

for by assuming that the rate is dependent on the sulfite ion concentration and the square root of the hydrogen ion concentration, but is independent of the acid sulfite ion concentration.

5. The analysis of the effect of cupric ion indicates that there is a primary process independent of heavy metal ions.

6. The mechanism of the oxidation has been discussed in terms of the characteristics of chain reactions. The roles of positive catalysts in the primary process and of inhibitors in the chain breaking process have been interpreted in the light of the data available.

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The Energy of Isomerization of *cis*- and *trans*-Dichloroethylene

BY REUBEN E. WOOD AND D. P. STEVENSON*

Introduction

Several discussions of the relative stability of *cis*- and *trans*-dichloroethylene have appeared in the literature. Stuart¹ from the estimates of the dipole-dipole, induction, and dispersion forces concluded that the *cis* form was the more stable by about 1 kilocalorie per mole. The single gaseous equilibrium constant determined by Ebert and Büll² at 300° seemed to confirm Stuart's conclusion provided one assumed that the isomerization involved no change in entropy. Altar³ disputed Stuart's conclusions and pointed out that Stuart's calculations ignored the steric repulsions. Altar's estimates of the steric interactions taken with Stuart's estimates of the other interactions led to the conclusion that the *trans* form is of slightly lower energy. A preponderance of the *cis* form in the equilibrium mixture was found by Ebert and Büll² and confirmed by Olson and Maroney.⁴ Altar explained this by showing that the rotational entropy of the *cis* form is considerably greater than that of the *trans* form. He assumed that the vibrational entropy of the two forms is the same, the translational entropy of the two forms being equal, of course. Later experiments by Maroney⁵ at higher temperatures seemed to indicate the *cis* form to be the lower energy form in agreement with the conclusions of Stuart.

In order to resolve these difficulties we have undertaken the analysis, with the aid of the en-

ergy difference calculated by statistical methods, of new equilibrium data obtained at lower temperatures than the data of Olson and Maroney,⁴ Maroney,⁵ and Ebert and Büll.²

Equilibrium Measurements.—The preparation and storage of the dichloroethylenes has been described in a previous paper.⁶ The iodine was twice sublimed from potassium iodide. The Pyrex reaction vessel has a volume of about 850 cc. It was heated in a tubular electric furnace controlled by a mercury temperature regulator. The temperature of the reactants was measured by a thermometer intruding into the vessel in a well.

The reactants, weighed and sealed into glass capsules, were introduced into the reaction vessel through a side arm. After the vessel had been evacuated and sealed off, the tips of these capsules were broken by shaking. The vessel was then put into the furnace and was maintained at the reaction temperature for the desired length of time.

After the heating period the vessel was removed from the thermostat and cooled rapidly. In the experiments at the highest temperatures cooling was hastened by the use of an electric fan and by the application of a wet towel to the flask. To condense out the dichloroethylene the side-arm of the reaction flask was immersed for about one-half hour in a dry ice-alcohol mixture. The side-arm was then broken off, a clean copper wire was quickly inserted into the condensed solution to remove iodine, and the tube was corked. After the solution had become colorless the extent of the isomerization was determined by a dielectric constant measurement. Care was taken during these operations to minimize the time the solutions were exposed to the air in order to prevent fractionation and water absorption. Table I presents the experimental data. It will be observed that at every temperature the equilibrium was approached from both sides. In the case of the first set of experiments at 185° it appears that the duration of the heating was too short to permit a close approach to equilibrium.⁷ For this reason the results of

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(1) H. A. Stuart, "Molekülstruktur," Verlag Julius Springer, Berlin, 1934.

(2) Ebert and Büll, *Z. physik. Chem.*, **A152**, 451 (1931).

(3) W. Altar, *J. Chem. Phys.*, **3**, 460 (1935).

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

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

(6) R. E. Wood and R. G. Dickinson, *ibid.*, **61**, 1581 (1939).

