Homogeneous Catalytic Hydrogenation of Sorbic Acid with Pentacyanocobaltate II[1]

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Abstract

The homogeneous hydrogenation of sodium sorbate, with pentacyanocobaltate II used as the catalyst, was followed manometrically at room temperature and atmospheric hydrogen pressure. One mole of hydrogen was absorbed by one mole of sorbate. UV and IR analyses demonstrated the reduction of sorbate to hexenoate. Gas liquid chromatography (GLC) of hexenoate indicated 82, 17, and 1% yields of 2-,3-, and 4-hexenoates, respectively, with traces of sorbate. Increasing either the period of hydrogenation or the ratio of catalyst to sorbate, or both, did not cause the formation of caproate or change the ratio of the three isomers. Homogeneous catalytic hydrogenation in methanolic solutions showed higher selectivity since 2-hexenoate was present in 96% yield.

To standardize GLC columns, hexenoic acid isomers were synthesized by the Knoevenagel condensation. *Trans*-2-hexenoic and *trans*-3-hexenoic acids were prepared in 75 and 85% yields by a condensation of *n*-butanal and malonic acid in the presence of pyridine and triethanolamine, respectively. *Trans*-4-hexenoic acid was prepared in 70% yield by condensing diethyl malonate with crotyl bromide. Physical properties, including UV and IR spectra, were determined for the purified synthetic acids and methyl esters.

Although the absolute specificity of attack at the 4,5-double bond of sorbic acid was not confirmed, the high degree of selectivity obtained does encourage further study of homogeneous catalysis on higher fatty acids.

Introduction

Certain metal ions (notably Cu^{++}, Ag^{+}, Hg^{++}, Hg_2^{++}, and MnO_4^{-}) and several transition-metal complexes can activate molecular hydrogen and function as homogeneous hydrogenation catalysts (12-15). These systems provide an unusual opportunity to understand the chemistry of catalysis. A catalyst molecularly dispersed in solution should lead to more easily explainable results than can be obtained with solid catalysts, since in solution the molecular compounds are better known.

Adding alkali cyanide to a solution of cobalt II salt, in molar ratio $CN^{-}/Co^{++}>5$, immediately forms pentacyanocobaltate II, $[Co^{II}(CN)_5]^{3-}$ (1,18). This complex can reduce water to hydrogen (22) and can react reversibly with molecular hydrogen to give a hydride ion $[Co^{III}(CN)_5H]^{3-}$ (22). During the past 2 years this complex was used for the homogeneous catalytic hydrogenation of conjugated systems. Sorbic acid was hydrogenated quantitatively and selectively to 2-hexenoic acid (7,23). In addition to conjugated systems, epoxides, allylic compounds, various nitrogen-containing compounds, and certain inorganic substrates such as hydrogen peroxide and metal salts were reduced (23,24). With pentacyanocobaltate II, isoprene was reduced to give a mixture of 85% 2-methyl-2-butene and 15% 2-methyl-4-butene (24). Butadiene was hydrogenated selectively to 1-butene, *trans*-2-butene, and *cis*-2-butene; cyclopentadiene was reduced to cyclopentene (35). Using chlororuthenate-II complex as catalyst, Halpern et al. (16,17) reported that maleic and fumaric acids were selectively hydrogenated to succinic acid, but ethylene and propylene remained unchanged.

Heterogeneous catalytic hydrogenation of sorbic acid results in the formation of 3- and 4-hexenoic acids. Relative proportions of the isomeric acids depend somewhat on reducing conditions; e.g., solvent (8–10,19), catalyst (19,26,34), and pH of aqueous solutions (8,19,26).

As indicated from the literature, homogeneous hydrogenation holds a possibility for specificity of attack on the double bond between carbon atoms 4 and 5. This degree of selectivity has not been reported for heterogeneous catalytic hydrogenation. Possibly this specificity of homogeneous catalysis might increase the flavor stability of soybean oil by selectively hydrogenating the 15,16-double bond of linolenic acid over those in the 9,10- and 12,13-positions. Due to discrepancies regarding the selectivity of pentacyanocobaltate II in the literature (7,23–25), additional analyses, such as gas chromatography and IR and UV spectrophotometry, were used for studying the products of hydrogenation of sorbic acid. Effects of the reaction environments, such as the solvent and temperature, on products of hydrogenation were also studied. The isomeric unbranched hexenoic acids were synthesized for standards in identifying the products of sorbic acid hydrogenation.

Experimental Procedures

Materials Used. The following commercially available reagents were used: *n*-butanal (Eastman, White Label), crotyl bromide (Chemicals Procurement Laboratories, Inc.), diethyl malonate (Eastman, White Label), malonic acid (Eastman, White Label), piperidine (Matheson Coleman and Bell, Practical), pyridine (Baker, Purified), sorbic acid (Eastman, Practical), and triethanolamine (Eastman, Practical). These chemicals were purified until their physical constants agreed with well-established literature values (2,20,25,31,36).

