ACKNOWLEDGMENT

The Indian Central Oilseeds Committee sponsored the research work reported here.

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Deuterium Tracer Studies of the Mechanism of Homogeneous Catalytic Hydrogenation of Sorbic Acid with Pentacyanocobaltate II[1]

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Abstract

Exchange of deuterium and hydrogen during homogeneous catalytic reduction of sorbic acid with pentacyanocobaltate II has been investigated three ways: isotopic exchange between D_2 and H_2O, H_2-D_2O exchange, and D_2-anhydrous methanol exchange. In contrast to experiments with heterogeneous catalysts, where complete exchange and equilibration occur readily, mass spectrometric analysis of the gas phase above the pentacyanocobaltate II shows slow, incomplete exchange during the course of reduction of either catalyst alone or catalyst and substrate.

Mass spectra of methyl hexenoates from the deuterium exchange experiments have been examined. The fragmentation patterns of the esters reduced in the presence of D_2O were compared with those reduced in H_2O and with authentic 2-, 3-, and 4-hexenoates. Little or no exchange occurred with the hydrogen of valeric acid in the presence of pentacyanocobaltate deuteride ion $[DCo(CN_5)]^{3-}$ and deuterium oxide. Experimental results indicate that either the hydrogen or deuterium that adds to the double bond originates predominantly from the solvent. It appears that the hydrogen atoms on the δ-carbon atoms in both 2- and 3-hexenoates exchange with deuterium during reduction in heavy water solutions.

Introduction

RECENT WORK IN THIS LABORATORY has confirmed that sorbate is selectively hydrogenated by pentacyanocobaltate II and has demonstrated that in aqueous and methanolic solutions 2-hexenoate is produced in 82 and 96% yield, respectively (14). In this reduction it was not known whether the hydrogen in reduced sorbate came from the hydrogen in the gas phase or in the water phase; such a question could be answered by labelling the hydrogen in question. By using a solvent labeled isotopically, its role in the reaction could be investigated.

Since the original experiments described by Iguchi (10), several others have published on this subject. Many of the earlier reports were concerned with the structure of the catalyst (1,2,7,9). Nuclear magnetic resonance studies have shown the presence of a hydrido complex ion $[HCo^{III}(CN)_5]^{3-}$ in reduced aqueous pentacyanocobaltate solutions (7). Visible and ultraviolet studies indicate that $[Co(CN)_5]^{3-}$ reacts reversibly with H_2 to form the hydrido complex ion (11). Furthermore, the aging process involves the homolytic scission of water to yield hydrido and hydroxo complex ions (4,11).

In 1953, Ogg (16) reported that when an acidified pentacyanocobaltate II solution liberated hydrogen in the presence of D_2, hydrogen deuteride was formed. Formation of HD was considered due to the presence of "nascent" hydrogen and cobalt species thought not to be active catalytically. When $[Co(CN)_5]^{3-}$ was prepared in D_2O from anhydrous salts, no proton resonance appeared in the high field region even after H_2 had been passed through the solution for 1 hr. Since resonance is found when solutions in H_2O are prepared under nitrogen, these observations can only be interpreted to mean that the $[HCo(CN)_5]^{3-}$ ion must be formed by interaction of pentacyanocobaltate II ions with water (7). Mills, Weller, and

TABLE I

Effect of Pentacyanocobaltate II[a] Concentration and Anions in Aqueous Solutions on Deuterium Absorption

Co, concn mM/liter	Anion	Observed D_2 absorbed mM	D_2 absorbed %
74.8	Acetate	25.31	67.67
81.7	Acetate	26.31	64.47
86.8	Acetate	29.12	67.07
149.2	Acetate	48.26	64.68
84.8	Chloride	32.22	75.97
86.4	Chloride	32.27	74.70
152.8	Chloride	56.58	74.05

[a] Ratio of CN ions to Co ions was 6:1; 25C.

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[1] Presented at the AOCS meeting, Minneapolis, 1963.

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Wheeler (15) reported that reduced solutions and aged nonreduced solutions of pentacyanocobaltate II catalyze D_2-H_2O exchange. Recently, Kwiatek et al. (12) reported that when pentacyanocobaltate II was prepared in an atmosphere containing equimolar quantities of deuterium and butadiene gases, di-, mono-, and nondeuterated *trans*-2-butene, *cis*-2-butene, and 1-butene were identified by mass spectrographic analysis and unreduced butadiene was shown to contain small quantities of mono- and dideutero-butadienes.

