26.3% V and 73.7% I, that is, at a result that is no easier to explain. There seems to be, however, no justification for adding this residue. Here again X-ray analysis could help a good deal in elucidating the problem.

Properties of the Low Vanadium Iodide.—It neither melts nor vaporizes at red heat. Its density was determined under carbon tetrachloride in the same state as used for analysis, that is, slightly contaminated with metallic vanadium, to be d_{15} 5.30. Its specific electric resistivity in the form of hand compressed powder was 10^6 ohm cm. at room temperature and 10^4 ohm. cm. in a boiling water-bath. It consists of garnet-red crystalline lamellae, resembling chromium trichloride in its consistency. It does not dissolve in water but evolves hydrogen slowly when treated with alkali; the low speed of this reaction may be partly due to the fact that it is moistened very slowly. It does not dissolve in organic solvents but splits off traces of iodine in contact with some of them (see above under Cb_2I_5). After standing for about one-fourth hour in the air it splits off some iodine and becomes moist.

Summary

1. Tantalum, columbium and vanadium react with iodine vapor at the temperature of dull red heat; the primary reaction products are the pentaiodides.

2. Tantalum pentaiodide vapor is reduced by incandescent tantalum. One product of this reaction dissolves in water to a deep green solution and is probably an analog of Chapin's green chloride and bromide.

3. Columbium and vanadium pentaiodide dissociate on heating and form compounds that gave the formulas $Cb_6I_{14}(Cb_2I_5?)$ and V_2I_3 on preliminary analysis. Some of their physical properties and chemical reactions are described.

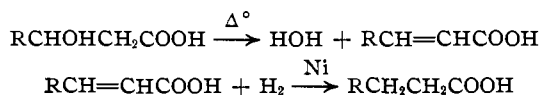## The Catalytic Hydrogenation of Some Organic Acids in Alkaline Solution

BY BRUCE B. ALLEN,[1] B. WOODROW WYATT[2] AND HENRY R. HENZE

During the course of another investigation identification of certain acidic substances, obtained as end-products of the high temperature–high pressure catalytic hydrogenation of cellulose suspended in alkaline solution,[3] necessitated attempts to hydrogenate some of the more common hydroxy acids in alkaline solution. The results of such experiments were of interest and importance sufficient to warrant the inclusion in this study of the behavior of keto acids and unsaturated acids under the same conditions.

The conditions of hydrogenation imposed upon the acids in alkaline solution were such that the temperature was not to exceed 250°, and the pressure at this temperature to be not more than 330 atmospheres. From the study made has come definite and quite interesting information. Thus, if the behavior of lactic acid be accepted as typical of the α-hydroxy acids, then it may be concluded that acids of this structure are not affected by catalytic hydrogenation under the conditions imposed. Apparently, γ-hydroxy

acids, too, are stable toward hydrogenation under our conditions since γ-hydroxyvaleric acid was identified as the primary reduction product of levulinic acid.

In contrast with the behavior of the α- and γ-hydroxy acids is that exhibited by the examples of β-hydroxy acids studied. Thus, hydracrylic acid, entirely typical of this class of compound, readily underwent hydrogenation at 175° to form propionic acid in excellent yield. Likewise, subjecting malic acid to the same conditions of alkali and hydrogen and also at 175° resulted ultimately in the replacement of the hydroxyl group by hydrogen, succinic acid being the product. In view of the ease with which β-hydroxy acids are known to become dehydrated at elevated temperatures, the following series of equations represent the reactions involved in the catalytic hydrogenation of β-hydroxy acids in alkaline solution