Cobaltous chloride, lithium chloride, potassium cyanide, potassium chloride, and sodium chloride reagent grade; methanol, ACS grade; and sodium metal were also used.

Hydrated salts of lithium chloride and cobaltous chloride were converted to the anhydrous form according to Mellor (29). Anhydrous potassium cyanide was prepared by drying potassium cyanide over phosphorus pentoxide in a desiccator under vacuum.

Absolute ethanol was prepared from 95% ethanol according to Vogel (39).

Method of Studying Hydrogen Absorption. Hydrogenation was followed by measuring hydrogen absorption at room temp and atm pressure in apparatus similar to that described by Johnston et al. (20), except that a 250-ml Erlenmeyer flask served as the

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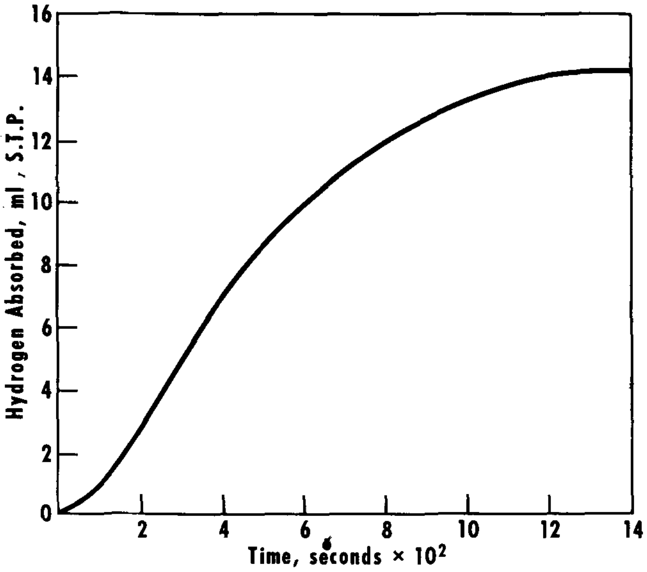

FIG. 1. Hydrogen absorption by sodium sorbate (0.683 mM) in the presence of pentacyanocobaltate II (8.03 mM) at 25C.

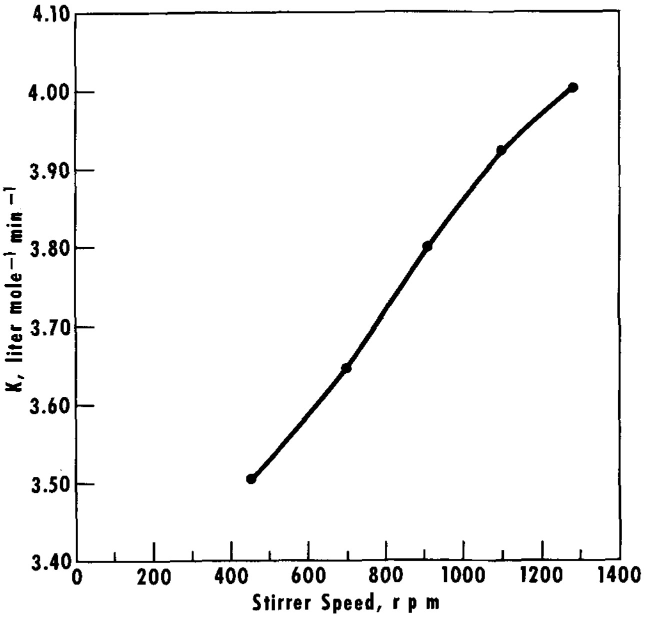

FIG. 2. Influence of different stirring speeds at 25C on hydrogenation rate of sodium sorbate.

reaction vessel. To achieve reproducible results, it proved necessary to use the same flask in each series of experiments.

Preparation of Pentacyanocobaltate II and Hydrogenation of Sorbic Acid. The catalyst was prepared according to the method of De Vries (7) with a slight modification adopted from the work of King and Winfield (21). Pure hydrogen at atm pressure was used to flush and fill the apparatus and also to saturate the catalyst. A solution containing 5.46 mM cobaltous chloride was introduced into the flask through the serum cap. Other hydrogen-saturated solutions containing 32.76 mM potassium cyanide, 3.40 mM NaOH, and 17.23 mM KCl were introduced consecutively into the reaction vessel while hydrogen was bubbled through the solution. The solution was stirred at 1,280 rpm with a Teflon-molded magnetic bar. The speed of the magnetic stirrer was measured by a photoelectric tactometer. Sodium sorbate (0.562 mM) was introduced, and hydrogen uptake was recorded every 40–60 sec. A blank determination in the presence of 0.562 mM sodium valerate was made.

To prevent loss of hydrogen cyanide during the bubbling of hydrogen, the gas was passed first through a potassium cyanide solution of the same concentration and temp as that in the reaction vessel. All reagents were always freshly prepared.

