Hydrogenolysis of Saturated, Oleic and Ricinoleic Acids to the Corresponding Alcohols

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Abstract

Fatty acids are hydrogenolysed to corresponding alcohols in 90% yield at 220–250C at pressures of 3500–4000 psi. For saturated acids the catalyst is one per cent of copper and for oleic and ricinoleic acids 2% of copper and one per cent of cadmium, all present as their soaps. Only 10% of the unsaturation is lost. The main side product is the acid-alcohol ester. In hydrogenolysis of ricinoleic acid, the alcohol obtained contains 15% of ester and 10% of lower alcohols such as undecenyl.

Introduction

The classical researches of Adkins and his collaborators (1) on the preparation of fatty alcohols by high-pressure hydrogenation or hydrogenolysis set the subsequent patterns of study for a considerable period. Since the presence of free acids was stated to be harmful, later workers continued to use mainly esters (2,3,4). The carefully-prepared mixed copper-chromium oxide catalyst, called copper chromite for short, which Adkins used at ca. 5% level is employed for commercial ester hydrogenolysis even today. Other oxides such as those of iron, vanadium, cobalt or nickel (3) have been extensively studied without clear advantages. Later, metal soaps such as those of lead, copper, zinc or cadmium were tried for hydrogenolysis either as such (5) or in gross admixture with fatty esters (6).

From the beginning, attempts were made to retain the starting unsaturation under the drastic hydrogenolysis conditions. Usually a second metal oxide such as that of zinc, cadmium, lead, bismuth or molybdenum (2,3) was used. Several studies point to the beneficial effect of cadmium oxide in protecting initial unsaturation (6,7,8).

The hydrogenolysis of ricinoleic acid (or of castor oil) containing a secondary hydroxyl group has so far yielded only the corresponding saturated diol (9,10). Frequently stearyl alcohol appeared as the major hydrogenolysis product (11,12,13), as a result of dehydration of the secondary hydroxyl group to yield a new ethenoid linkage followed by saturation of both double bonds.

The most promising approach to unsaturated alcohols appeared to be the use of fatty acids in conjunction with copper-cadmium catalysts (14,15,16). In the present study, this technique has been followed for the hydrogenolysis of oleic and ricinoleic acids to the corresponding alcohols. The procedure was extended to stearic acid. For comparison, the conventional Adkins process using copper chromite catalyst was applied to methyl stearate. Attempts to obtain fatty alcohols by alternative procedures based on literature claims are briefly recorded. The following abbreviations have been used in the text and tables: SV—saponification value, HV—hydroxyl value, I.V.—iodine value, AV—acid value and RI—refractive index at 25C.

Experimental

Fatty Acids and Esters. A very high degree of purity was not particularly essential, and therefore not striven for in the starting materials for hydrogenolysis. Since many lots of each raw material were prepared, the analytical data given for each are only representative.

Stearic acid (Distillation Products) was esterified with methanol and one per cent H_2SO_4 and the isolated ester vacuum-distilled to give methyl stearate (SV 187, calc 188.3). Oleic acid (USP grade, I.V. 90.5, over 90%) was used after a single vacuum-distillation. Ricinoleic acid was simply the mixed fatty acids of castor oil (which contains 90% of this acid), isolated by alcoholic saponification with shaking at at room temp. A marked drop in hydroxyl value occurred on shelf storage of ricinoleic acid and the product was freshly prepared when required.

The fatty alcohols required for reference purposes were obtained by reduction of the corresponding pure esters, in refluxing xylene with metalic sodium and *t*-butanol, using Hansley's procedure (17). The crude fatty alcohols were saponified, washed with water and finally purified by vacuum-distillation.

