tion and the residue, containing the acetylmethylcarbinol and the unfermented glycol, is carefully fractionated. The fraction boiling between 135 and 150° is further purified by the use of an efficient fractionating column. The final fraction of the acetylmethylcarbinol obtained in a typical experiment had a boiling range of 142–144°, and the refractive index at 15° was 1.4192 as compared with the literature value of 1.4194.

The Properties of the Unfermented Glycol.—The unfermented glycol fraction recovered by the ether extraction and subsequent fractionation was purified by three distillations and was entirely free from the carbinol. The boiling range of the glycol was 179–182°. The angle of rotation of the glycol using the D line of sodium was $[\alpha]^{25}\text{D}$ +10.15. The highest rotations previously reported for *d*-2,3-butylene glycol are $[\alpha]^{25}\text{D}$ +5.0 by Böeseken and Cohen[12] and $[\alpha]^{25}\text{D}$ +6.9 by Chappell.[13] For the 2,3-butylene glycol used in the fermentations of the present investigation, produced by the action of *Aerobacter aerogenes* upon sugar, it was $[\alpha[^{25}\text{D}$ +1.0°. The freezing point of this glycol was 27°, which, according to the data of Wilson and Lucas,[9] corresponds to a mixture containing about 90% of the *meso*-glycol. The results of the above experiments indicate that the *Acetobacter suboxydans* preferentially attacks the *meso*-glycol and that the original glycol contained little or none of the *l*-form. Experiments are being conducted for the production of larger amounts of the *d*-glycol and its further purification.

Preliminary data indicate the feasibility of a dual fermentation for the production of acetylmethylcarbinol. The carbohydrate medium is first fermented with *Aerobacter aerogenes* to produce the 2,3-butylene glycol. The fermented medium is then sterilized, any needed adjustments in *p*H are made, and the medium inoculated with *Acetobacter suboxydans* to produce the acetylmethylcarbinol. By this procedure it is not necessary to isolate the glycol before subjecting it to the carbinol fermentation.

Summary

1. A procedure has been described for the production of acetylmethylcarbinol by the action of *Acetobacter suboxydans* upon 2,3-butylene glycol. The yields of the carbinol are 90–94% of theory.

2. The unfermented 2,3-butylene glycol is dextrorotatory with an angle of rotation much higher than that previously reported in the literature. These results indicate that the organism attacks the *meso*-glycol preferentially and that the glycol produced by the action of *Aerobacter aerogenes* consists of the *meso*-glycol and *d*-glycol with little or none of the *l*-glycol.

Ames, Iowa Received April 9, 1943

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[12] J. Böeseken and R. Cohen, *Rec. trav. chim.*, **47**, 839 (1928).

[13] C. H. Chappell, "A Study of 2,3-butylene glycol and its derivatives," Thesis, Iowa State College, 1935.

[Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology, No. 931]

The Equilibrium of Gaseous Dibromoethylenes

By Richard M. Noyes and Roscoe G. Dickinson

The kinetics of the iodine catalyzed liquid phase isomerization of the *cis* and *trans* 1,2-dichloroethylenes have been studied by Wood and Dickinson,[1] and the vapor phase equilibrium has been investigated by Wood and Stevenson.[2] However, much less work has been done on the dibromoethylenes. Olson and Maroney[3] have studied the liquid phase equilibrium at 25 and at 150°, but no vapor phase work has been done. Since the techniques had already been developed in this Laboratory in connection with the work on the dichloroethylenes,[2] it was felt that it might be instructive to extend the study to the dibromoethylenes.

Experimental

Materials.—The iodine used as a catalyst in the reaction was sublimed from potassium iodide–iodine mixture and resublimed.

The dibromoethylene was prepared by adding commercial tetrabromoethane to a mixture of zinc and alcohol as directed by Van de Walle.[4] The isomers were separated by fractional distillation with absolute alcohol, the fractionation being followed by the index of refraction of the distillate. The dibromoethylene was removed from the alcohol by extracting with six molar sulfuric acid, washed with water, and dried with potassium carbonate.

The dielectric constant of *cis*-dibromoethylene obtained by the above method was not appreciably affected by subsequent attempts at purification. The dielectric constant of the *trans* isomer could be lowered somewhat by crystallization from methanol at dry-ice temperatures. The dielectric constants at 25° and 1.7 megacycles were 2.47 and 6.96 for the *trans* and *cis* isomers, respectively.

The *cis* isomer was quite stable, but the *trans* turned yellow on standing in air. The dielectric constant of *trans*-dibromoethylene exposed to the air changed rapidly and reached a value corresponding to 62% *cis* in agreement with the equilibrium observation of Olson and Maroney.[3] It was found that both isomers could be stored indefinitely under nitrogen without appreciable isomerization.

Procedure.—The composition of isomeric mixtures was determined by means of the dielectric constant. Mix-

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[1] Reuben E. Wood and Roscoe G. Dickinson, This Journal, **61**, 3259–3263 (1939).

[2] Reuben E. Wood and D. P. Stevenson, *ibid.*, **63**, 1650–1653 (1941).

