_{25^\circ C.}} = \frac{35,200}{2.303 \times 1.988}\left(\frac{97.5}{298.1 \times 395.6}\right) = 6.356$$

$$\therefore \frac{K_{122.5^\circ C.}}{K_{25^\circ C.}} = 2.27 \times 10^{6}$$

$$\text{or } K_{122.5^\circ C.} = (2.98 \times 10^{-15})(2.27 \times 10^{6}) = 6.77 \times 10^{-9}$$

When the concentrations are expressed in mols per cubic centimeter, the equilibrium constant, K, is equal to $\frac{6.77 \times 10^{-9}}{82.06 \times 395.6} = 2.09 \times 10^{-13}$ which is the value to be substituted for K in the equation for $S\sigma_{12}^2$

$$\therefore \sqrt{K} = 4.57 \times 10^{-7}$$

$$\therefore S\sigma_{12}^2 = \frac{0.00387}{4.57 \times 10^{-7} \times 10^{28.4427} \quad 395.6\left(\frac{126.92 \quad 148.06}{126.92 \times 148.06}\right)}$$

$$\cdot\, \frac{1}{e^{-\left(\frac{4,780}{1.988 \times 395.6}\right)}}$$

$$= 5.53 \times 10^{-23}$$

If the collision diameter is assumed to be 10^{-7} cms., then the "steric and orientation factor", S, is equal to 5.53×10^{-9}.

SUMMARY

1. The kinetics of the cis-trans isomerization of cinnamic acid was studied and the reaction was found to be first order with respect to the cis-cinnamic acid concentration and half order with respect to the iodine concentration: $-\frac{dc}{dt} = k' I_2^{\frac{1}{2}} C$.

2. With a large increase in the product of the cis-cinnamic acid concentration and the iodine concentration the specific reaction rate constant decreased.

3. The specific reaction rate constant is equal to 0.441 AT 122.5°C. where the concentrations are expressed in mols per litre and the time in hours (= 0.00387, where the concentrations are expressed in mols per cubic centimeter and the time in seconds.)

4. The temperature coefficient of the specific reaction rate constant between 99.4°C. and 122.5°C. is 2.29 for 10°C.

5. From the photochemical and thermal kinetic data of the cis-trans isomerization of cinnamic acid the heat of reaction for the reaction Cis + I $\rightarrow$ Cis I was found to be 4,780 calories and the heat of reaction for the reaction $I_2 \rightleftarrows 2I$ was found to be 38,220 calories.

6. From the kinetic theory collision rate expression the value of $S\sigma_{12}^2$, where S is the "steric and orientation factor" and σ_{12} is the mean collision diameter of cis-cinnamic acid and iodine, was found to be 5.53×10^{-23} cms.

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