Catalysts. To prepare oleic soaps, copper carbonate and cadmium oxide were added directly to a small portion of fatty acids at the required percentage, heated till solution occurred and the mass kept at almost 120C for 1–2 hr under reduced pressure till no more moisture and/or carbon dioxide was evolved. Copper and cadmium ricinoleates were precipitated from a neutral aqueous potassium soap solution by the addition of an equivalent proportion of copper nitrate or cadmium chloride solution. The copper salt being soluble in ether was extracted with this solvent and washed free of inorganic salt. The cadmium salt was filtered, washed with water and then acetone, and dried. Copper stearate was obtained by double decomposition, filtration and washing. The material charged to the autoclave consists of a fatty acid solution of metal soaps. During the early stages of hydrogenolysis these are believed to be reduced to colloidal metals (18). After hydrogenolysis they are filtered off as metallic powders. Barium-stabilised copper chromite was prepared as directed by Conner et al. (1c), by adding a mixed solution of hydrated copper nitrate and barium nitrate to another containing ammonium dichromate and ammonium hydroxide, the precipitate being dried, ignited over a free flame and leached with acetic acid.

Hydrogenolysis. A Parr high-pressure hydrogenation apparatus was used. By employing an inner vessel of stout stainless steel with a perforation for gas in the loose-fitting lid, the charge was cut down to 25–30 g fatty material/run. The charge and the catalyst were taken in the vessel and the latter placed in the bomb, which was then sealed gas-tight. The bomb was flushed with hydrogen gas (500 psi) and more gas pumped in from the hydrogen booster till the pressure had been built up. The temp was then raised. The pressure also increased during heating and the figures recorded are the final pressures attained. With a little experience and using the charts supplied with the equipment, any desired final pressure could be achieved. The bomb was rocked for the

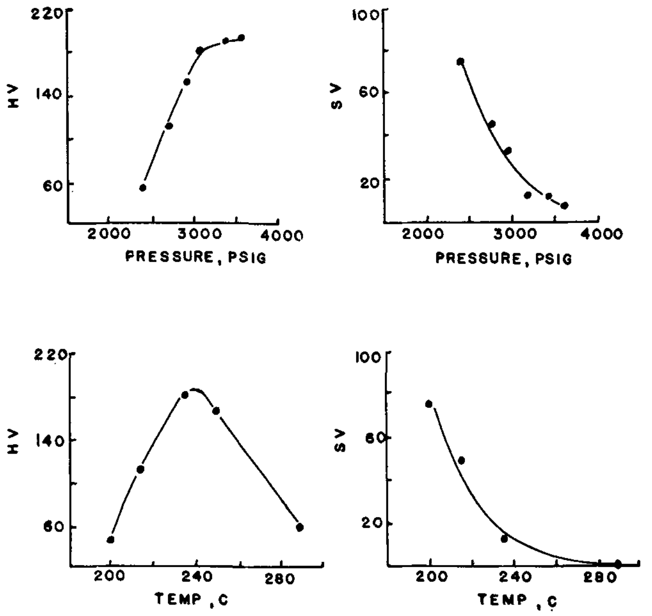

FIG. 1. Hydrogenolysis of oleic acid. Catalyst 3.75% $CuCO_3$ and 1.25% CdO used as soaps. Top: temp. 230C, pressure varied. Bottom: pressure 3500 psi, temp varied.

specified time. In the runs with fatty acids, hydrogen absorption was rapid, being over in ca. 20 min. Completion was judged by the levelling of pressure. The heating was now cut off and after cooling overnight the fatty material was removed, using ether, and filtered free of catalyst. To remove any traces of catalyst still remaining, the product in ether was shaken vigorously with 50% HCl in a separatory funnel.

Analysis. The RI, AV, SV and I.V. (Wijs) were determined by the usual methods. The HV was carried out according to B.S. 684:1950, Method I of British Standard Specifications, in which the material is refluxed with acetic anhydride-pyridine and back titrated in butanol solution with dilute alkali.

Results and Discussion

Oleyl Alcohol. Hydrogenolysis of oleic acid was conducted using as catalysts oleic soaps corresponding to 3.75% copper carbonate and 1.25% cadmium oxide. This salt wt will correspond to metal wt percentages of 1.9 and 1.1, or to 8.5 atoms copper and 2.7 atoms cadmium/100 moles oleic acid. Keeping temp constant at 230C, the final pressure was raised to various levels from 2400–3550 psi. Next the temp was varied from 200–290C at a constant pressure of 3500 psi. These results show in Figure 1.

