

has $\Lambda_0 = 57.40$ in ethylene chloride at 25°) we find 2.10×10^{-8} for the dissociation constant of tributylammonium picrate. This value of K gives a value of 2.4 \AA. for the parameter a (effective ion size),¹⁰ which seems unexpectedly small.

(10) Fuoss and Kraus, *THIS JOURNAL*, **55**, 1019 (1933).

Summary

The conductance of tributylammonium picrate in ethylene chloride has been measured at 25° . The concentration range covered was $1.8 \times 10^{-4} N$ to $0.5 N$.

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RECEIVED AUGUST 30, 1939

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 734]

The Equilibrium and Kinetics of the Thermal Isomerization of Dichloroethylene Catalyzed by Iodine

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The conversion of *cis*- into *trans*-cinnamic acid, catalyzed by iodine in benzene solution, has been found¹ to proceed at rates which can be interpreted in terms of iodine-atom catalysis just as can the photochemical conversion sensitized by iodine.² We have found that iodine similarly catalyzes the *cis*-*trans*-isomerization of dichloroethylene, and have measured reaction rates in the pure liquids and in various solutions. Since the isomerization comes to a measurable equilibrium, we have measured equilibrium constants as well as rates of conversion in both directions.

Materials.—The *cis*- and *trans*-dichloroethylenes were prepared by fractional distillation of mixtures of the isomers obtained from the Eastman Kodak Company. It was found desirable to carry out the distillations under carbon dioxide to avoid oxidation by air; pure *trans*-dichloroethylene was noticeably subject to air oxidation. The distillations were carried out with a five-foot (1.5-meter) column; the final products had boiling-point ranges of less than 0.1° and dielectric-constant ranges of 0.003. The boiling point of the *cis*-dichloroethylene was 59.6° at 745 mm.; the dielectric constant was 9.20 at 25° . The boiling point of the *trans*-dichloroethylene was 47.2° at 745 mm.; the dielectric constant was 2.14 at 25° . After purification the liquids were stored in flasks under an atmosphere of carbon dioxide; liquid for use was forced out by carbon dioxide when desired. The same method of storage was applied to stock solutions of the dichloroethylenes in the various solvents. The liquids thus stored were found to retain their original dielectric constants throughout the duration of the experiments (several months).

Thiophene-free benzene was fractionally crystallized, dried, and distilled.

Cyclohexane (Eastman "Practical") was shaken with fuming sulfuric acid, washed with sodium hydroxide solution, then with water, dried, and distilled. Its dielectric constant was found to be 2.013 at 25° .

(1) R. G. Dickinson and H. Lotzkar, *THIS JOURNAL*, **59**, 472 (1937).

(2) A. Berthoud and Ch. Urech, *J. chim. phys.*, **27**, 291 (1930).

Decalin (decahydronaphthalene) (Eastman "Practical") was shaken with anhydrous aluminum chloride and then treated similarly to the cyclohexane. It was found that if the treatment with fuming sulfuric acid was not sufficiently prolonged, the decalin added iodine in the subsequent experiments. The dielectric constant of the purified decalin was 2.150 at 25° .

The iodine was sublimed from potassium iodide-iodine mixture, and resublimed.

Dielectric Constant Measurement.—A method of analysis based on dielectric constant measurement was employed to determine the extent of isomerization. This measurement was made by a substitution method in which the capacitance of a cell containing the solution in question was compared with that of a variable precision condenser. The apparatus involved two oscillating circuits coupled to produce an audible heterodyne beat on a telephone receiver. A quartz crystal oscillating at 1.7 megacycles controlled the frequency of one of these circuits. The frequency-controlling part of the other circuit comprised inductance and capacitance, a part of the latter being furnished either by the cell containing the solution, or by the precision condenser. The essence of the measurement was the rapid substitution, by means of a switch, of the measuring cell for the precision condenser in this circuit; the precision condenser was adjusted so that no perceptible change in pitch of the heterodyne beat occurred when this substitution was made.