For the methanol media, anhydrous chemicals were used in preparing the catalyst.

Extraction of Reduced Sorbic Acid. After hydrogenation, the solution was transferred to a separatory funnel, acidified with 10% aqueous hydrochloric acid, and after saturation with NaCl, extracted three times with diethyl ether. The extracts were combined, washed with saturated aqueous NaCl, and dried over anhydrous sodium sulfate. After ether was evaporated under vacuum at 30C in a rotary evaporator, 98.3% of the expected hexenoic acids was recovered. The residue was transferred to a small vial and kept under a blanket of pure nitrogen at −18C.

Synthesis of trans-Hexenoic Acids. Pure *trans*-2-hexenoic acid was prepared in 75% yield by condensing 0.5 mole *n*-butanal with 0.5 mole malonic acid in the presence of pyridine in a manner similar to that described by Boxer and Linstead (4). Pure *trans*-2-hexenoic acid was also obtained in 95% yield by condensing 23 ml *n*-butanal with 26 g malonic acid in the presence of 25 ml pyridine and 1 ml piperidine: Döebner condensation reaction (11). The pure acid was obtained by partial esterification followed by fractional distillation. The acid was characterized by determining its melting point [mp 32C] and by preparing the anilide (mp 110C) and *p*-toluidide (mp 124C).

Trans-3-hexenoic acid was prepared in 75% yield by condensing *n*-butanal with malonic acid in the presence of triethanolamine according to the method of Linstead et al. (27). The acid was purified by partial esterification followed by fractional distillation of the methyl ester fraction. The esters were saponified, acidified with HCl, and extracted with ether. The pure acid melted at 12C; *p*-toluidide at 95.5C.

Trans-4-hexenoic acid was synthesized in 70% yield by condensing 30 g diethyl malonate with 25 g crotyl bromide according to the procedure of Linstead and Rydon (28). The crude acid contains 25.5% 3-hexenoic acid. Fractional distillation was used to obtain the pure acid (mp 0C); *p*-toluidide melted at 103C.

The method of Stoffel et al. (37) was used for preparing the methyl esters of hexenoic acid isomers.

Gas Chromatographic Technique. GLC of solvent-free acids and esters was carried out in a radium-D ionization-chamber detector of a Pye-Argon chromatograph equipped with a 4-ft glass column. For acids, packing consisted of 8.2 g 10% diethyl glycol succinate and 1% phosphoric acid on Chromosorb W, 60–80 mesh (30). For methyl esters, 8.2 g of 10% Craig succinic acid polyester on Chromosorb W, 60–80 mesh, was used. Argon flow was controlled by a precision reducing valve and measured by a soap flow meter at the column outlet. The gas flow rate was 66 and 40 ml/min for acids and esters, respectively. Column temp were 120C for the acids and 90C for the methyl esters. Both columns were conditioned at 220C by flushing with argon for 2 days before analytical use. Quantitative analyses were made from measurements on the recorded chromatograms of the synthesized standards and of the hydrogenated products of sorbic acid.

TABLE I
Reaction Rate Contants in the Homogeneous Catalytic Hydrogenation of Sorbic Acid, 25C (1280 rpm)

Sorbic acid 10^{-3} mole/L	Pentacyanocobaltate II 10^{-3} mole/L	K L mole^{-1} min^{-1}
6.83	80.30	4.07
8.54	80.30	4.02
17.08	80.30	4.35
8.54	53.00	4.38
8.54	80.30	4.07
8.54	120.45	4.17
8.54	160.60	4.38

TABLE II
Synthesis of n-Hexenoic Acid Isomers by the Knoevenagel Condensation

Catalyst	K_b catalyst	2-Hexenoic acid, %	3-Hexenoic acid, %
Pyridine	2.3×10^{-9}	80.4	19.6
Pyridine and Piperidine	2.30×10^{-9} 2×10^{-3}	98.4	1.6
Triethanolamine	....	12.3	87.7

Results

Hydrogenation of Sodium Sorbate with Pentacyanocobaltate II. In the presence of pentacyanocobaltate II, sodium sorbate absorbs one equivalent of hydrogen. The amount of reduced sorbate at any given moment is calculated from curves representing hydrogen absorption in the presence of sodium sorbate and sodium valerate under identical conditions. Figure 1 shows hydrogen uptake as a function of time in seconds. Reproducibility of experiments under the same conditions is excellent, as the difference in triplicate runs never exceeded ± 3%. The curve shows an induction period of about 2 min during which the rate of hydrogen absorption is small. When about 7% of sorbate is reduced, the reaction settles to a steady state, which exists until nearly 80–85% of the diolefin is reduced. Subsequently, the rate of hydrogenation gradually declines. After 20 min, one double bond is completely saturated.