Beyond ca. 3200 psi, pressure is not critical for hydrogenolysis. Temp was far more critical. Dehydroxylation occurs rapidly beyond 240C. When the highest quantity of alcohol has been formed, an SV of between 5 and 10 is exhibited by the product. This may be caused by the presence of original, unreduced ester, or by oleyl oleate as suggested earlier by Normann and von Schuckmann (19), and also by our own subsequent work with ricinoleic acid.

TABLE I
Hydrogenolysis of Oleic Acid

Constants	Variable		Product characteristics			
			AV	SV	HV	I.V.
Temp 250C	Catalyst % [a]					
Pressure 3900 psi	Cu	Cd				
Time as required	3.75	1.25	Nil	4.4	198.4	84.0
	4.00	2.00	7.0	57.5	94.6	95.8
	2.50	2.50	2.5	62.9	85.0	87.5
	1.25	3.75	Nil	92.6	23.0	87.0
	0.50	3.75	37.9	118.1	9.0	91.7
	Nil	5.00	49.4	122.7	8.5	91.9
Temp 250C	Runs under		Nil	10.9	189.0	74.0
Pressure 3500 psi	optimum		Nil	9.4	190.0	82.0
Time as required	conditions		1.1	10.9	180.3	82.5
Catalyst 5%			Nil	7.2	190.0	70.0
Cu-Cd (3:1)[a]			Nil	4.5	198.4	81.0

[a] As $CuCO_3$ and CdO used to form soap, see text.

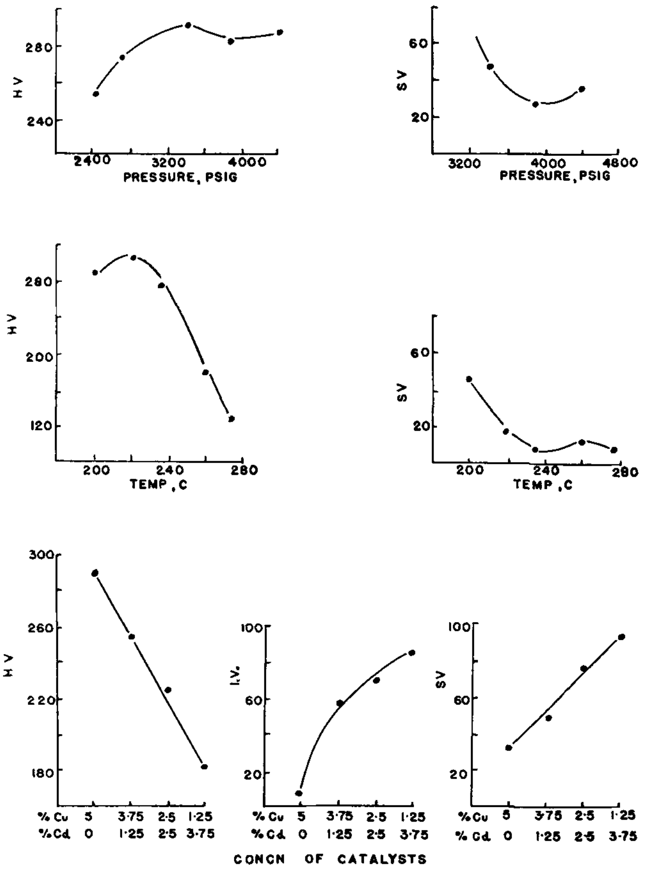

FIG. 2. Hydrogenolysis of ricinoleic acid. Top: catalyst 3.75% $CuCO_3$ and 1.25% CdO used as soaps, temp 200C, pressure varied. Middle: catalyst as above, pressure 3500 psi, temp varied. Bottom: temp 200C, pressure 3750 psi, catalyst proportions varied.