The precision condenser was a General Radio instrument; the capacitance range used was from 25 to 110 μmf . A calibration was made which gave corrections of the condenser readings to values linear with the capacitance.

The measuring cell was of glass and substantially of the type described by Doborzynski³; it was thermostated at 25° . For analytical purposes only a relation between composition of solution and precision condenser reading was necessary; nevertheless the apparatus was calibrated to give dielectric constants with the aid of a number of liquids of known dielectric constant.

Analytical Method.—The analytical problem was that of determining the fraction of dichloroethylene in the *cis*- or *trans*-form in a solution containing known amounts of solvent, iodine, and total dichloroethylene.

(3) D. Doborzynski, *Z. Physik*, **66**, 657 (1930).

Iodine was removed from the solution by inserting a clean, dry, helical coil of copper wire. Blank experiments showed that this method of deiodizing the solution brought about no isomerization of the dichloroethylene. After removal of iodine the solution contained a known ratio of total dichloroethylene to solvent so that a measurement of its dielectric constant enabled the fraction of dichloroethylene in each form to be determined from previous measurements on known solutions containing the same total dichloroethylene. Dielectric constants of some of these solutions are given in Table I.

TABLE I

Dielectric constants at 25° of solutions of *cis*- and *trans*-dichloroethylene undiluted (I), and diluted to ten mole per cent. of total (*cis* and *trans*) dichloroethylene in benzene (II), cyclohexane (III), and decalin (IV). Also shown are the measured dielectric constants of the solvents used.

% <i>cis</i> of total C ₂ H ₂ Cl ₂	Dielectric constant			
	I No solvent	II Benzene	III Cyclohexane	IV Decalin
0	2.14	2.256	2.018	2.149
20		2.347		
40	4.52	2.439		
50			2.192	2.274
60	5.93	2.530		
80	7.50	2.620		
100	9.20	2.714	2.375	2.405
Pure solvent		2.269	2.013	2.150

From the precision of the measurements it is estimated that the probable error of a determination of the ratio of *cis*- to total dichloroethylene is about 0.003 in a 10 mole per cent. solution in benzene; the error is, of course, somewhat larger in more dilute solutions.

Experimental Procedure.—Since the isomerizations were often carried out at temperatures considerably above the normal boiling points of the solutions, the reacting solutions were sealed up in thick glass ampoules. A stock solution of dichloroethylene in solvent, which had been made up by weight, was transferred to the ampoule, a weighed amount of iodine in a glass capsule was introduced, and the ampoule was sealed off. All fillings were carried out in such a way that oxygen was largely, although perhaps not completely, absent when the ampoules were sealed off. In the experiments without added solvent, this was accomplished either by filling the ampoule with carbon dioxide initially, or by boiling off considerable liquid after it had been introduced and cooling under carbon dioxide. In the rest, the solution usually was frozen down with solid carbon dioxide, and evacuated and sealed off while frozen. It was shown by blank experiments that no appreciable fractionation resulted from this treatment. In all manipulations care was exercised to keep moisture from the solutions because of the considerable effect of water on the dielectric constants.

After sealing off, the ampoules were placed in a light-tight thermostat. In some experiments this was an electric furnace with thermoregulator and in others a bath of vapor of a boiling liquid. In all rate experiments the average temperature was known to about 0.1°. At the conclusion of the experiment, the ampoule was removed from the thermostat and cooled and kept in the dark until analyzed. The duration of the experiments was sufficiently

great so that errors in timing due to the initial heating and final cooling period could be shown to be negligible.

Blank experiments were carried out in which ampoules were made up and treated as usual with, however, the omission of iodine. Such ampoules were made up with the pure dichloroethylenes, and with solutions in each of the solvents. In the absence of iodine, the isomerization was negligible. Similar blanks made with iodine and solvent only gave scarcely appreciable changes in dielectric constant.