Hydrogenation Rate Constants Depend on Stirring. Stirring should not be necessary with homogeneous solutions, except when one is added to another so as to bring a rapid intimate contact with the main solution. Stirring applies particularly where diffusion or adsorption of gases, or both, may occur or where heat generated locally may influence the reaction.

Dependence of the rate constants on stirring speed (Fig. 2) indicates that the rate of diffusion of hydrogen into the solution influences the reaction rate.

Kinetics of the Homogeneous Catalytic Hydrogenation of Sodium Sorbate. Two series of experiments were carried out. In the first, the concentration of sodium sorbate was constant (8.54 mM/L), whereas the concentration of pentacyanocobaltate II varied from 53.00 to 160.60 mM/L. In the second, the concentration of pentacyanocobaltate II was constant (80.30 mM/L), while the concentration of sorbic acid varied from 6.85 to 17.08 mM/L. Data in Table I show that the reaction is of a second order since reasonably constant values of K were obtained from second order equation calculations.

Synthesis of trans-Hexenoic Acids. To standardize GLC columns, *n*-hexenoic acid isomers were synthesized by the Knoevenagel condensation. Aliphatic aldehydes do not give exclusively α,β-unsaturated acids, but mixtures of α,β- and β,γ-unsaturated acids. The composition of the mixtures of hexenoic acids prepared in the presence of different catalysts was established by GLC.

Table II shows that the influence of the catalyst on the course of the chemical reaction is profound. By changing the catalyst, the products from *n*-butanal and malonic acid were completely different. Döebner condensation, whereby *n*-butanal is condensed with malonic acid in pyridine containing traces of piperidine, produced almost exclusively 2-hexenoic acid with only a very small amount of 3-hexenoic acid.

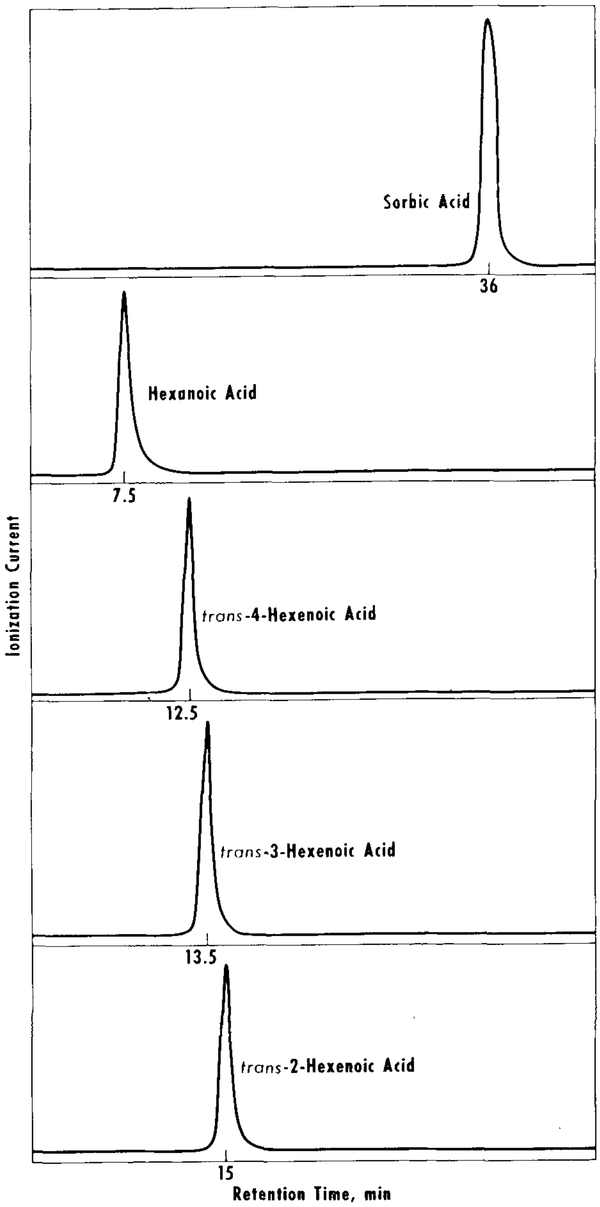

FIG. 3. Chromatograms of 2-,3-, 4-hexenoic, caproic, and sorbic acids on a glass column 4 ft x ¼ in., temp 120C, 10% DEGS plus 1% H_3PO_4, and an argon flow rate of 66 ml/min.

Evidence that the acids synthesized have a *trans* configuration is supported by the strong IR absorption in the 10.30 μ region (36).

Gas Chromatographic Analysis of Hexenoic Acid Isomers. Figure 3 shows typical chromatograms of *trans*-2-, 3-, 4-hexenoic, caproic, and sorbic acids. All acids yielded single peaks when tested individually. Well-defined separation of these acids was obtained on using a mixture of the three isomers.