$$RCHOHCH_2COOH \xrightarrow{\Delta^{\circ}} HOH + RCH{=}CHCOOH$$

$$RCH{=}CHCOOH + H_2 \xrightarrow{Ni} RCH_2CH_2COOH$$

This mechanism of reaction[4] was substantiated in the instance of malic acid which was converted
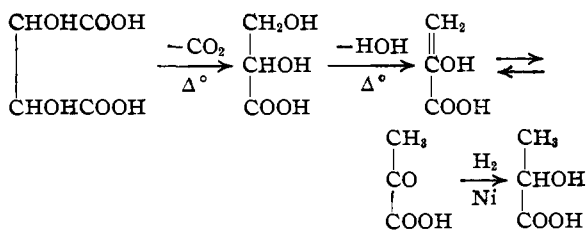
(3) We have found Raney nickel to catalyze hydrogenation in alkaline aqueous solution (5–10% sodium hydroxide); in this connection cf. Adkins, "Reactions of Hydrogen," University of Wisconsin Press, Madison, 1937, p. 25 and Covert, Connor and Adkins, THIS JOURNAL, **54**, 1661 (1932).

(4) In discussing the possible mechanism involved in the hydrogenolysis of certain organic compounds oxygenated in 1,3-positions, Connor and Adkins, THIS JOURNAL, **54**, 4678 (1932), consider the mechanism here formulated as a possibility in the instances which they studied, but conclude it to be not a probability.

by dehydration into fumaric acid by heating under the conditions of temperature and concentration of alkaline solution used in hydrogenation; the fumaric acid subsequently was hydrogenated to succinic acid.

In addition to the γ-keto acid, levulinic acid, the behavior of an α-keto acid, pyruvic acid, was studied under our selected conditions. In both cases rapid hydrogenation occurred below 100° and a molar equivalent of hydrogen reacted. After hydrogenation was complete at this temperature, heat was applied until the temperature had been elevated 'to 250°; in both instances, no reaction at this higher temperature had been noted after two hours, thereby establishing the stability of both α- and γ-hydroxy acids toward hydrogenation under these conditions.

Since it is our viewpoint that an α,β-unsaturated acid is formed as an intermediate in the hydrogenation of β-hydroxy acids, it was desirable to demonstrate the ease of reduction of a typical unsaturated acid in alkaline solution. Maleic, fumaric, and aconitic acids were hydrogenated rapidly and quantitatively at 100° or less to the corresponding saturated acids. Incidentally, the tribasic carballylic acid formed in the last instance was found to be stable toward hydrogenation at 250°.

A consideration of the behavior of tartaric acid, which may be looked at both as an α- and a β-dihydroxy acid, is of interest. Tartaric acid is decarboxylated and hydrogenated under our conditions to form lactic acid. Decarboxylation of tartaric acid should result in the formation of glyceric acid, which in turn is dehydrated, yielding pyruvic acid at the temperature used. The latter acid has been shown to be reduced readily at a much lower temperature.

$$\begin{array}{ccccc}
\text{CHOHCOOH} & & \text{CH}_2\text{OH} & & \text{CH}_2 \\
| & \xrightarrow[\Delta°]{-\text{CO}_2} & | & \xrightarrow[\Delta°]{-\text{HOH}} & \| \\
| & & \text{CHOH} & & \text{COH} \rightleftarrows \\
\text{CHOHCOOH} & & \text{COOH} & & \text{COOH}
\end{array}$$

$$\begin{array}{ccc}
\text{CH}_3 & & \text{CH}_3 \\
| & \xrightarrow[\text{Ni}]{\text{H}_2} & | \\
\text{CO} & & \text{CHOH} \\
| & & | \\
\text{COOH} & & \text{COOH}
\end{array}$$

Such conclusions as may be drawn relative to the ease with which α-, β-, and γ-hydroxy acids undergo hydrogenation when subjected to our experimental conditions might be considered as further substantiation of similar generalizations of Adkins based upon the hydrogenation of com-

pounds containing hydroxyls alpha, beta, or gamma to such groups as hydroxyl, carbonyl, carbethoxy, etc.[5] The similarity is quite striking in the case of glycols, the 1,3-type readily undergoing "hydrogenolysis" at one of the oxygen–carbon linkages, while 1,2- and 1,4-glycols show little or no tendency to undergo the same cleavage. This comparison is even more interesting in view of the fact that Adkins' experiments were carried out almost exclusively with copper chromite catalyst.