Equilibrium Experiments.—In Table II are summarized the results of experiments which were long enough so that equilibrium between the *cis* and *trans* isomers was substantially achieved. Some of these experiments were made with no added solvent; the rest were made with solutions of about ten mole per cent. dichloroethylene in benzene, cyclohexane, or decalin. The dichloroethylene at the start was always all *cis* or all *trans* as shown by the fourth column. The final composition shown in the seventh column is the percentage of the total dichloroethylene which was in the *cis* form at the end of the experiment. The equilibrium constant is given as the ratio of *trans* to *cis* isomer; its value is, of course, independent of whether concentrations or mole fractions are used. Mean values for various solvents and temperatures are given in the last column.

In the solutions studied here the values of the equilibrium constants are seen to depend relatively little either on the temperature or on the solvent. From the equation $-\Delta F^\circ = RT \ln K$, the following values for ΔF° for the conversion of *cis*- into *trans*-dichloroethylene in solution at 150° are obtained: in benzene, 750 cal.; cyclohexane, 630 cal.; decalin, 640 cal. Using the van't Hoff equation, $\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$, and values of the equilibrium constant at different temperatures, ΔH may be calculated; the values obtained are, in benzene, 1200 cal.; cyclohexane, 1200 cal.; decalin, 600 cal. Since the probable error of these is at least 200 or 300 calories, it is not certain that the difference between the value for decalin and that for the other solvents is significant.

Values for the equilibrium constant for this reaction in the gaseous state have been given^{4,5,6} which are of the same general magnitude as those found here.

The iodine-catalyzed conversion of *cis*- into *trans*-cinnamic acid has been found,¹ in dilute

(4) E. Ebert and R. Büll, *Z. physik. Chem.*, **A152**, 451 (1931).

(5) A. R. Olson and W. Maroney, *THIS JOURNAL*, **56**, 1322 (1934).

(6) W. Maroney, *ibid.*, **57**, 2397 (1935).

TABLE II
 EQUILIBRIUM MEASUREMENTS

Expt.	Solvent	Temp., °C.	Original isomer	Duration, hr.	Mole % iodine in soln.	Mole % <i>cis</i> in C ₂ H ₂ Cl ₂ at end	Equil. const., K = (T)/(C)	Mean K
7	None	150	<i>cis</i>	495	0.32	70.8	0.412	
8	None	150	<i>cis</i>	239	.71	71.1	.406	
24	None	150	<i>trans</i>	281	.36	70.6	.417	0.412
42	Benzene	150	<i>cis</i>	252	.40	71.1	.406	
41	Benzene	150	<i>trans</i>	252	.30	70.7	.414	.410
50	Benzene	185	<i>cis</i>	21	.43	68.6	.458	
57	Benzene	185	<i>cis</i>	5.8	.60	70.0	.447*	
55	Benzene	185	<i>trans</i>	7.5	.59	68.1	.453*	
51	Benzene	185	<i>trans</i>	21	.43	70.1	.427	
58	Benzene	185	<i>trans</i>	21.5	.57	68.5	.460	.455
67	Cyclohexane	150	<i>cis</i>	92	1.1	67.6	.479	
60	Cyclohexane	150	<i>cis</i>	308	0.67	67.3	.486	
68	Cyclohexane	150	<i>trans</i>	92	1.3	68.2	.467	
61	Cyclohexane	150	<i>trans</i>	308	0.77	69.0	.449	.470
71	Cyclohexane	185	<i>cis</i>	7	.64	66.3	.515*	
72	Cyclohexane	185	<i>trans</i>	7	.60	63.9	.531*	.523
96	Decalin	150	<i>cis</i>	116	1.33	68.1	.468	
95	Decalin	150	<i>trans</i>	100	0.84	68.1	.468	.468
100	Decalin	186	<i>cis</i>	10	1.36	66.8	.497	
105	Decalin	186	<i>cis</i>	10	1.17	67.3	.486	
101	Decalin	186	<i>trans</i>	10	1.31	66.5	.503	.495 ±0.010

* Since the starred experiments were not quite long enough, a small correction of the observed final composition to that at infinite time was made in computing the corresponding K ; this required a rough knowledge of the rate constants.