Gas Chromatographic Analysis of Reduced Sorbic Acid. A typical chromatogram produced by reduced sorbic acid is seen in Figure 4. The three peaks are identified by comparing their retention times with those for synthesized hexenoic acid isomers. No caproic acid is present, and the respective yields of 2-, 3-, and 4-hexenoic acids are 81.7, 17.3, and 1%. Of course, confirmatory evidence is necessary before any claims as to the actual identity of the unknown components

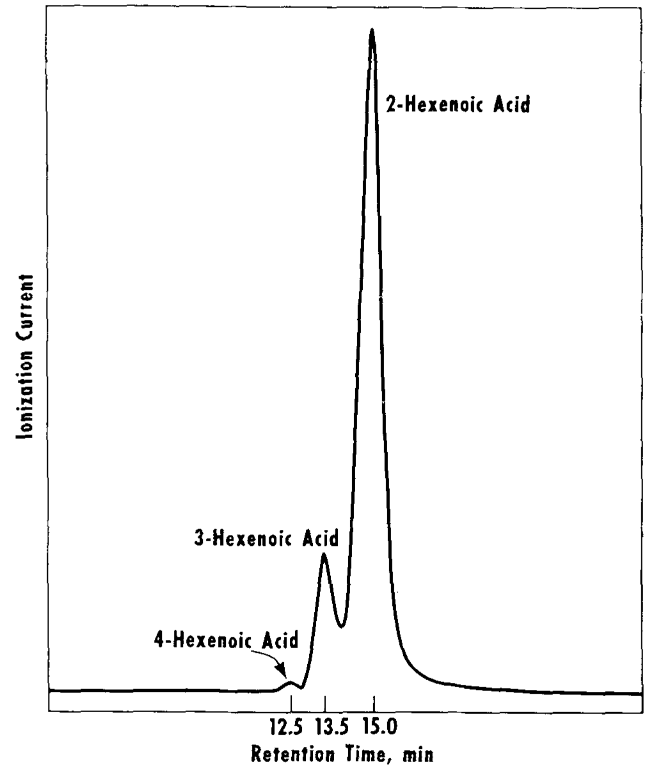

FIG. 4. Chromatograms of reduced sorbic acid on a glass column 4 ft x ¼ in., temp 120C, 10% DEGS plus 1% H_3PO_4, and an argon flow rate of 66 ml/min.

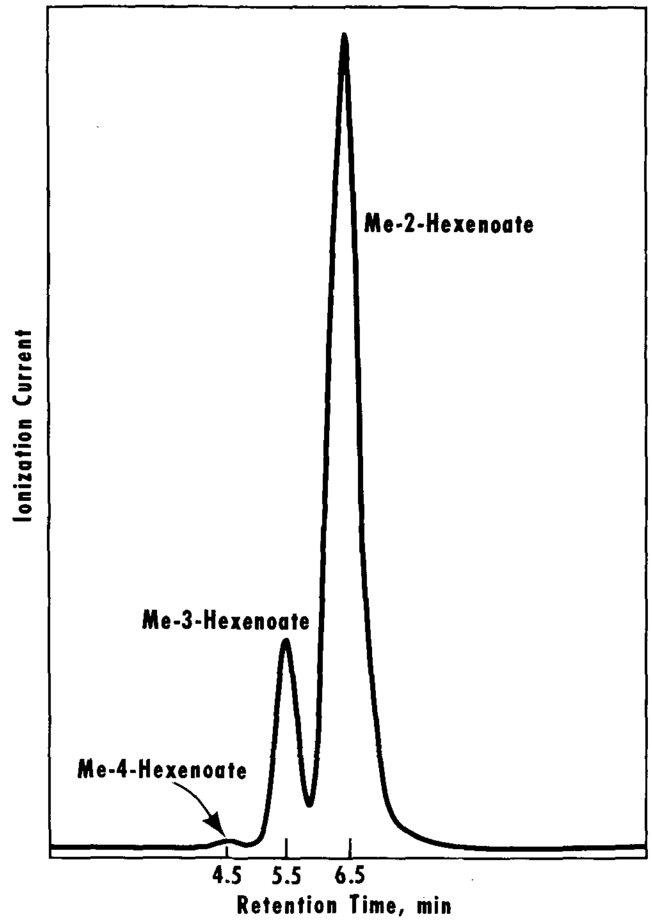

FIG. 5. Chromatograms of methyl esters of reduced sorbic acid on a glass column 4 ft x ¼ in., temp 90C, 10% Craig succinic polyester, and an argon flow rate of 40 ml/min.