(7) Because of the fact that equilibrium was not attained in these first two experiments, it is possible to use them as very rough reaction-rate measurements. Although this research was not planned

TABLE I

Expt.	Temp., °C.	Starting isomer	Duration, hours	C ₂ H ₂ Cl ₂ , g.	I ₂ , g.	Final % <i>cis</i>	K = Final <i>cis/trans</i>	K ^b
1	185	<i>trans</i>	93	3.06	0.035	61.55	1.601	
2	185	<i>cis</i>	112	3.09	.032	64.22	1.795	
3	185	<i>trans</i>	118	3.32	.179	63.32	1.726	1.730
4	185	<i>cis</i>	165 ^a	3.43	.177	63.47	1.738	
5	215	<i>trans</i>	51	3.07	.169	62.06	1.636	1.646
6	215	<i>cis</i>	46	3.36	.179	62.36	1.657	
7	245	<i>trans</i>	46	3.08	.136	61.40	1.591	1.579
8	245	<i>cis</i>	46	3.20	.134	61.10	1.571	
9	245	<i>trans</i>	15.5	3.22	.190	61.10	1.571	
10	245	<i>cis</i>	16	3.15	.186	61.40	1.591	
11	275	<i>trans</i>	4	3.24	.204	60.38	1.524	1.518
12	275	<i>cis</i>	4	2.90	.204	60.10	1.506	
13	275	<i>trans</i>	2	3.05	.202	60.32	1.520	
14	275	<i>cis</i>	2	3.04	.202	60.45	1.528	

^a The temperature was about 200° from the seventieth to the ninety-fifth hour. ^b $\ln K = 0.364 (1/T \times 10^3) - 0.247$ (least squares).

these experiments have not been used in the plot (Fig. 1) of the experimental $\ln K$ vs. $1/T$ line.

From Fig. 1 the value of ΔH^0 for the reaction $\text{trans-C}_2\text{H}_2\text{Cl}_2 \rightarrow \text{cis-C}_2\text{H}_2\text{Cl}_2$ over the temperature range studied may be computed to be -720 cal./mole. The observed equilibrium constant at 458°K. leads to a value of -500 cal./mole for ΔF_{458}^0 . Combining these one obtains a value for ΔS^0 at this temperature of -0.49 cal./mole degree.

Discussion.—It is shown by Fowler and Guggenheim⁸ that for an isomeric equilibrium of the type $\text{trans} \rightleftharpoons \text{cis}$, the equilibrium constant $K = (\text{cis})/(\text{trans})$ is given by the equation

$$K = (f'/f'') \exp(-\Delta E_0^0/RT) \quad (1)$$

to yield kinetic data and consequently did not include experiments testing the homogeneity of the reaction, it seems worth while to make rate constant calculations which would assume significance should the reaction prove to be homogeneous.

Putting the results of Experiment 1 into the equation

$$k_1 = \frac{-K'}{t(1+K')} \ln [1 - (1+K')\alpha]$$

a value of $k_1 = 3.9 \times 10^{-6}$ sec.⁻¹ results. In a similar manner Experiment 2 gives a value of $k_1 = 3.5 \times 10^{-6}$ sec.⁻¹. Here K' is the equilibrium constant (assumed to be 0.577 at 458°K.), α the fraction of *cis* C₂H₂Cl₂ in the mixture after t seconds, and k_1 a specific rate constant for the reaction $\text{cis C}_2\text{H}_2\text{Cl}_2 \rightarrow \text{trans C}_2\text{H}_2\text{Cl}_2$. These values are very roughly 100 times as large as would be predicted from the data of Jones and Taylor (J. L. Jones and R. L. Taylor, THIS JOURNAL, 62, 3483 (1940)) for the reaction had it been carried out at this temperature without iodine.

Another interesting comparison may be made if we treat the data of these two experiments in the way that Wood and Dickinson⁹ treated the results of rate experiments on this same reaction in solution. This may be done by dividing the above k_1 's by the square roots of the respective iodine concentrations. The resulting two values of k_1' are 9.0×10^{-3} and 9.5×10^{-3} mole^{-1/2} cc.^{1/2} sec.⁻¹. By extrapolating to 185° the data⁹ for the reaction in decalin solution, a corresponding value of $k_1' = 8.8 \times 10^{-3}$ mole^{-1/2} cc.^{1/2} sec.⁻¹ is obtained. The fact that the gaseous k_1' 's are identical to their precision with this solution k_1' at least suggests the possibility that the gas reaction has the same mechanism as the reaction in solution.

