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# The Heterogeneous Catalytic Racemization of *l*-Butanol-2

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The racemization of an optically active organic compound is formally one of the simplest possible reactions. An investigation of the possibilities of the gas phase heterogeneous catalytic racemization thus appeared to be of interest. It was felt, further, that such an investigation might yield information about the nature of catalytically active adsorption. This paper reports the results of certain orienting experiments in this field.

The simplest optically active organic alcohol, butanol-2, was selected for this investigation. Low pressures were employed so that the point of equilibrium in the dehydrating and dehydrogenating reactions might be displaced as far as possible in the direction of decomposition. Such would facilitate the separation of a racemization *per se* from one proceeding by a dehydrogenation-hydrogenation or a dehydration-hydration mechanism.

## Experimental

**Materials.**—The *l*-butanol-2 employed in this research was kindly furnished by Professor E. S. Wallis.[1] It was refluxed for one day over lime and distilled; b. p. 99.2–99.8°.

Copper catalyst: Schering-Kahlbaum "copper oxide for anal." was crushed and sieved: 1.5 g. of 20–40 mesh material was reduced with hydrogen *in situ* at up to 254° to provide the copper catalyst employed.

Zinc chromite: this was prepared following Taylor and Strother.[2] The material was pelleted, crushed and sieved: 1.0 g. of the 20–40 mesh product was reduced for eight hours at 455° to form the zinc chromite catalyst.

The Pyrex "catalyst" consisted of 0.9 g. of 20–40 mesh Pyrex glass which had been boiled with nitric acid and then aqua regia.

Chromium oxide: 0.85 g. of 20–40 mesh chromium oxide gel prepared as Preparation 9 of Burwell and Taylor[3] was reduced with hydrogen at 400°. During this treatment the material underwent the "glow phenomenon" and became green. Another sample of chromium oxide called here "by urea" was prepared as Preparation 7 of Burwell and Taylor; one gram of 20–40 mesh material was reduced with hydrogen, the temperature rising slowly to 360°. In the course of the experiments the catalyst was subjected to temperatures slowly rising to 425°. At the conclusion of the experiments the catalyst was subjected to temperatures rising to 550°. It remained black and failed to undergo the "glow phenomenon." This behavior contrasts with the results of Burwell and Taylor who reported that the material underwent the "glow phenomenon" at below 400° upon a more rapid initial temperature rise.

**Apparatus and Procedure.**—The apparatus employed in this research is illustrated in Fig. 1. From J, the system was connected with a McLeod gage and a mercury vapor pump backed by an oil pump. From K, the system was connected to an automatic Sprengel collecting pump. Electrolytic hydrogen passed over copper turnings heated to 450°, soda lime, calcium chloride and through a liquid air trap could be introduced through H. Tank nitrogen passed through a similar purification train could be introduced at G.

The catalyst was contained at F. Upon removal of the ground glass caps R and S, samples could be inserted or removed from traps M and N by means of a specially constructed pipet. When the system was thus open, a stream of nitrogen, passed through the apparatus, prevented oxygen from having access to the catalyst.

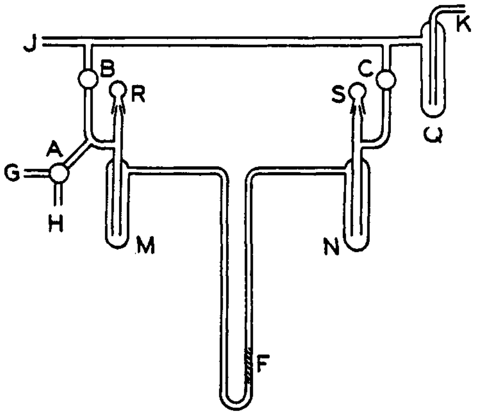

Fig 1.