[3] A. R. Olson and William Maroney, *ibid.*, **56**, 1322 (1934).

[4] H. Van de Walle, *Bull. soc. chim. belg.*, **27**, 209–217 (1913).

tures of known composition were measured, and a calibration curve of isomeric composition against dielectric constant was prepared for analytical purposes. The calibration data are given in Table I.

The dielectric constant was determined with the apparatus constructed by Wood and described by him.[1,5] The cell employed was that described by Lucas and Gould.[6]

TABLE I

DIELECTRIC CONSTANTS OF DIBROMOETHYLENE MIXTURES AT 25°

The calibration data were obtained using samples of *cis* and *trans* isomers each of which contained a slight impurity of the other isomer as indicated by its dielectric constant. The impurities amounted to no more than about one per cent. in each case and were estimated from the calibration data themselves. The weights given in this table have been corrected for the estimated impurities.

Weight *cis*	Weight *trans*	Percentage *cis*	Dielectric constant
		0.00	2.467
0.6726	3.9432	14.57	3.020
1.1393	3.4010	25.09	3.451
1.9083	2.8341	40.24	4.105
2.2761	2.3265	49.45	4.515
2.8235	1.6551	63.04	5.088
3.2340	1.0527	75.44	5.669
3.9216	0.6531	85.72	6.248
		100.00	6.962

The experimental procedure was the same as that used by Wood and Stevenson[2] in the study of the gas phase equilibrium of the dichloroethylenes. The dibromoethylene and the iodine catalyst were sealed in a small ampule with a drawn-out tip. The air was swept out of the ampule by dibromoethylene vapors in the process of sealing so that no more than a trace of oxygen was present. The ampule was introduced into the reaction vessel which was then evacuated and sealed off. The tip of the ampule was broken by shaking, and the dibromoethylene and iodine vaporized into the reaction vessel. The system was placed in an electrically heated furnace with a uniform and measured temperature.

At the end of the run, the vessel was removed from the furnace, and the side-arm was immersed in a bath of dry-ice and isopropyl ether. When condensation was complete, the side-arm was broken off, and a coil of clean copper wire was introduced. The system was stoppered and set aside in the dark to deiodize. The copper was removed when the liquid became clear, and the dielectric constant was measured. In trial experiments the liquid did not change dielectric constant appreciably when iodine was added and then removed by this method.

The first five experiments were made without catalyst. Isomerization at around 150° was too slow to measure easily. When a sample of either isomer was exposed for about seventy hours at 185°, the dielectric constant of the resulting mixture was approximately that later found for the iodine catalyzed equilibrium mixture. However, the resulting liquids were cloudy, and their dielectric constants could not be measured accurately. When the liquids were placed in the measuring cell, the readings went up rapidly with time, and they came out of the cell yellow. It seemed probable that the platinum in the cell caused some reaction of a decomposition product of the dibromoethylene which increased the dielectric constant of the mixture. It was found desirable to use iodine as a catalyst and to work at a lower temperature.

In the iodine-catalyzed experiments a small, dark deposit formed on the walls of the reaction vessel and was removed before each run by boiling with fuming nitric acid. It seemed to be a polymerization product which contained iodine or at least whose formation was catalyzed by iodine. The deposits were always quite small, and good dielectric constant readings were obtained from the liquids from all runs at temperatures below 180°. One run made for fifteen hours at 192° with iodine as a catalyst gave the same yellowing and variable condenser reading which was observed in the uncatalyzed runs at high temperatures.

Experimental Results.—The iodine catalyzed runs are summarized in Table II. Absolute values of percentage composition are probably good to about one per cent., although the relative values in different runs are good to better than that. Almost all runs were made from the *cis* side of equilibrium because of the air induced isomerization described above which led to the loss of most of the supply of *trans* isomer. After several runs from the *cis* side had been made, the residues were pooled and distilled. In this process a small amount of iodine color was formed, indicating that there had been some addition or substitution of iodine in the compounds during the isomerization reaction. However, the total iodine present in any run was only one or two mole per cent.; the most of it certainly remained unreacted. Any iodine compounds formed in

TABLE II

EQUILIBRIUM OF GASEOUS DIBROMOETHYLENES

Run	Mole fraction I_2 in %	Temp. in °C.	Time in hours	Dielectric constant	% *Cis*	*K*, [*cis*]/[*trans*]
6	*ca.* 1	144.6	48.0	4.546	50.2	1.006
7	*ca.* 1	144.6	43.5	4.571	50.7	1.028
8	*ca.* 1	144.6	20.4	4.823	56.4	1.29
9	*ca.* 1	144.6	46.2	4.544	50.1	1.004
10	1.3	144.6	44.7	4.559	50.4	1.018
11	1.6	170.5	41.2	4.508	49.3	0.972
12	1.2	170.5	19.2	4.513	49.4	0.977
13	0.8	170.5	19.2	4.518	49.5	0.981
15	1.0	170.5	41.0	4.507	49.3	0.971
19	1.3	178.4	17.5	4.498	49.1	0.963
20	2.7	178.4	17.5	4.528	49.8	0.990
21	1.3	178.2	20.0	4.499	49.1	0.964
22	2.6	126.6	93.6	4.626	52.0	1.08
23	2.3	126.6	117.7	4.616	51.7	1.07
24	2.4	144.6	96.5	4.523	49.6	0.986
25[a]	2.2	126.6	137.8	4.514	49.4	0.978
26[a]	2.2	170.6	41.0	4.546	50.2	1.006
28	1.4	144.6	158.0	4.517	49.5	0.980
29	1.4	144.3	237.4	4.522	49.6	0.985

[a] Runs 25 and 26 were made from the *trans* side of equilibrium.