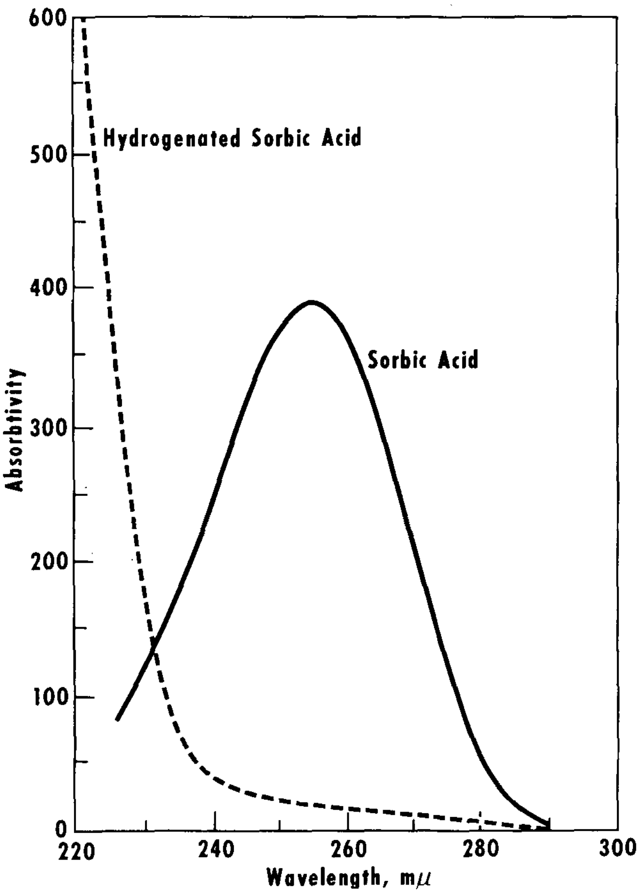

FIG. 6. UV spectra of sorbic acid and reduced sorbic acid in spectro-grade n-hexane.

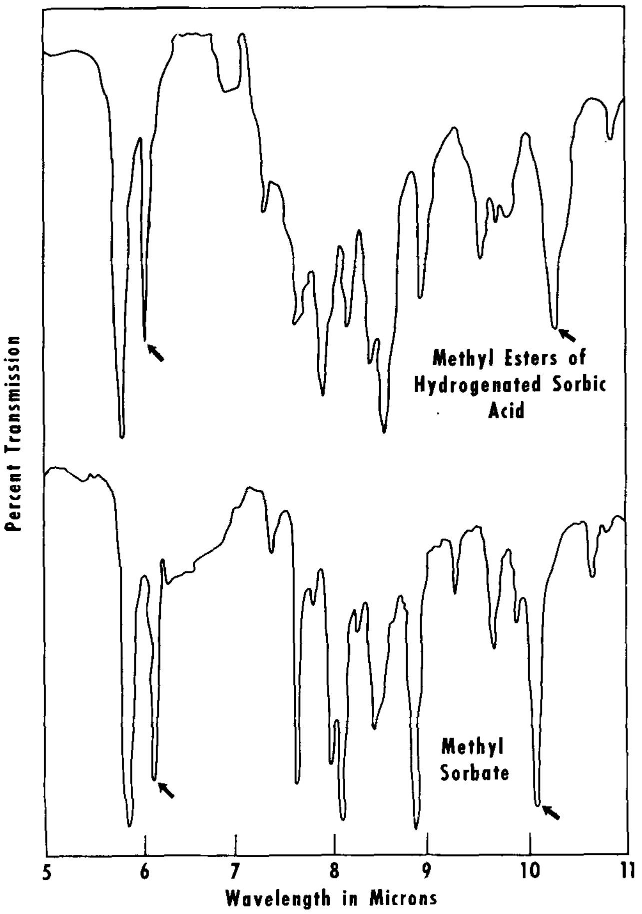

FIG. 7. IR spectra of methyl esters of sorbic acid and reduced sorbic acids.