At the start of a run, a sample of *l*-butanol-2 was placed in trap N, the cap replaced, liquid air placed about the trap, and the apparatus exhausted with the catalyst at F maintained at some suitably elevated temperature. To eliminate dissolved gases, a little of the alcohol (about 5%) was allowed to boil off on momentary removal of the liquid air flask. After pumping off the catalyst for about four hours, the furnace was replaced by a vapor-bath of a boiling organic liquid to maintain the catalyst at that temperature desired during the run.

The mercury vapor pump was then cut out and the collecting pump started, liquid air was placed about trap Q and solid carbon dioxide–toluene mush about trap M. Trap N was brought to and maintained at 25°. Butanol thus distilled from trap N to trap M passing over the catalyst in so doing. Water and butanone would also have been retained in trap M. Any hydrogen formed would

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(1) For preparation see Sprung and Wallis, THIS JOURNAL, **56**, 1717 (1934).

(2) Taylor and Strother, *ibid.*, **56**, 586 (1934).

(3) Burwell and Taylor, *ibid.*, **58**, 697 (1936).

have been collected in the Sprengel pump. Butylenes (no attempt was made to determine which of the four varieties were present) would have passed through trap M but would have been retained in trap Q. The vapor pressures[4] of the butylenes are about 5 to 20 mm. at −79°. The operating pressure to the left of the catalyst was less than 2 mm. After all the alcohol had distilled (this required about one hour) it dropped to less than 0.01 mm. Thus but little butylene should have remained dissolved in the butanol-2 in trap M.

After the volume of hydrogen liberated had been determined, trap Q was allowed to warm and the butylene therein condensed was collected and its volume measured.

The optical rotation of the condensate in M was determined in a 1-dm. micro polarimeter tube; 0.3 g. of each condensate was dried with anhydrous copper sulfate. It was then dissolved in 25 cc. of pyridine containing 2.5 g. of 3,5-dinitrobenzoyl chloride. After twenty-four hours, the pyridine solution was treated with 3 *N* sulfuric acid and ether. The ether layer was washed successively several times with 3 *N* sulfuric acid, water, dilute sodium hydrogen sulfite solution, water, dilute sodium carbonate solution and water. The ether solution was dried over calcium chloride, decolorized with Norite, and evaporated. The resulting crystals of the *s*-butyl esters of 3,5-dinitrobenzoic acid were white but gave a pale yellow solution which, however, passed the sodium D line without difficulty. Further purification by fractional crystallization was prohibited by the possibility that one of the optical forms might thereby be concentrated. The rotations of the esters were determined at 21 ± 1° in chloroform solution in a 1 dm. semimicro polarimeter tube. The concentration of esters was 0.134 ± 0.002 g. per cc. (20°). Inasmuch as the observed rotations were multiplied by about 7.5 in obtaining the specific rotations, the specific rotations are reported merely to the nearest tenth degree.

Three samples of butyl dinitrobenzoate prepared from the inactive alcohol by the method described above exhibited melting points of 74.5–76.5, 74.5–75.5, and 73.5–75.5° (uncorr.). Three samples were prepared from an alcohol of rotation, $\alpha^{21}\text{D}$ −4.67°. The melting points were 79.5–82, 78.5–80.5, and 79.5–81.5° (uncorr.) and the rotations, $[\alpha]^{21}\text{D}$ were −13.0, −12.8, and −13.1°. The rotation of the ester from an alcohol of $\alpha^{21}\text{D}$ −4.67° will be taken as −13.0.

Malone and Reid[5] report 75.6° as the m. p. of *dl-s*-butyl 3,5-dinitrobenzoate. The agreement between the rotations and melting points indicates that degrees of racemization calculated from the rotations of the esters are correct to about ±1%. It will be noted that the melting points of the esters increase with decreasing rotation.

The experimental results are exhibited in Tables I and II. In the cases of catalysts: "Pyrex glass," chromium oxide, "glowed," and zinc chromite, the butanol-2 employed had a rotation, $\alpha^{21}\text{D}$ −3.20°. The dinitrobenzoyl ester corresponding to an alcohol of this rotation would have a rotation, $[\alpha]^{21}\text{D}$ −8.9°. For the catalysts: copper and chromium oxide gel by urea, the alcohol of rotation, $\alpha^{21}\text{D}$ −4.67° was employed.