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[5] Saul Winstein and Reuben E. Wood, THIS JOURNAL, **62**, 549 (1940).

[6] H. J. Lucas and C. W. Gould, Jr., *ibid.*, **63**, 2550 (1941).

such small amounts would have had a negligible effect on the dielectric constant. The distillate was deiodized with copper and fractionally distilled with absolute alcohol to separate the isomers. Runs 25 and 26 were made with the *trans* isomer so obtained. The apparent slightly higher percentage of *cis* in the final equilibrium mixture in run 26 may be due to some impurity. The runs from the *cis* side are probably more reliable, and the others agree sufficiently to indicate that the state reached in these reactions was indeed an equilibrium between the two isomers as was assumed.

The changes in free energy, entropy, and heat content on isomerization are all zero within experimental error. As good an estimation as can be made is to say that the equilibrium constant, K, for the reaction *trans*-$C_2H_2Br_2 \rightleftarrows$ *cis*-$C_2H_2Br_2$ is 0.984 at 145° and 0.975 at 170°. The changes in thermodynamic quantities on isomerization at 158° become $\Delta F^0 = 17 \pm 40$ cal./mole. $\Delta H^0 = -130 \pm 300$ cal./mole. $\Delta S^0 = -0.34 \pm 0.8$ cal./mole degree.

So little is known about the vibration frequencies of the isomers that it is impossible to make a statitstical mechanical treatment of the equilibrium as was done by Wood and Stevenson.[2]

Summary

The gaseous equilibrium of *cis* and *trans* dibromoethylenes catalyzed by iodine has been studied in the range from 144 to 178° and has been found to correspond to equal amounts of the two isomers over the entire interval within the experimental error in analysis. Hence the standard free energy, entropy and heat content changes are all zero for the isomerization.

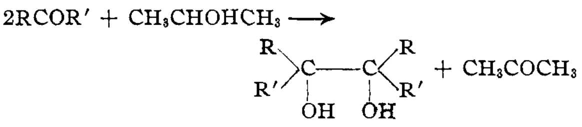
PASADENA, CALIFORNIA RECEIVED APRIL 27, 1943

NOTES

Photochemical Pinacolization

BY FELIX BERGMANN AND YEHUDA HIRSHBERG

In a previous paper from this Laboratory,[1] pinacolization of ketones under the influence of ultraviolet light was studied with the aim of elucidating the elementary process in the mutual oxidation and reduction of ketones and secondary alcohols, according to the scheme



$$2RCOR' + CH_3CHOHCH_3 \longrightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>\!\underset{OH}{\overset{}{C}}-\underset{OH}{\overset{}{C}}\!<\!\!\begin{matrix} R \\ R' \end{matrix} + CH_3COCH_3$$

We have now extended this investigation and found very narrow structural limits for the applicability of this type of reaction.

1. The fact that benzophenone and acetophenone are pinacolized quantitatively according to the above scheme would indicate that at least one aryl group is necessary to activate the carbonyl group. However, neither α- nor β-acetyl-naphthalene gave any reaction, and, likewise, α-naphthyl phenyl ketone and di-α-naphthyl ketone remained unchanged. Also, phenyl *p*-biphenylyl ketone, like its *o*-isomer, was not attacked, although the *m*-compound has been reported to yield the pinacol.[2] It is apparent that a change in the type of the aromatic substituent both in benzophenone and acetophenone nearly always impairs the photochemical reactivity.

2. Systematic changes were now applied to the non-aromatic part of acetophenone. Desoxybenzoin yielded the (higher-melting) α-pinacol in about 80% yield; no trace of the β-form was detected. The next higher homolog, benzyl-acetophenone, was inactive, but 1,4-diphenylbutanone-1 yielded a small amount of a liquid pinacol, which perhaps represents a mixture of both stereoisomers. It is very significant that the same behavior was encountered in the cyclic analogs of the last two ketones: α-indanone (I), comparable to $C_6H_5COCH_2CH_2C_6H_5$, was not pinacolized, but yielded, instead, the condensation product II: α-tetralone corresponding to $C_6H_5COCH_2CH_2CH_2C_6H_5$ yielded the pinacol in yields up to 75%.

3. On the principle of vinylogy, the styryl group was presumed to behave like the phenyl

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(1) Weizmann, E. Bergmann and Hirshberg, THIS JOURNAL, **60**, 1530 (1938).

(2) Hatt, Pilgrim and Stephenson, *J. Chem. Soc.*, 478 (1941).