(8) Fowler and Guggenheim, "Statistical Thermodynamics," The Macmillan Co., New York, N. Y., 1939, p. 157.

in which f' and f'' are the partition functions for the *cis* and *trans* molecules, respectively, of the form

$$f = V(2\pi mkT/h^2)^{3/2} 8\pi^2 (8\pi^3 k^3 T^3 ABC/h^6 \sigma^2)^{1/2} \prod_{i=1}^n (1 - e^{-h\nu_i/kT})^{-1} \quad (2)$$

and ΔE_0^0 is the energy difference between the two forms at 0°K. The use of Eq. 2 for the f 's involves the assumption that the molecules may

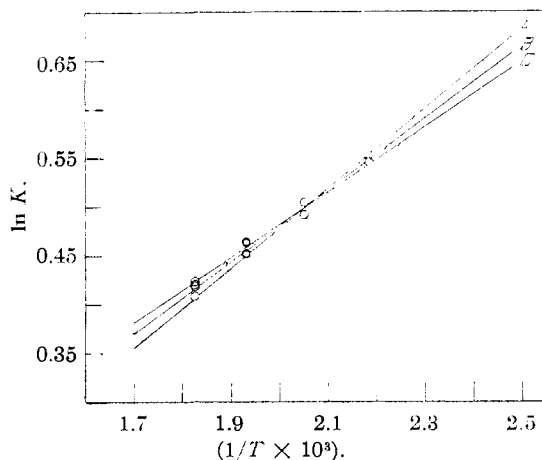


Fig. 1.—

- Curve A $\delta_4 + \tau = 420$ cm.⁻¹; $\Delta E_0^0 = -577$ cal./mole
 Curve B $\delta_4 + \tau = 435$ cm.⁻¹; $\Delta E_0^0 = -528$ cal./mole
 $\ln K = 0.364 (1/T \times 10^3) - 0.247$
 Curve C $\delta_4 + \tau = 450$ cm.⁻¹; $\Delta E_0^0 = -481$ cal./mole
 Circles are experimental points from Table I.

be treated as rigid rotators and harmonic oscillators and that the gases are perfect. For the *cis*- and *trans*-dichloroethylenes, if we take the dimensions found by Pauling, Brockway and Beach⁹

(9) L. Pauling, L. O. Brockway and J. Y. Beach, THIS JOURNAL, 57, 2693 (1935).

Eq. 1 becomes

$$K = 1.376 \kappa(T) \exp(-\Delta E_0^0/RT) \quad (3)$$

in which we write

$$\kappa(T) = \frac{12}{\pi} \left[(1 - e^{-h\nu_1/kT})_{cis}^{-1} / (1 - e^{-h\nu_1/kT})_{trans}^{-1} \right] \quad (4)$$

The extensive literature on the Raman spectra of *cis*- and *trans*-dichloroethylene has been reviewed by Hibben¹⁰ and the infrared absorption has been observed by Wu.¹¹ Of the twelve frequencies possessed by each molecule eleven are known for the *cis* form and nine are known for the *trans* form. The frequencies may be divided into two classes: those for which $\omega > 1150 \text{ cm.}^{-1}$ (five for each molecule) and those for which $\omega < 1000 \text{ cm.}^{-1}$ (seven for each molecule). In Table II those of the first class are given. Over

TABLE II

	$\nu_1(\text{C-C})$	$\nu_2(\text{C-H})$	$\nu_3(\text{C-H})$	$\delta_1(\text{C-H})$	$\delta_2(\text{C-H})$
<i>cis</i>	1586	3077	3100	1179	1300
<i>trans</i>	1576	3070	3100	1271	1200

the temperature range in which we shall be interested the effects of these frequencies cancel in the equilibrium constant. In Table III are given those frequencies which are important in determining the equilibrium constant. Wu¹¹ found

TABLE III

	$\nu_4(\text{C-Cl})$	$\nu_5(\text{C-Cl})$	$\delta_3(\text{C-Cl})$	$\delta_4(\text{C-Cl})$	τ	δ_5	δ_6
<i>cis</i>	711	875	174	406	561	694	?
<i>trans</i>	848	803	351	?	?	820	?

the non-planar vibration corresponding to δ_6 to have a frequency of $\sim 1000 \text{ cm.}^{-1}$ in vinyl chloride and $\sim 900 \text{ cm.}^{-1}$ in trichloroethylene. Thus we may fairly safely assume that δ_6 is rather close to 950 cm.^{-1} in both *cis*- and *trans*-dichloroethylene. Using force constants derived by Verleyesen¹² for the symmetric planar frequencies of the *trans* molecule one may calculate ν_5 and δ_4 to be 810 and 240 cm.^{-1} , respectively. The value calculated for ν_5 is in excellent agreement with that found by Wu,¹¹ but the value calculated for δ_4 may be in considerable error. We have taken as parameters τ (*trans*), ΔE_0^0 , and δ_4 subject to the restriction that $180 < \delta_4 < 300 \text{ cm.}^{-1}$.