Ipatiew,[6] who has investigated the catalytic hydrogenation of the aqueous salts of both malic and tartaric acids but under conditions which differed from those employed in this investigation, reported formic acid as being one of the major products in both instances. Since in this study we have not encountered formic acid as an end-product, it became imperative to observe the behavior of this acid under our conditions. It was surprising indeed to note the relative rapidity with which the formate was hydrogenated. As carbonate, methane, and water were the only results of the reduction, being formed in the proportions represented by the equation $2\text{HCOONa} + 2\text{H}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{CH}_4 + \text{H}_2\text{O}$, the presence of these substances among the products in Ipatiew's work may be explained easily: namely, from the incomplete hydrogenation of formic acid previously formed. Likewise, this behavior of formic acid under our conditions explains the absence of this acid as a product in this investigation.

Because of the fact that oxalic acid can be converted into formic acid, it was of interest to test the stability of the former in alkaline solution toward hydrogen. No evidence of absorption of hydrogen or alteration of the oxalate was observed.

Experimental

General Procedure for the Hydrogenation of Organic Acids in Alkaline Solution.—The apparatus employed for the hydrogenation experiments was of the type described by Adkins[7] and included an autoclave of 325 cc. capacity and a heater controlled by means of a temperature indicating control pyrometer. The procedure followed in

(5) Adkins, *op. cit.*, pp. 71–73; p. 104 *et seq.*

(6) Ipatiew and Rasuwajew, *Ber.*, **60B**, 1973 (1927).

(7) Ref. 3, Chapt. III.

the hydrogenation of the acids studied was essentially the same in all instances: from 0.25–0.50 mole of the acid under consideration was dissolved in a solution containing 100 g. of distilled water and an amount of sodium hydroxide as would represent an excess of 5 g. over that equivalent to the acid. The resulting solution was transferred to the reaction vessel, 5–8 g. of Raney nickel catalyst[6] was introduced, and a hydrogen pressure of 2500 pounds per square inch (170 atmospheres) applied. Heat was then supplied gradually until reaction had commenced; i. e., during the heating period a corresponding rise in the pressure (at 250°, an increase to about 325 atmospheres) was noted, this rise ceasing abruptly and being followed by a gradual decrease when reaction had begun. The temperature was maintained at this point until hydrogenation was complete, the criterion of completion of reaction being no further decrease in pressure.

The isolation, purification, and identification of the product or products were dependent upon the starting material and anticipated substances and necessarily differed in the various instances. In general, however, the reaction mixture was separated from the catalyst by filtration, the filtrate neutralized with the calculated amount of sulfuric acid, extracted with ether, and then evaporated to either a mush or mixture of solids (depending upon the ether-insoluble products present). The residue was then extracted repeatedly with absolute alcohol. The ether and alcohol extracts were examined separately and in appropriate manners.

The pertinent data from this investigation of the hydrogenation of organic acids in alkaline solution have been summarized in tabular form and are included as Table I. When necessary for clarity, appropriate footnotes to the tabulated material have been added.

TABLE I

EXPERIMENTAL DATA FOR THE CATALYTIC HYDROGENATION OF SOME ORGANIC ACIDS

Acid	Moles acid	Moles H₂	t, °C.	Time, min.	Yield, %	Products
Maleic	0.50	0.53	100	26	98.0[a]	Succinic acid[a]
dl-Malic[d]	.50	.50	175	49	92.7[b]	Succinic acid[b]
					1.0[c]	Acids volatile with water
Hydracrylic[e]	.38	.38	175	30	91.6	Propionic acid[f]
Levulinic	.44	.48	75[h]	27	84.1	γ-Hydroxyvaleric acid[g]
Pyruvic[i]	.44	.43	60[h]	36	82.3	Lactic acid[j]
Tartaric	.26	.56	235	150	71.3	Lactic acid[j]
					1.2[c]	Acids volatile with water
Formic	.50	.58	250	135	48.5	Carbon dioxide[k]
					51.0	Methane[l]
Aconitic[m]	.25	.22	100[h]	12	93.3	Tricarballylic acid[n]
Lactic	.30	.00	250	120	..	...
Oxalic	.25	.00	250	120	..	...