In the experiments reported in Table I, after all the alcohol had distilled over, the system was pumped at the temperature of the run until the rate of evolution of the gas was negligible. Columns 3 and 4 report the amounts of gas passing traps at −190 and −80°, respectively. Thus column 3 reports the amount of hydrogen expressed as 100 times the ratio of amount of hydrogen collected to the amount of hydrogen which would have been formed if the dehydrogenation reaction had gone to completion. Column 2 reports the rotation of the condensate, column 5 the rotation of the ester prepared from the condensate.

In Table II the first 4 columns have the same meaning as in Table I. After the system had been pumped at the temperature of the run until gas evolution was negligible, the temperature of the catalyst was elevated to about 400° in the cases of zinc chromite and chromium oxide gel by urea and to 254° in the case of copper and the pumping continued until the rate of gas evolution was again very small. The additional quantities of hydrogen and butylene are reported in columns 5 and 6. The rotations and melting points of the esters prepared from the condensate are reported in columns 7 and 8.

TABLE I

| Temp., °C. | $\alpha^{21}\text{D}$ of condensate | $H_2$, % | Butene, % | $[\alpha]^{21}\text{D}$ of ester | M. p. of ester, °C. |
|---|---|---|---|---|---|
| | Catalyst: | "Pyrex glass," 20–40 mesh | | | |
| 456 | −3.14 | 0.3 | 0.2 | | |
| 592 | −3.14 | 2.4 | 1.6 | | |
| 618 | −3.10 | 3.2 | 3.7 | | |
| 612[a] | −2.76 | 10.6 | 16.7 | −8.9 | 77–79 |
| | Catalyst: | Chromium oxide, "glowed" | | | |
| 132 | −3.13 | 0.4 | 1.0 | | |
| 184 | −1.71 | 3.9 | 2.0 | | |
| 218 | −0.03 | 46.6 | 9.1 | | |

[a] In the experiment at 612°, the alcohol was passed across the catalyst five times.

## Discussion

**Pyrex Glass.**—The reaction on Pyrex glass was not demonstrated to be catalytic and might indeed have been wholly or partly homogeneous. At the temperatures employed in these experiments, products formed by the dehydrogenation and dehydration reaction might have been decomposed further. Thus the collected gases cannot be assumed to have been exclusively hydrogen and butene. While the figures entered in columns 3 and 4 of Table I are thus not capable of any clear interpretation, they suffice, nevertheless, to show the approximate amount of decomposition.

Under the conditions of the experiments, butanol-2 began to decompose with any rapidity only above 600°. The experiment at 612° demonstrates that although 25% of the starting material had decomposed, the recovered alcohol had the same rotation as the initial. This indicates that probably the decomposition reaction or reactions under these conditions have a smaller activation

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[4] Landolt-Börnstein, "Physikalisch-chemische Tabellen," 5th ed., Springer, Berlin, Eg. IIb, p. 1303, and Eg. IIIc, p. 2453.

[5] Malone and Reid, THIS JOURNAL, **51**, 3424 (1929).