solution in benzene, to proceed at rates which are first order with respect to cinnamic acid and half order with respect to iodine. The assumption of similar kinetics for the dichloroethylenes is found to be in agreement with the data provided that account is taken of the occurrence of reverse reaction. If k_1 and k_2 are specific rate constants for the reactions $cis\text{-C}_2\text{H}_2\text{Cl}_2 \xrightleftharpoons[k_2]{k_1} trans\text{-C}_2\text{H}_2\text{Cl}_2$, and if $K = (trans)_{eq}/(cis)_{eq}$ be the equilibrium constant, then $K = k_1/k_2$. The assumption that each reaction is of first order with respect to the reacting isomer and of half order with respect to iodine leads to the integrated expression

$$k_1 = - \frac{K}{t(I_2)^{1/2}(K+1)} \ln \frac{(K+1)\alpha - 1}{K} \quad (1)$$

for experiments in which the initial dichloroethylene is all *cis*, and to

$$k_1 = - \frac{K}{t(I_2)^{1/2}(K+1)} \ln [1 - (K+1)\alpha] \quad (2)$$

for experiments in which the initial dichloroethylene is all *trans*. In both of these equations α is the fraction of dichloroethylene in the *cis* form at the time t .

The results of determinations of k_1 are given in Table III. Values of the equilibrium constant needed were taken from the results of Table II

calculated to the desired temperature by means of the van't Hoff equation. The numerical values of k_1 in Table III were obtained expressing t in hours and (I_2) as mole fraction of I_2 in the reaction mixture.⁷

Inspection of the values of k_1 shows that these exhibit satisfactorily constant values in a given solvent at a given temperature. In each solvent, the iodine concentration was varied more than 10-fold (22-fold in the case of decalin). In Table III all experiments with added solvent had a total dichloroethylene mole fraction of about 0.1 except experiments 35 and 46. In these the mole fractions were made 0.2 and 0.01, respectively, without producing any significant change in rate constant. Indeed the experiments without added solvent gave values not much different from the others at the same temperature. It may be further noticed that the values found for k_1 are not dependent on which isomer was originally present; this is nearly true even when no added solvent was present so that the medium was largely different in the two cases. In fact the values of k_1 at a given temperature differ by less than 25% in the various media examined.

(7) If the value of K as well as the relation $K = k_1/k_2$ be assumed, it becomes arbitrary whether a given experiment be regarded as a determination of k_1 or of k_2 .