In turn, we investigated the solvent in the reaction in order to elucidate the mechanism of reduction of sorbate. Our experiments on pentacyanocobaltate II solutions included: stoichometric study of pentacyanocobaltate reduction; measurement of deuterium- and hydrogen-solvent exchange in presence of pentacyanocobaltate II; and D_2-H_2O, H_2-D_2O, and D_2-MeOH exchange during homogeneous catalytic reduction of sorbate with pentacyanocobaltate II.

Experimental Procedures

Details of the experimental procedures have been given previously (14), and only exceptions or additions will be noted. Anhydrous chemicals were used in preparing the catalyst in D_2O and methanolic solutions. Clear solutions were used throughout, and each determination was made at least in triplicate.

Materials. Deuterium gas and D_2O of 99.7+% isotopic purity were obtained from General Dynamics Corp.

Hydrogen deuteride used for mass spectrometer calibration was prepared by reducing D_2O with $LiALH_4$.

Deuterated hexenoates were prepared for mass spectrometer calibration by reducing sorbate in deuterium with pentacyanocobaltate II dissolved in heavy water.

Isotopic Exchange. Isotopic exchange experiments were carried out with the same hydrogenation apparatus described for the nonisotopic experiments (14). Zero time was taken at the moment stirring began. Gas samples were collected at intervals during the run. Before filling the evacuated gas bottles, the gas was passed through a drying tube containing Drierite. Gas samples were analyzed for H_2, HD, and D_2 with a Bendix model 12 time-of-flight mass spectrometer, under standard operating conditions and with an ionization potential of 70v.

Mass Spectrometric Analysis of Methyl Hexenoates Formed During Reduction of Sorbate. Since small samples (2 µl) are required to obtain a satisfactory mass spectrum, it was decided to separate reduced sorbate samples to their components by gas-liqiud chromatography (GLC) with a single injection rather than in a preparative column. A column (8 ft, ¼ in.) packed with 25% diethylene glycol succinate on Chromosorb W 60–80 mesh was used. Up to 30 µl of reduced sorbate was injected into an F and M chromatograph. The separate fractions were trapped in a Hamilton fraction collector and "U" tubes partially filled with acid and alkali-washed sand. The tubes containing the separated esters were attached to the mass spectrometer liquid inlet with a double-ended needle device, one end for insertion through the tube septum and the other, for the mass spectrometer inlet septum. Helium was pumped out of the "U" tube inlet vacuum system while it was immersed in liquid N_2. The vacuum system was "valved off" and the "U" tube was connected to the inlet reservoir before heating with boiling water. About 50% recovery of the injected sample was obtained. The sample was then analyzed in the mass spectrometer like any ordinary sample.

TABLE II

Effect of Temperature on Deuterium Absorption by Pentacyanocobaltate II[a] Prepared in Deuterium Oxide

Temp C	Observed D_2 absorbed mM	D_2 absorbed %
25	53.40	72.28
18	59.20	80.00
10	68.20	92.00

[a] Ratio of CN ions to Co ions was 6:1; 157 .32 mM pentacyanocobaltate II/l. absorbs theoretically 78.66 mM D_2, chloride anions are present in solution.

Results and Discussion

Stoichiometric Study of Hydrogen Uptake by Pentacyanocobaltate II in H_2O and D_2O. When $[Co^{II}(CN)_5]^{3-}$ was prepared in D_2O, it was observed that H_2 absorbed corresponded to 60% of that calculated to reduce the cobalt present from the divalent to the monovalent state. When experiments were conducted in H_2O, the amt of reduced cobalt corresponded to 81% of the theoretical value. This increase might be caused by the difference of hydrogen gas solubility in H_2O and D_2O (14,15). Lack of complete correspondence between H_2 uptake and $Co^{II} \longrightarrow Co^{I}$ stoichiometry seems due to the aging process, whereby loss of reducibility is experienced (4,7,11).