In another series, the proportions of copper and cadmium were varied. The results shown in Table I stress the importance of proper catalyst balance, both absolute and relative. Even when the copper-cadmium ratio drops from 3:1–2:1, keeping the copper content almost the same, as in the first two runs, a marked reduction of free alcohol formation occurs and the esters predominate. At 0.5% copper, the starting acids remain unchanged and almost all the alcohol formed is converted to ester.

Also shown in Table I are five separate hydrogenolysis runs on oleic acid under optimum conditions. The crude alcohols were mixed and distilled under vacuum, when the total distillate (178–182 C/1.5 mm) analysed thus: SV and AV Nil, HV 210.8 (Calc 209.7), I.V. 84.1 (Calc 94.7), RI 1.4579 (RI of reference sample prepared by sodium reduction, 1.4597). Thus the major departure of this oleyl alcohol from purity is the saturation of the double bond by ca. 10 units, corresponding to the presence of ca. 12% stearyl alcohol.

Ricinoleyl Alcohol. As in the trials with oleic acid, the total amt of copper-cadmium catalyst (ratio 3:1 as salts) employed to form soaps was first kept at 5%. The effect of altering at a time only one variable, pressure or temp, on the hydrogenolysis of ricinoleic acid was examined, with the results shown in Figure 2.

As with oleic acid, a pressure above 3200 psi is not highly critical. Above ca. 3800 psi, the increase in SV and decrease in HV are consistent with the formation of esters between the alcohol and fatty acid analogous to estolide formation between two molecules of ricinoleic acid. Temp is critical at ca. 220C, considerable lowering of HV occurring beyond this figure. This is the well-established temp for dehydration of the secondary hydroxyl group present in castor oil products. Dehydration would cause little change in the SV pattern, but an increase in the I.V., and this actually obtains. At high hydrogenolysis levels, the SV will mirror two reactions: ester formation (increase of SV), and hydrocarbon formation caused by dehydration of the primary alcoholic group (decrease of SV). The slight kink in the SV graph at 260C may be a result of such reactions.

Ricinoleic acid was hydrogenolysed at 200C and 3750 psi using various proportions of copper and cadmium catalyst. The percentages as $CuCO_3$ and CdO show in Figure 2 against each characteristic of the products. Use of copper alone, even at a low level of 1.25% (as carbonate) appears to cause total hydrogenolysis (low AV) but the double bond is entirely reduced. Increasing proportions of cadmium spare the double bond to increasing extents, but also promote coupling of the acid with the alcohol formed. At 3.75% level of cadmium (as oxide), the product corresponds almost entirely to ricinoleyl ricinoleate.

In later runs, max yields of free ricinoleyl alcohol were obtained at 220C and 3800–4000 psi using 3.75% by wt of copper carbonate and 1.25% of cadmium oxide as their ricinoleate soaps. A typical product analysing to SV 27, HV 280, I.V. 75.5, AV 9.0, RI 1.4675 was vacuum-distilled using a fractionating column into four fractions:

	I	II	III	IV
B.P., C/1.5 mm	88	192–96	298–302	Residue
% Wt.	9.1	65.3	15.3	10.3
AV	Nil	2.4	32.4	......
SV	Nil	8.7	94.2	......
HV	346	309	141.0	......
I.V	57	78	97.0	......
Main components(s)	Undecenyl alcohol, other lower alcohols(?)	Ricinoleyl alcohol	Ricinoleyl ricinoleate, ricinoleic acid	Polymers

Undecenyl alcohol was identified in Fraction I by thin-layer chromatography on silica gel G against an authentic sample. IR spectra, measured in a Perkin-Elmer Model 21 instrument with sodium chloride optics, were consistent with the components postulated. Fraction I showed the presence of a vinyl group (11.00 μ). Both Fractions II and III showed absorptions (9.0 μ, O—H deformation and 7.25 μ, C—O stretching) corresponding to the secondary hydroxyl group present in ricinoleate products. Only Fraction II showed evidence of a primary hydroxyl (9.50 μ, O—H deformation)and Fraction III of an ester group (5.75 μ, C=O stretching). Fraction III, containing mainly ricinoleyl ricinoleate, was saponified, acidified and separated into acid and alcohol components by alkali washing. These products answered to slightly saturated ricinoleyl alcohol and ricinoleic acid respectively. In every instance where such esters were hydrolysed, the I.V.s of the acid and alcohol moieties were similar, showing that the ethenoid linkage in each has been hydrogenated to the same degree, probably before combination to form the ester.