TABLE III
 RATE MEASUREMENTS

Expt.	Solvent	Temp., °C.	Original isomer	Mole % iodine in soln.	Duration, hr.	Mole % <i>cis</i> in C ₂ H ₂ Cl ₂ at end	K assumed	<i>k</i> ₁ hr. ⁻¹
9	None	150.0	<i>cis</i>	0.1103	31.2	87.6	0.412	0.156
10	None	150.0	<i>cis</i>	.2718	30.4	83.3	.412	.157
11	None	150.0	<i>cis</i>	.722	18.6	83.3	.412	.158
12	None	150.0	<i>cis</i>	1.457	13.0	83.2	.412	.160
19	None	149.7	<i>trans</i>	0.686	22.8	44.0	.412	.150
23	None	149.7	<i>trans</i>	.2704	24.8	34.3	.412	.150
26	None	149.7	<i>trans</i>	.1261	53.2	44.1	.412	.151
35	Benzene	149.6	<i>cis</i> 20%	.343	18.0	87.5	.410	.156
47	Benzene	150.0	<i>cis</i>	.944	17.5	82.7	.410	.154
48	Benzene	150.0	<i>cis</i>	.1104	47.2	83.9	.410	.149
44	Benzene	149.5	<i>trans</i>	.1403	40.0	37.6	.410	.148
45	Benzene	149.5	<i>trans</i>	1.262	20.8	49.0	.410	.147
46	Benzene	150.0	<i>trans</i> 1.09%	0.482	37.5	52	.410	.15
52	Benzene	140.5	<i>trans</i>	.2237	91.0	44.4	.396	.0637
56	Benzene	140.5	<i>trans</i>	.839	42.6	42.0	.396	.0643
53	Benzene	158.9	<i>trans</i>	.801	7.3	35.8	.422	.323
54	Benzene	159.5	<i>trans</i>	.0854	28.3	42.8	.423	.339
70	Cyclohexane	150.0	<i>cis</i>	.521	22.0	80.5	.470	.191
69	Cyclohexane	150.0	<i>trans</i>	.729	21.1	42.9	.470	.177
62	Cyclohexane	150.7	<i>trans</i>	1.127	21.0	49.1	.471	.188
63	Cyclohexane	150.7	<i>trans</i>	0.2503	21.2	31.4	.471	.187
73	Cyclohexane	159.2	<i>trans</i>	.591	8.3	35.8	.486	.389
74	Cyclohexane	159.2	<i>trans</i>	1.173	8.3	44.0	.486	.387
99	Decalin	131.1	<i>trans</i>	0.812	69.9	31.5	.454	.0303
102	Decalin	131.1	<i>trans</i>	1.540	69.9	39.2	.454	.0304
94	Decalin	150.2	<i>trans</i>	0.947	18.9	41.5	.468	.163
97	Decalin	150.4	<i>trans</i>	.0690	28.8	22.0	.468	.165
104	Decalin	159.9	<i>cis</i>	.885	8.6	80.4	.475	.376
98	Decalin	159.4	<i>trans</i>	.1427	25.2	43.5	.475	.344
103	Decalin	159.9	<i>trans</i>	1.027	8.6	43.5	.475	.378

The variation of the rate constant k_1 with the temperature is shown in Fig. 1 in which $\ln k_1$ is plotted against $1/T \times 10^3$ for each of the solvents. From the slopes of these lines, the values of Q_1 in the Arrhenius equation $d \ln k_1/dT = Q_1/RT^2$ can be calculated. The values so obtained are, for benzene solutions 31,200 cal., for cyclohexane solutions 30,800 cal., for decalin solutions 30,200 cal. Values of k_2 , the specific rate constant for the *trans* to *cis* reaction, may be obtained from the relation $k_2 = k_1/K$. Values of Q_2 may be obtained from the relation $Q_1 - Q_2 = \Delta H$; those values for Q_2 are 30,000, 29,600, and 29,600 cal., respectively. The probable experimental error is such that it is not certain whether the apparent changes in Q_1 and Q_2 with solvent are real.

In Table IV are given, for different solvents, average values at 150° of the equilibrium constant, and of the rate constants k_1 and k_2 for the *cis* to *trans* reaction and its reverse. It is desirable also to compute rate constants, k_1 and k_2 , with (I₂) expressed as a volume concentration

instead of a mole fraction. It is easy to show that $k' = kv^{1/2}$ where v is the volume of solution containing a total of one mole of substance. Estimated values of v at 150° for pure dichloroethylene, and for 10 mole per cent. solutions in the various solvents are given in the fifth column. These values were obtained from measurements on the pure substances at lower temperatures on the assumption of additivity of volumes and constancy of thermal expansion coefficient with temperature; their uncertainty probably does

TABLE IV

CONSTANTS IN VARIOUS SOLVENTS AT 150° COMPARING VALUES COMPUTED WITH (I₂) EXPRESSED IN MOLE FRACTIONS WITH THOSE IN VOLUME CONCENTRATIONS

Solvent	K	$k_1 \times 10^7$ sec. ⁻¹	$k_2 \times 10^7$ sec. ⁻¹	v , cc.	k_1'	k_2'
					$\times 10^5$ moles ^{-1/2} cc. ^{1/2} sec. ⁻¹	$\times 10^5$ moles ^{-1/2} cc. ^{1/2} sec. ⁻¹
None	0.412	430	1044	92	41	100
Benzene	.410	425	1036	104	43	106
Cyclohexane	.470	497	1058	123	55	118
Decalin	.468	445	950	177	59	126

not affect the k 's by more than 2%. It is interesting to notice that, in passing from one solvent to another, the k 's in which (I_2) is expressed as a mole fraction are much more constant than the k 's in which (I_2) is expressed as a volume concentration.