Effect of Solvent on D_2 Absorbed by Pentacyanocobaltate II. The data for D_2 absorption by freshly prepared $[Co(CN)_5]^{3-}$ in H_2O, D_2O, and MeOH are given in Tables I, II, and III. D_2 uptake measurements show that the amt of reduced $[Co(CN)_5]^{3-}$ is much greater in methanol than in H_2O and D_2O. This increase might be attributed to the greater solubility of D_2 in methanol. Using methanol containing 0.06% H_2O decreases the amount of D_2 absorbed by 5%. This reaction suggests that the traces of water in the solvent are removed by the aging process resulting in the formation of hydrido and hydroxo complex ions. In turn, the hydroxo complex ions react with excess CN^- present in solution to form the stable hexacyanocobaltate ions.

Effect of Temperature, Cobalt Concentration, and Anions in Aqueous Solutions on Deuterium Absorption. In the presence of chloride ions, the amt of reduced $[Co(CN)_5]^{3-}$ with D_2 is 12% higher than in the presence of acetate ions (Table I).

Changing the initial cobalt concentration by a factor of two had no effect on the reducibility of the catalyst with deuterium (Table I). Similar results were found by De Vries (5) on hydrogen uptake by aqueous solutions of pentacyanocobaltate II (Tables II and III).

Isotopic Exchange. Mass spectrometric analysis of the gas phase shows that pentacyanocobaltate II and pentacyanocobaltate-sorbate catalyze D_2-H_2O and H_2-D_2O exchange. In contrast to heterogeneous catalysts,

TABLE III

Deuterium Absorption by Pentacyanocobaltate II[a] in Methanolic Solutions

Co, concn mM/liter	Temp C	H_2O in MeOH %	Observed D_2 absorbed mM	D_2 absorbed %
0.0594	5	Anhydrous	0.0288	97.00
0.372	0	0.04	0.184	99.00
0.372	20	0.04	0.176	94.55
0.446	5	0.06	0.206	92.10

[a] Ratio of CN ions to Co ions was 6:1; chloride anions are present in solutions.

TABLE IV

Isotopic Exchange,[a] 25C

Co, concn mM/liter	Anion	Sorbate mM/liter	Sample taken after sec	Volume, %		
				H_2	HD	D_2
Deuterium-H_2O						
86.4	Chloride	....	3600	53.07	0.6	46.87
84.75	Chloride	12.34	8400	64.18	0.8	35.74
86.8	Acetate	....	3600	40.74	0.54	58.72
85.3	Acetate	12.34	8400	60.28	0.62	39.10
Hydrogen-D_2O						
86.40	Chloride	....	3600	60.31	0.92	38.77
85.30	Chloride	12.34	8400	59.87	1.10	39.03

[a] Molar ratio of gas phase to liquid phase was 0.5:100.

where complete exchange and equilibration occur readily (3), the composition of the gas phase shows slow, incomplete exchange during the course of reduction. Unpublished data from this laboratory (13) show that at 25C no isotopic exchange takes place until 50% of reduced $[Co(CN)_5]^{3-}$ is formed. In the presence of either pentacyanocobaltate II, or pentacyanocobaltate-sorbate, the isotopic exchange was slow and incomplete (Table IV).

Of particular interest is the influence of added anions on the isotopic distribution in the gas phase during D_2-H_2O exchange. Acetate ions increase the hydrogen content in the gas phase but do not change the H_2/HD ratio (Table IV). Because this effect is not fully understood, further work is being done to clarify this point.

The slight exchange obtained with anhydrous methanol in the presence of 0.3 mM Co/liter might be due to the fact that the concn of the catalyst is so small the exchange between D_2 and MeOH is undetected by mass spectrometric analysis (Table V).

On using ACS grade methanol containing 0.04 to 0.06% H_2O, the solubility of pentacyanocobaltate II can be increased to 4.5 mM/liter and a slight D_2-MeOH exchange occurs. D_2-MeOH exchange experiments show a much lower H_2/HD ratio than in either D_2-H_2O exchange or H_2-D_2O exchange.