[a] Neutralization of the reaction mixture and removal of the water by evaporation under reduced pressure was followed by extraction of the solid residue with absolute ethanol. Evaporation of the alcohol under reduced pressure resulted in the separation of 57.8 g. of white solid. When recrystallized from water, the product melted at 184.0–185.0° (corr.) and gave no depression of the m. p.

(8) Ref. 3, p. 20; Covert and Adkins, THIS JOURNAL, 54, 4116 (1932).

when mixed with known succinic acid. [b] The solid product from malic acid was obtained in the same manner as that from maleic acid. This product when recrystallized from water melted at 184.0–185.0° (corr.) and also showed no depression of the m. p. when mixed with succinic acid. [c] Determined by titration of the aqueous distillate obtained on evaporation of the neutralized reaction mixture. [d] In a separate experiment, in which an effort was made to clarify the mechanism of the hydrogenation of malic acid, the same quantities of acid, alkali, and water were first heated for two hours at 175° and under the pressure developed by the water present, but in the absence of hydrogen and the catalyst. The resulting suspension (the separated solid was shown to be sodium fumarate by comparison of its p-nitrobenzyl bromide derivative with that of known sodium fumarate) was combined with the usual weight of catalyst and hydrogenated. Whereas malic acid is hydrogenated only at temperatures above 175°, in this case 0.27 mole of hydrogen was absorbed at 75°. An additional 0.25 mole of hydrogen was absorbed when the temperature was raised to 175°. When the reaction mixture was treated as in a and b, 50.5 g. or a yield of 85.6% of succinic acid was obtained. [e] Prepared by the alkaline hydrolysis of β-hydroxypropionitrile.[9] [f] Obtained by ether-extraction of the acidified mixture resulting from hydrogenation. The propionic acid obtained had the following physical properties: b. p. 139.5–140.0° (745 mm.); d^{20}_4 0.9940; n^{20}D 1.3870; MR calcd., 17.59; MR found, 17.55. [g] Obtained as the lactone following acidification and ether-extraction. Physical properties and analytical data for the γ-valerolactone: b. p. 97.5° (21 mm.); d^{20}_4 1.0526; n^{20}D 1.4330; MR calcd., 24.74; MR found, 24.72. Anal. Calcd. for $C_5H_8O_2$: C, 59.98; H, 8.06. Found: C, 60.19; H, 8.01. [h] After completion of reaction at the temperature indicated, the temperature was raised to 250° and maintained thus for two hours. Since no decrease in pressure was noted after this time, the acid already formed apparently is resistant to hydrogenation under these conditions. [i] Synthesized by the dry distillation of a mixture of tartaric acid and potassium bisulfate.[10] The portion hydrogenated had the following physical properties: b. p. 78° (30 mm.); n^{20}D 1.4287. [j] Product identified by customary qualitative tests; namely, conversion to acetaldehyde with dilute acid, to carbon monoxide with concd. sulfuric acid, and by oxidation with permanganate. Complete conversion of the pyruvic acid to lactic acid was indicated since the typical color reactions of the former with β-naphthol[11] and with ammonia–sodium nitroprusside reagent[12] were not obtained with the product. [k] Determined by titration of the alkaline reaction mixture subsequent to hydrogenation. [l] Determined by means of a Fisher gas analyzer employing palladium black as an adsorbent for hydrogen. [m] Prepared from citric acid by dehydration with concd. sulfuric acid[13]; m. p. 186.5° (dec., corr.). [n] Obtained from the reduction mixture as in a. The purified tricarballylic acid melted at 158.5–159.5° (corr.) after recrystallization from water.

(9) "Organic Syntheses," John Wiley & Sons, New York, 1927, Vol. VII, p. 54.
(10) Ibid., Vol. IV, p. 63.
(11) Alvarez, Bull. soc. chim., [3] 33, 716 (1905).
(12) Simon, Compt. rend., 125, 534 (1897).
(13) Hentschel, J. prakt. Chem., [2] 35, 205 (1887).