Discussion.—Just as was the case with the isomerization of cinnamic acid, the kinetics of the dichloroethylene isomerization can be accounted for in terms of iodine atom catalysis, and indeed in terms of the same mechanism as discussed in the case of cinnamic acid. In this mechanism atomic iodine is assumed to be in thermal equilibrium with molecular iodine so that proportionality of the rate¹ with the square root of the iodine concentration results.

The same proportionality would exist if the catalyst were iodine ions in equilibrium with molecular iodine, *e. g.*, $I_2 \rightleftharpoons I^+ + I^-$. Evidence that an ionic mechanism is, however, not involved here has been obtained somewhat unexpectedly. It was originally planned to measure the dielectric constants of the reacted solutions without first removing iodine. When this was attempted with solutions of iodine in pure *cis*-dichloroethylene the electric oscillations in the dielectric constant apparatus were feeble, and with the more concentrated iodine solutions, entirely absent. On the assumption that this quenching of oscillation resulted from conductance of the solution some approximate conductance measurements were made. It was found that *cis*-dichloroethylene containing 0.02 g. per cc. of iodine had a specific conductance of 3×10^{-6} mho; this was 100 times the conductance of the dichloroethylene alone, and over 1000 times the conductance of a similar solution of iodine in benzene. Since the mobility of iodine ion in dichloroethylene could hardly be of a different order of magnitude from that in benzene, its concentration in benzene must be comparatively low; nevertheless, the specific rate constants are little different in dichloroethylene and benzene. An atomic rather than ionic catalysis accordingly is indicated here.

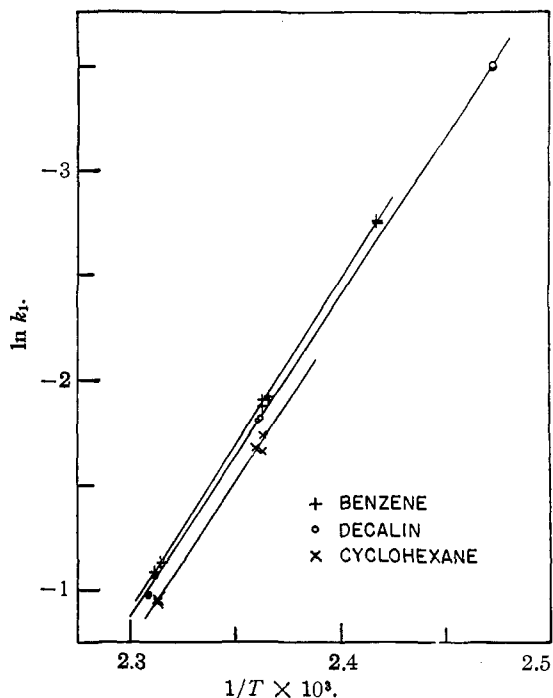


Fig. 1.—Dependence of rate constant on temperature: +, benzene; o, decalin; x, cyclohexane.

Summary

Dielectric constants of various liquid mixtures of *cis*- and *trans*-dichloroethylene and of their solutions in benzene, cyclohexane, and decahydronaphthalene have been measured.

Using iodine as a catalyst, equilibria between the *cis* and *trans* isomers have been established and measured in the pure liquids and in the solutions at various temperatures.

Rates of isomerization in the various media have been measured starting with each isomer. Neither the activation energies nor the actual rates vary much from one medium to another of those examined. The rate constants vary somewhat less from solvent to solvent when computed with the iodine expressed as a mole fraction than when computed with it expressed as a volume concentration.

The kinetics are compatible with an iodine-atom catalysis. Evidence against an ionic catalysis is mentioned.