TABLE II

| Temp., °C. | $\alpha^{21}_{\text{D}}$ of cond. | $H_2$, % (a) | Butene, % (a) | $H_2$, % (b) | Butene, % (b) | $[\alpha]^{21}_{\text{D}}$ of ester | M. p. of ester, °C. |
|---|---|---|---|---|---|---|---|
| Catalyst: Zinc chromite | | | | | | | |
| 132 | −2.80 | 2.9 | 0.4 | 1.6 | 0.9 | − 8.4 | 77–79 |
| 184 | −0.32 | 29.2 | .3 | 2.5 | .9 | − 1.1 | 72.5–75 |
| 184 | − .20 | 31.8 | | 1.9 | 1.3 | | |
| 154 | −2.02 | 5.4 | .2 | 1.7 | 0.7 | − 5.7 | 75.5–78 |
| Catalyst: Copper | | | | | | | |
| 132 | −0.20 | 48.2 | 0.7 | | | | |
| 100 | −4.10 | 7.7 | .1 | | | | |
| 111 | −3.90 | 10.9 | .3 | 0.1 | nil | −11.5 | 78.5–80.5 |
| 132 | −1.50 | 33.5 | .2 | .1 | nil | − 5.6 | 73.5–76.5 |
| 111 | −4.60 | nil | nil | | | | |
| 132 | −3.91 | 10.9 | 0.1 | | | | |
| 154 | −2.24 | 32.6 | 1.2 | | | − 8.0 | 75–77 |
| Catalyst: Chromium oxide gel by urea | | | | | | | |
| 184 | −1.72 | 6.0 | 3.1 | 7.0 | 1.6 | − 5.0 | 74–76 |
| 111 | −4.54 | 0.1 | 0.3 (Passed over the catalyst twice) | | | | |
| 218 | −0.19 | 15.1 | 6.3 | | | | |
| 154 | −3.94 | 1.7 | 1.7 | | | −11.6 | 79–80.5 |
| 218 | −0.12 | 19.1 | 5.8 | | | − 0.3 | 72–74 |
| 184 | −1.75 | 6.3 | 2.0 | 9.1 | 1.8 | − 5.3 | 75–77.5 |
| 184 | −1.86 | 6.5 | 1.4 | 8.1 | 1.7 | − 5.7 | 75.5–77.5 |
| 218 | −0.12 | 21.1 | 5.0 | 7.4 | 1.6 | | |

energy than any of the possible racemization reactions.

**The Catalytic Racemization.**—The alcohol recovered after passage over the two chromium oxides, zinc chromite and copper at suitable temperatures had an optical rotation distinctly lower than that of the starting material. Of the possible mechanisms of this racemization, that involving dehydration to butene followed by rehydration to secondary butyl alcohol and the corresponding dehydrogenation–rehydrogenation reaction will be considered first.

In the reaction

$$n\text{-}C_4H_8 + H_2O(g) = C_2H_5CHOHCH_3$$

let $k_1$ be the rate constant of the hydration reaction, $k_2$ the rate constant of the dehydration. Then

$$\text{rate}_1 = k_1 \text{ (pressure factor)}_1$$
$$\text{rate}_2 = k_2 \text{ (pressure factor)}_2$$

and

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k_1 \text{ (pressure factor)}_1}{k_2 \text{ (pressure factor)}_2}$$

Since at equilibrium rate $_1$ = rate $_2$

$$\frac{\text{rate}_1}{\text{rate}_2} = K_p \frac{p_{\text{butene}}\, p_{H_2O}}{p_{\text{alcohol}}}$$

This relation involves the assumption that the equations valid at equilibrium may be employed to represent the rates over the entire composition range to which the relation is applied.

For the above reaction, Stanley, Youell and Dymock[6] report the value of the equilibrium constant for pressure in atmospheres to be 9.4 × $10^{-3}$ at 150°. At a total pressure of 20 mm. with 20% decomposition of butyl alcohol the value of the ratio rate$_1$/rate$_2$ would be 1.0 × $10^{-5}$. Thus the back reaction in the dehydration could have contributed but negligibly to the racemization in any of the experiments reported in this paper.