Stearyl Alcohol. Under our conditions, the Adkins procedure for hydrogenolysis of methyl stearate using 5% copper chromite was very sensitive to temp and time. Figure 3 illustrates the various trials in which three parameters were varied. Opt conversions occurred in one hr at 260C at a pressure of 2200 psi.

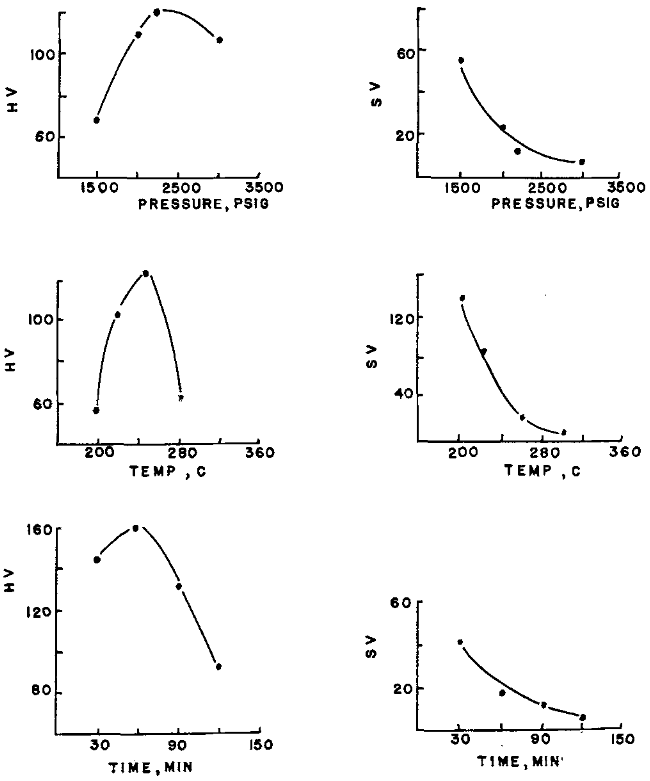

FIG. 3. Hydrogenation of methyl stearate using 5% barium-stabilised copper chromite catalyst. Top: temp 250C, time 2 hr, pressure varied. Middle: pressure 2000 psi, time 2 hr, temp varied. Bottom: temp 250C, pressure 2000 psi, time varied.

The oleic and ricinoleic acid trials had shown that copper acted as the hydrogenolysis catalyst. In stearic acid there is no unsaturation to protect, and cadmium can perhaps be dispensed with. Table II shows the effect of lowering the percentage of copper catalyst. Between 5 and 2%, the alcohol yield is only slightly reduced, but thereafter drops sharply. Conversion to alcohol is 90% when the soap corresponding to 2% of copper carbonate is used as catalyst. This is equivalent to one per cent of metal by wt, or to 4.5 atoms copper in 100 mole stearic acid.

Miscellaneous Trials. Various procedures suggested in the literature were tested for hydrogenolysis of oleic and ricinoleic acids, without promise. As already known, use of barium-stabilised copper chromite catalyst for hydrogenolysis of methyl or *n*-butyl oleate, or of methyl ricinoleate, led to considerable reduction of unsaturation. Mixed copper (10%) and cadmium (5%) soaps used with methyl ricinoleate or castor oil gave products containing very little alcohol and of high acid value. Hydrogenolysis of lead ricinoleate appeared to result in estolide forma-

TABLE II

Hydrogenolysis of Stearic Acid

Constants	Variable	Product characteristics		
		AV	SV	HV
Temp 250C	Cu catalyst, % [a]			
Pressure 3800 psi	5	1.4	4.9	192.7
Time as required	5	Nil	2.5	191.0
	3	Nil	7.0	191.8
	3	Nil	8.0	187.2
	2	Nil	4.9	187.2
	1	10.3	38.0	161.0

[a] As $CuCO_3$ used to form soap, see text.

tion. Hydrogenolysis of actylated ricinoleic acid using copper-cadmium soaps for short periods caused dehydration; longer periods led to almost complete ester formation.