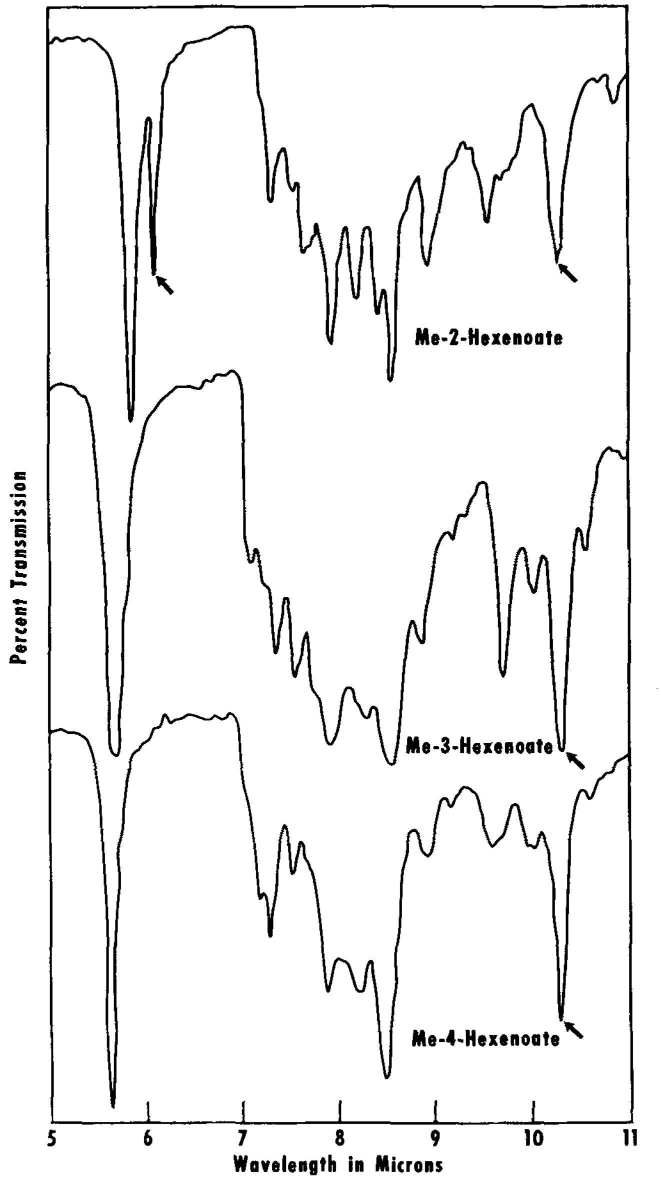

FIG. 8. IR spectra of methyl esters of 2-,3-, and 4-hexenoic acids.

can be made. Comparing the chromatograms of the methyl esters of reduced sorbic acid with the retention times of methyl esters of isomeric hexenoic acids gave satisfactory results.

During preparation of the methyl esters of reduced sorbic acid with diazomethane, 85% of the methyl-4-hexenoate was lost. Müller (32) attributed poor quantitative results in preparing methyl esters of unsaturated acids with diazomethane (33) to the formation of pyrazolines or other side reactions. Using methanol-boron trifluoride (31) for preparing the methyl esters of reduced sorbic acid proved unsuccessful. About 98% of 4-hexenoic acid present in reduced sorbic acid appeared on the chromatogram of the methyl esters (Fig. 5) prepared by methanol-HCl. No difference was observed in the components of reduced sorbic acid when homogeneous hydrogenation was carried out at 10,20,25,29, and 34C.

Homogeneous Catalytic Hydrogenation of Sorbic Acid in Methanol. Using methanol as the solvent, instead of water, increases the rate of hydrogen uptake probably because of increase in hydrogen solubility. GLC of reduced sorbic acid indicates respective yields of 96.2 and 3.8% of 2- and 3-hexenoic acids. Caproic and 4-hexenoic acids were not present.

UV Spectrophotometric Analysis. UV spectra of sorbic acid and reduced sorbic acid in spectro-grade *n*-hexane are given in Figure 6. Sorbic acid shows maximum absorption at 255 mμ, while reduced sorbic acid did not show any absorption in the range characteristic of linearly conjugated diene acid. Reduced sorbic and 2-, 3-, and 4-hexenoic acids possess strong absorption in the region 210 mμ, although no distinct maximum was observed. These results agree with the findings of Braude (5) and Van der Hulst (38). On comparing absorption spectra of sorbic and reduced sorbic acids, the saturation of one double bond clearly caused the disappearance of a band at 255 mμ. As 3- and 4-hexenoic acids possess strong absorption in the region 210 mμ without any distinct maximum, it is hard to establish their absence in reduced sorbic acid by UV measurements alone.

IR Spectrophotometric Analysis. Figures 7 and 8 show IR spectra of methyl esters of sorbic and reduced sorbic acids, as well as 2-, 3-, and 4-hexenoic acids. A comparison of the IR spectra of methyl sorbate and of reduced sorbate shows the disappearance of a band at 10.1 μ, which arises from *trans,trans* configuration, and the appearance of a band at 10.30 μ due to isolated *trans* (3). The strong absorption band at 5.82 μ indicates the presence of C=C—C=O in sorbate, reduced sorbate, and 2-hexenoate.

Figure 9 illustrates that in the region between 5.50 and 11.00 μ, a series of relatively strong, equally spaced bands exists. The strength and the frequencies of the individual bands in 2-hexenoate and reduced sorbate are not identical, indicating that reduced sorbic acid contains other compounds besides 2-hexenoate.

Discussion

The sequence of the chemical reactions that follow mixing of cobaltous chloride and potassium cyanide solutions as assembled from the literature are:

1. Formation of pentacyanocobaltate II ions(1):

$$Co^{++} + 5CN^- \longrightarrow [Co^{II}(CN)_5]^{3-}$$

2. Hydrogenation of pentacyanocobaltate II ions(22):

$$[Co^{II}(CN)_5]^{3-} + H_2 \overset{\text{Slow}}{\rightleftharpoons} [Co(CN)_5H_2]^{3-}$$

$$[Co(CN)_5H_2]^{3-} + [Co^{II}(CN)_5]^{3-} \overset{\text{Fast}}{\rightleftharpoons} [Co^{III}(CN)_5H]^{3-}$$