The equilibrium constant for the dehydrogenation of *s*-butyl alcohol has not been recorded. However, Parks and Kelley[7] report the value of the equilibrium constant in the hydrogenation of acetone to *s*-propyl alcohol to be 2.8 at 184°. One may calculate from the data of Parks and Kelley that the equilibrium constant at 132° would be 24. It is probable that the equilibrium constant for the corresponding reaction with methyl ethyl ketone would have a value not far removed from that for acetone and that assumption will be made in this paper. With rate$_1$ applying to the hydrogenation and rate$_2$ applying to the dehydrogenation, the value of the ratio, rate$_1$/rate$_2$ would be at a total pressure of 20 mm. and 20% decomposition 3.0 × $10^{-3}$ at 184° and 2.6 × $10^{-2}$ at 132°. Provided then that the equilibrium constant for the hydrogenation of methyl ethyl ketone is less than or but little greater

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[6] Stanley, Youell and Dymock, *J. Soc. Chem. Ind.*, **53**, 205–208T (1934).

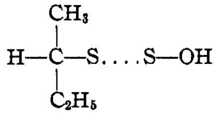
[7] Parks and Kelley, *J. Phys. Chem.*, **32**, 740 (1928).

than that for acetone, the contribution of the back reaction in the dehydrogenation of *s*-butyl alcohol to the racemization is small at temperatures above 132° and at total decompositions less than 20%.

The copper catalyst employed sintered rapidly or was poisoned. At the lower range of temperatures at which the copper was employed the equilibrium constant may have been sufficiently large to permit the back reaction to play an important part in causing the observed racemization although it appears unlikely that the whole of the racemization resulted from this effect.

Apparently, however, mere adsorption of *l*-butanol-2 on certain sections of the surfaces of chromium oxide, zinc chromite and probably copper results in the racemization of the alcohol. Such an adsorption must involve either dissociation or such a weakening of one or more of the valence bonds as almost to amount to dissociation.

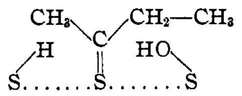
Mere dissociation of the alcohol into fragments such as



$$\begin{array}{l} \quad\; CH_3 \\ \quad\;\; | \\ H\text{—}C\text{—}S\ldots S\text{—}OH \\ \quad\;\; | \\ \quad\; C_2H_5 \end{array}$$

where S represents a surface atom, would probably not admit racemization as the bond between the asymmetric carbon atom and the hydroxyl radical would be replaced by a bond of considerable strength between the carbon atom and an unsaturated atom of the surface.

If the butanol-2 be dissociated thus



racemization would not take place on reëvaporation if the original fragments recombine unless free rotation be possible about the bond holding the hydrocarbon residue to the surface. However, if upon reëvaporation, the hydrocarbon residue combine with hydrogen and hydroxyl radicals produced by the dissociative adsorption of other butanol molecules on neighboring surface atoms or if migration of the fragments about the surface be possible, racemization could occur. While it cannot be decided whether or not the same type of activated adsorption produces both racemization and reaction it should be noted that the above hypothesis can account for dehydration and dehydrogenation as well as racemization. Evaporation of the hydrocarbon residue with an oxygen atom would produce butanone, while evaporation of the hydrocarbon residue would with rearrangement produce butene.

Lazier and Vaughen[8] observed that the reduction in the catalytic activity of chromium oxide resulting from "glowing" was much smaller for the decomposition of ethanol than for reactions involving hydrocarbons. Their results were obtained at temperatures of the order of 400°. That the "glowed" and gel chromium oxides have about the same activity at the lower temperatures employed in this research results probably from the greater inhibiting effect of water vapor upon the gel catalyst.

## Summary

1. The butanol-2 recovered from the passage of *l*-butanol-2 over "Pyrex" glass at 612° had an optical rotation equal to that of the starting material under conditions where 25% of the starting material had decomposed.

2. The butanol-2 recovered from passage of *l*-butanol-2 over zinc chromite, copper, gel chromium oxide and "glowed" chromium oxide had an optical rotation lower than that of the starting material.

3. The racemization cannot result from the reverse reactions of the dehydrogenation and dehydration except possibly in the case of copper but results most likely from suitable dissociative adsorption of the alcohol.

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[8] Lazier and Vaughen, THIS JOURNAL, 54, 3086 (1932).