Our experiments provide data which in theory should more than suffice to fix the three unknown parameters, but the temperature range over which

(10) J. H. Hibben, "Raman Spectra," Reinhold Publ. Corp., New York, N. Y., 1939.

(11) T. Y. Wu, *Phys. Rev.*, **46**, 465 (1934).

(12) W. Verleyesen, *Ann. soc. sci. de Bruxelles*, **59**, 267 (1939).

it was convenient to study the reaction was such that the trend of K with T was sensitive only to the sum of the two unknown frequencies¹³ and ΔE_0^0 . In Fig. 1 are shown plots of calculated $\ln K$ vs. $1/T$ curves. The sum of the two unknown frequencies and ΔE_0^0 were so chosen that all curves go through the experimental point at 215° . The curves calculated for the sum $\delta_4 + \tau = 420$ and 450 cm.^{-1} may be seen to be extremes. It should be remarked that it is not possible to distinguish between the curve calculated assuming $\delta_4 = \tau = 225$, and that calculated assuming $\delta_4 = 175$ and $\tau = 275$. The curve for the frequency sum equal to 435 cm.^{-1} and ΔE_0^0 equal to -530 cal./mole is indistinguishable from the least squares $\ln K = A + B/T$ line derived from the experimental data.

The value of ΔE_0^0 , -530 cal./mole , favoring the *cis* form, indicates that Altar's³ estimate of the steric and van der Waals forces—obtained from his potential curve for ethylene chloride—overcorrects the energy difference found by Stuart.¹ The great difficulty of these calculations has been made quite clear by the failure of the theory to discuss adequately the hindered rotation in ethane and related molecules.¹⁴ The stabilization of the *cis* form with respect to the *trans* form may depend in part on resonance between the normal structure and two structures involving conjugation of an unshared electron pair of one of the chlorine atoms with the double bond. This conjugation would leave a positive formal charge on the double-bonded chlorine atom, giving rise to decreased dipole-dipole repulsion. This effect would be more pronounced in the *cis* molecule because of the greater proximity of the chlorine atoms. Certainly the greater stability of the *cis* isomer seems to depend on the interaction between the halogen atoms and the double bond, for *trans*-butene-2 is 950 calories more stable than *cis*-butene-2,¹⁵ and the ethylene halides all exist preponderantly in the *trans* configuration.¹⁶

It is of interest to note that the difference in vibrational entropy of the two forms almost exactly balances the difference in rotational entropy giving a resultant $\Delta S \sim 0$, a fact which Altar³ was not in a position to foresee.

(13) J. G. Aston and G. H. Messerly, *THIS JOURNAL*, **62**, 1917 (1940), have given a clear discussion of the reason for this situation.

(14) E. Gorin, J. Walter and H. Eyring, *ibid.*, **61**, 1876 (1939).

(15) G. B. Kistiakowsky, *et al.*, *ibid.*, **57**, 876 (1935).

(16) J. Y. Beach and co-workers, *J. Chem. Phys.*, **6**, 639 (1938); *THIS JOURNAL*, **61**, 303, 3127 (1939); V. Schomaker and D. P. Stevenson, *J. Chem. Phys.*, **8**, 637 (1940).

In order to resolve the two unknown low frequencies of the *trans* molecule, whose sum we find to be 435 cm.^{-1} , it would be necessary to investigate the infrared absorption of the molecule in the region below 300 cm.^{-1} to find δ_4 . The torsional frequency, τ , could then be found by difference. Heat capacity measurements alone would not suffice since δ_8 would become important, giving rise to three parameters and making extraordinarily accurate measurements necessary.

The authors are indebted to Professor Roscoe G. Dickinson and to Dr. Verner Schomaker for helpful discussion and suggestions during the course of this research.

Summary

The gaseous equilibrium between *cis*- and *trans*-dichloroethylene has been studied between 185 and 275°, iodine being used to catalyze the isomerization. From the equilibrium data the value for ΔH^0 for the isomerization of *cis*-dichloroethylene has been calculated to be 723 cal./mole.