Conclusions

Over 90% hydrogenolysis of fatty acids to alcohols can thus be effected at 220–250C at pressures from 3500–4000 psi using as catalyst one per cent copper present as the fatty acid soap. Use of a catalyst consisting of 2% copper and one per cent cadmium will protect almost 90% of any monoethenoid unsaturation present. Ricinoleyl alcohol resulting from hydrogenolysis also contains 10% short-chain alcohols and 15% acid-alcohol esters.

Except that high pressures are necessary, the use of fatty acids as described has several advantages over esters. Pure acids are commercial products which can be used as such. Metal soap catalysts are easy to prepare. Against 5% copper chromite used tc hydrogenolyse esters, the soap corresponding to 2% copper carbonate suffices for saturated acids. Hydrogenolysis of acids occurs very rapidly, and is easily judged by hydrogen absorption. An important further advantage is that unsaturation is preserved simply by having a cadmium soap also present.

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Physical Properties of Fatty Acid Methyl Esters. III. Dispersion

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Abstract

The dispersion and the molar dispersions, according to Lorentz-Lorenz and to Gladstone-Dale, are presented at 20C and at 40C for the saturated fatty acid methyl esters from acetate to nonadecanoate and for methyl oleate, linoleate, linolenate, and erucate. Regression equations for these two additive properties have been computed for the saturated series. The limiting dispersion is computed for the Gladstone-Dale specific dispersion.

Introduction

FOR CONSTITUTIVE STUDIES the dispersion is an attractive property because it is closely related to the fine structure of the molecule. It has the advantage of being independent of errors in absolute units of calibration because the values are differential in origin. The temp dependence is small which obviates the need for critical temp adjustments during measurements.

The M dispersion, product of the dispersion and the M volume, may be expected to possess additive properties. According to Bruhl (1), however, this property is pre-eminently constitutive.

The failure of many earlier attempts to compute the M dispersion by summation of the contributing elements can be ascribed to this reason, as constitutive differences affect the dispersion much more than the refraction.

The majority of the papers on the application of the dispersion to structural problems is found in the field of hydrocarbon analysis (2,3,9,12). The scope and applicability has especially been expanded by the investigations of Grosse and Wackher (8) and Thorpe and Larsen (11). Applications are generally based on the constant value which the specific dispersion possesses for a class of compounds. This property can be deduced from the fact that mol wt are additive. Numerical values obtained from pure hydrocarbons proved to be consistent in synthetic mixtures, and this has substantiated the applicability of the specific dispersion to type analysis of hydrocarbons (10).

Dispersion and Molar Dispersion

In a previous communication (6,7) we have reported the refractive indices of the saturated fatty acid methyl esters from acetate to nonadecanoate, methyl oleate, linoleate, linolenate, and erucate, at 20C and 40C, for the H_α, H_β, Na_D, and the H_γ spectral lines. The dispersion, which is discussed in this paper, has been obtained as the difference between the refractive indices of the H_β and the H_α lines, although $n_\gamma - n_\alpha$ would have been more obvious. The gain in accuracy by using the larger values is, however, more than offset by the lower accuracy of the n_γ determinations.

Expressions most commonly used for the M dispersion are the Gladstone-Dale dispersion

$$D_{GD} = (n_\beta - n_\alpha) \cdot M/d = \sum_i c_i D_{i,GD} \qquad [1]$$

and the Lorentz-Lorenz expression

$$D_{LL} = R_\beta - R_\alpha = \sum_i c_i D_{i,LL} \qquad [2]$$

In these equations D_i is the increment of the contributing element i, c_i the number of these elements, R_m the Lorentz-Lorenz M refraction (7), and d the density.

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