Mass Spectrometric Analysis of Reduced Sorbate. The mass spectrometric analyses for deutrium content of 2- and 3-hexenoate fractions in reduced sorbate are given in Table VI. During the catalytic reduction of sorbate in either aqueous or methanolic solution, no exchange of deuterium in solvent for carbon-bonded hydrogen was evident except for hydrogens on the δ-carbon atoms (18). From the fragmentation patterns of deuterated 2- and 3-hexenoates, it was concluded that hydrogen atoms on δ-carbon atoms exchanged with deuterium. These findings were confirmed with nuclear magnetic resonance studies (18). Also, no exchange occurred with the hydrogen of valerate in the presence of $[DCo(CN)_5]^{3-}$ and deuterium oxide. These findings are in contrast with those reported by Rohwedder et al. (17) with heterogeneous catalysts where extensive exchange of deuterium for carbon-bonded hydrogen took place during reduction of methyl oleate with gaseous deuterium.

TABLE V

Deuterium-Methanol Exchange[a]

Co, concn mM/liter	Temp, C	H_2O % in methanol	Sorbate mM/liter	Sample taken after, sec	Volume, %		
					H_2	HD	D_2
0.32	5	Anhydrous	....	1200	00.00	00.00	100.00
0.32	5	Anhydrous	0.55	4200	00.00	00.00	100.00
4.78	5	0.06	....	2076	00.00	00.00	100.00
4.76	5	0.06	4.01	6489	0.30	0.40	99.30
4.46	0	0.04	....	2600	00.00	00.00	100.00
4.43	0	0.04	3.72	6600	0.30	0.40	99.30

[a] Ratio of CN ions to Co ions was 6:1.

TABLE VI

Mass Spectrometric Analysis of 2- and 3-Hexenoate Fractions in Reduced Sorbate

System	Temp C	2-Hexenoate, %			3-Hexenoate, %		
		d_0[a]	d_2	d_3	d_0	d_2	d_3
D_2-D_2O	29	0	16	84	0	26	74
D_2-D_2O	10	0	13	87	....	....	....
D_2-H_2O	25	100	0	0	100	0	0
H_2-D_2O	25	0	27	73	0	36	64

[a] d_0, d_2, d_3 = Number of deuterium atoms/mole ester.

Pentacyanocobaltate II is the most active homogeneous catalyst so far reported for the activation of molecular hydrogen. The studied exchange reactions offer remarkable evidence for the catalytic properties of pentacyanocobaltate II solutions. Our experimental results indicate that we have, as part of the D_2-H_2O exchange process, a hydrogen evolution reaction which is due to the reversal of hydrogen uptake and which therefore yields, as product, an active cobalt complex that can again take up D_2 from the gas phase. The chemical equations representing the reactions taking place in D_2-H_2O system are:

$$2[Co(CN)_5]^{3-} + D_2(g) \rightleftharpoons 2[DCo(CN)_5]^{3-} \qquad [1]$$

$$2[DCo(CN)_5]^{3-} + H_2O(l) \longrightarrow 2[HCo(CN_5]^{3-} + D_2O(l) \qquad [2]$$

$$2[HCo(CN)_5]^{3-} \rightleftharpoons 2[Co(CN)_5]^{3-} + H_2(g) \qquad [3]$$

$$2[HCo(CN)_5]^{3-} + \text{sorbate} \longrightarrow 2[Co(CN)_5]^{3-} + \text{hexenoic acid isomers} \qquad [4]$$

In this hypothesis, we assume that the reduced catalyst (eq. 1) exchanges with the solvent (eq. 2) and that the exchanged catalyst can evolve H_2 (eq. 3) or reduce sorbate (eq. 4), if it is present in solution.

Experimental results show the same explanation is true for H_2-D_2O exchange. Of particular significance is the absence of deuterium atoms in reduced sorbate prepared in the D_2-H_2O system and the presence of deuterium atoms in reduced sorbate prepared in H_2-D_2O (Table VI) indicating that (eq. 2) takes place after reduction of the catalyst and that the resulting catalyst after exchange reduces sorbate.

Of greater significance is the absence of exchange between D_2 and carbon-bonded hydrogen under experimental conditions that favor exchange between D_2 and water or D_2 and MeOH. These results are different from those reported by Horrex et al. (8) and Greenhalgh et al. (6) who found that benzene, cyclohexane, and isopentane exchanges with D_2O in the presence of heterogeneous catalysts.

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[Received September 8, 1964—Accepted February 16, 1965]