By combining these data with the available spectroscopic and electron diffraction data a value for the sum of two unknown frequencies in *trans*- $\text{C}_2\text{H}_2\text{Cl}_2$ has been calculated; and it has been shown that at 0° K. the *cis* form is more stable than the *trans* by about 530 cal./mole.

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The Reduction of Tartaric Acid¹

BY H. J. LUCAS AND W. BAUMGARTEN

Within recent years there has been a marked revival of interest in the tetroses and related compounds. Aside from the ozonolysis of diacetyl-*d*-xylal² the tetroses have been prepared mainly from the pentoses by the well-known degradation methods of Ruff,^{3a} Wohl^{3b,c,4} and Weermann.⁵

The desirability of using the tartaric acids as sources for tetroses and related compounds was recognized by Emil Fischer,⁶ who was unsuccessful in attempts to reduce tartaric acid. Following the realization that the lactones, rather than the acids themselves, are the compounds which undergo reduction he planned to reduce esters of tartaric acid.⁷ Since no subsequent statement has appeared, it is presumed that results were negative.⁸ This report is made now, since the synthesis of *l*-threitol has been accomplished.

The extension of the Rosenmund⁹ method to

(1) Dextrorotatory tartaric acid, *l*-(+)-*threo*-dihydroxysuccinic acid, is referred to simply as tartaric acid.

(2) W. Freudenberg, *Ber.*, **65**, 168 (1932).

(3) (a) Hockett, *THIS JOURNAL*, **57**, 2260, 2265 (1935); (b) Hockett, Deulofeu, Sedoff and Mendive, *ibid.*, **60**, 278 (1938); (c) Hockett and Maynard, *ibid.*, **61**, 2111 (1939).

(4) Iwaware, Fukunaga and Kubota, *Bull. Chem. Soc. Japan*, **12**, 116 (1937); *Chem. Abs.*, **31**, 5767 (1937).

(5) Weermann, *Rec. trav. chim.*, **37**, 16 (1917).

(6) E. Fischer, *Ber.*, **22**, 2204 (1889).

(7) E. Fischer, *ibid.*, **23**, 930 (1890).

(8) The method of Bouveault and Blanc, *Compt. rend.*, **136**, 1676 (1903); **137**, 60 (1903), has been applied to the reduction of isobutyl tartrate, ethyl isopropylidene tartrate and isobutyl isopropylidene tartrate without success. Glattfeld and Mochel, *THIS JOURNAL*, **60**, 1011 (1938), have shown that esters of α,β -dihydroxyisobutyric acid cannot be reduced this way.

(9) Rosenmund, *Ber.*, **51**, 585 (1918).

sugar chemistry by Cook and Major¹⁰ and by Glattfeld and co-workers,¹¹ who have reduced the acid chlorides of acetylated hydroxy acids to acetylated hydroxy aldehydes with hydrogen in the presence of palladinized barium sulfate, suggested a similar method of attack here.

When tartaric acid, I, is heated with acetic anhydride¹² or with benzoyl chloride,¹³ it is converted into diacetyltartaric anhydride, II, or dibenzoyltartaric anhydride. The dibenzoyl anhydride is converted by water into dibenzoyltartaric acid monohydrate. The anhydride was obtained when attempts were made to convert the acid to the acid chloride, as noted by others.¹⁴ Diacetyltartaric acid was not obtained in satisfactory yields from the diacetyl anhydride.¹⁵

An acid chloride can be prepared from a half ester, obtained from one of the anhydrides through a reaction with an alcohol. Although dibenzoyltartaric anhydride reacts readily with primary alcohols, the resulting products are liquids. Moreover, they cannot be distilled without decomposition. However, diacetyltartaric anhy-

(10) Cook and Major, *THIS JOURNAL*, **58**, 2410 (1936).

(11) Glattfeld and Mochel, *loc. cit.*; Glattfeld and Straitiff, *THIS JOURNAL*, **60**, 1384 (1938); Glattfeld and Kribben, *ibid.*, **61**, 1720 (1939).

(12) Chattaway and Parkes, *J. Chem. Soc.*, **123**, 663 (1923).

(13) Butler and Cretcher, *THIS JOURNAL*, **55**, 2605 (1933).

(14) Zetzsche and Hubacher, *Helv. chim. acta*, **9**, 291 (1926).

(15) Austin and Park, *J. Chem. Soc.*, **127**, 1926 (1925), state that diacetyltartaric acid results from the action of water in acetone. No yield is given.