Summary

1. A study has been made of the behavior of certain aliphatic organic acids, chiefly typical hydroxy, unsaturated, or keto, toward reduction catalyzed by Raney nickel and in the presence of sodium hydroxide and under high hydrogen pressure.

2. At temperatures below 250° and hydrogen pressures not exceeding 330 atmospheres, α- and γ-hydroxy acids are not affected, whereas β-hydroxy acids are converted into the corresponding unsubstituted acids.

3. The unsaturated acids studied were hydrogenated rapidly at temperatures of 100°, or less.

4. α- and γ-keto acids were hydrogenated with ease to the corresponding hydroxy acids at quite moderate temperatures.

5. Of particular importance was the conversion, in alkaline solution at 250° and under a hydrogen pressure of 330 atmospheres, of formic acid into methane and carbon dioxide.

Austin, Texas

Sterols. LIII. The Structure of the Side Chain of Sarsasapogenin*

By Russell E. Marker and Ewald Rohrmann

In the course of extensive experiments undertaken to obtain hormone intermediates from relatively inexpensive starting materials, we have made many observations on the sapogenins which can hardly be reconciled with the present conception of the side chain of these substances. Up to the present it has been assumed that this side chain contains two rather non-reactive oxygen atoms. In accordance with this assumption Tschesche and Hagedorn[1] suggested a double tetrahydrofuran structure, I.


I. Sapogenin side chain   II. C_{22} Lactone
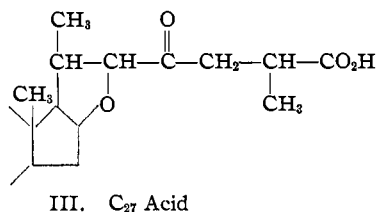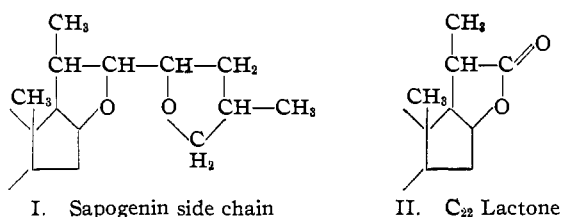
III. C_{27} Acid
Formulations of Tschesche and Hagedorn[1]

The existence of an oxide linkage at C-16 is well established from the degradation of the C_{22} lactone from tigogenin to etio-allo-bilianic acid by Tschesche and Hagedorn[1] and of the C_{22} lactone from sarsasapogenin to etio-bilianic acid by

Farmer and Kon.[2] The linkage between C-16 and C-22 is based upon the formation of lactone II. The definite proof of the structure of this lactone will require a stepwise degradation to a known compound such as an allo-pregnane, a pregnane derivative or a known bile acid.

The corresponding C_{27} acid from sarsasapogenin was prepared by Fieser and Jacobsen[3] and was designated as sarsasapogenoic acid. In later work[4] they presented evidence interpreted as offering support to the formulation suggested by Tschesche and Hagedorn for the sapogenin and the C_{27} acid.

We have found that the two oxygen atoms in the sapogenin side chain are inert only in neutral or alkaline media. *In acid media they are unusually reactive.* While the evidence presented here is not yet complete, all of the results are consistent with the presence of a protected carbonyl group existing as a ketone spiro acetal. The following formulation is suggested on the basis of the accepted structure of the lactone (II) and on the assumption that the sapogenins possess the cholesterol skeletal side chain.

IV. Sapogenin side chain (suggested)

* Paper LII, This Journal, **61**, 588 (1939).

(1) Tschesche and Hagedorn, Ber., **68**, 1412 (1935).
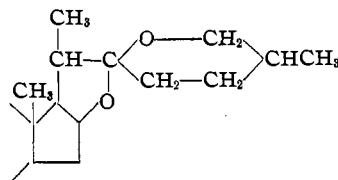
(2) Farmer and Kon, J. Chem. Soc., 414 (1937).

(3) Fieser and Jacobsen, This Journal, **60**, 29 (1938).

(4) Fieser and Jacobsen, ibid., **60**, 2753 (1938).