H-evolving cobaltic complex; one ligand is a hydride ion

3. Hydrogenation of sorbic acid(7, 23):

$$2[Co^{III}(CN)_5H]^{3-} + CH_3{-}CH{=}CH{-}CH{=}CH{-}COOH \xrightarrow{\text{Nonreversible}} 2[Co^{II}(CN)_5]^{3-} + \text{Hexenoic acids}$$

4. Decay reactions or aging(22):

$$[Co^{II}(CN)_5]^{3-} + H{-}OH + [Co^{II}(CN)_5]^{3-} \longrightarrow [Co^{III}(CN)_5H]^{3-} + [Co^{III}(CN)_5OH]^{3-}$$

$$[Co^{III}(CN)_5OH]^{3-} + CN^- \longrightarrow [Co^{III}(CN)_6]^{3-} + OH^-$$

Stable Hexacyanocobaltate

The high selectivity of pentacyanocobaltate II in hydrogenating sorbic acid in aqueous solutions to 2-, 3-, and 4-hexenoic acids is indicated by GLC and by UV and IR spectra of reduced sorbic acid and its methyl esters. Homogeneous catalytic hydrogenation in methanolic solutions shows higher selectivity as 2-hexenoic acid was present in 96% yield. Although the present work does not confirm the absolute specificity of attack at the 4,5-double bond of sorbic

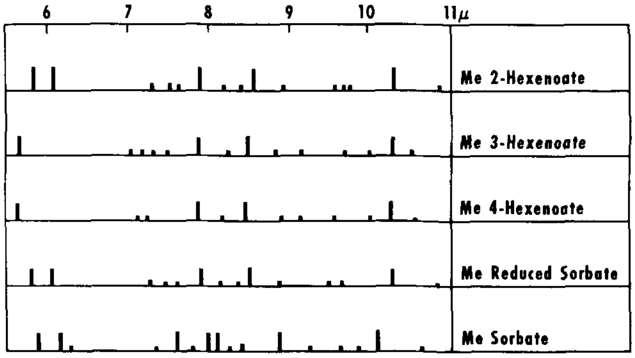

FIG. 9. Schematic presentation of absorption bands of methyl esters of 2-,3-, 4-hexenoic, reduced sorbic, and sorbic acids.

acid, the high degree of selectivity does encourage further study of homogeneous catalysis on higher fatty acids.

ACKNOWLEDGMENT

UV and IR spectrophotmetric work done by Helen M. Peters.

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Report of the Instrumental Techniques Committee, AOCS, 1962-1963

THE INSTRUMENTAL TECHNIQUES COMMITTEE held its inaugural meeting during the first International Convention of the Society in Toronto, Canada. The Committee Meeting was held in the Tudor Room of the Royal York Hotel as part of the 36th Fall Meeting, on October 1, 1962. Thirteen members and guests, including the Chairman and Chairmen of all Subcommittees, attended this first meeting.

The general organization of the New Instrumental Techniques Committee was reviewed by the Chairman. The Committee at present consists of three Subcommittees: 1) Gas Chromatography, a joint Subcommittee with the Association of Official Agricultural Chemists, consisting of twenty members with E. M. Sallee, Chairman; 2) Spectroscopy Subcommittee, with thirteen members and R. R. Allen, Chairman; and 3) Color Subcommittee with nineteen members and W. T. Coleman, Chairman. In addition, the Instrumental Techniques Committee has an active Special Task Group for the Preparation of Methyl Esters under J. R. Chipault, Chairman, consisting of nine members.

At this initial organizational meeting it was agreed that at each Fall Meeting of the Society a general meeting of the Instrumental Techniques Committee would be held. This meeting, to which all members of the Committee would be urged to attend and all members of the Society are invited, is to consist of more or less executive reports of the Subcommittee Chairmen as to progress made since the last Annual Meeting of the Society and their plans for the immediate future.

At each Annual meeting of the Society, each Subcommittee will conduct an individual meeting under the direction of its respective Subcommittee Chairman. At these sessions, details of the progress of the Subcommittee during the past year will be reviewed and plans and suggestions for future activities will be considered. These meetings will be followed by a meeting of the Instrumental Techniques Committee as a whole to be held later during the Annual Spring Meeting.

In accordance with the decisions at the inaugural meeting of the Instrumental Techniques Committee, each of the Subcommittees met during the 54th Annual Meeting of the Society at the Biltmore Hotel in Atlanta, April 22–24, 1963, and these individual Subcommittee meetings were followed by a meeting of the entire Committee.

Color Subcommittee

The Color Subcommittee, with Chairman W. T. Coleman presiding, met April 21, at 2:00 p.m. Only four members were in attendance. The Subcommittee has only one pending project, possible specifications and methods for surface color. Considerable subcommittee effort has been expended on a study of this problem. It was decided that the next step in this project is the poll of the industry for an indication of the needs and interest so that any ex-