

## ACKNOWLEDGMENT

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

## REFERENCES

- Meyer, H., Arch. Pharm. 237, 184 (1897).
- Morrel, R. S., and E. O. Phillips, J. Soc. Chem. Ind. 57, 245 T (1938).
- Francois, M. T., Compt. rend. 194, 731 (1932).
- Jakes, M., and J. Hokel, Chem. Listy. 32, 15 (1938).
- Jakes, M., and J. Hokel, Fette und Seifen 45, 306 (1938).
- Berry H., and A. M. Cook, J. Pharm. Pharmacol 2, 217 (1950).
- Jones, R. O., J. Soc. Chem. Ind. 36, 359 T (1917).
- Langton, H. M., *Ibid.* 50, 213 T (1931).
- Rassow, B., and J. Rubinsky, Z. angew. Chemie 26, 316 (1913).
- Stefanescu, D., and N. Stanesco, Rev. Univ. 'C. I. Parhon' Politech. Bucharesti Ser. Stunt nat 4, No. 8, 73 (1955).
- Bolley, D. S., Private communication.
- Rowe, R., Paint Technol. 19, 79 (1955).
- Scheiber, J., Ger. 832,751 (1952).
- Brod, J. S., U.S. 2,212,385.
- Scheiber, J., U.S. 1,942,778.
- Hawke, F., and E. A. Kohil, J. South Afr. Chem. Inst. 12, 1, 17 (1959).
- Sreenivasan, B., N. R. Kamath, and J. G. Kane, JAOCS 33, 61 (1956).
- Mikush Von, J. D., and C. Frazier, Ind. Eng. Chem., Anal. Edn. 13, 788 (1941).
- Burton, D., and G. F. Robertshaw, "Sulfated Oils and Allied Products," A. Harvey, London, 1939, 129.
- Smith, L., Ann. Chim. Phys. (3), 6, 40 (1842). Cited in "Fatty Acids" by K. S. Markley, Vol. II, 1961, 1026.
- Heintz, W., Ann Physik. 93, 481 (1854). Cited by Markley. See reference 20 above.
- Grummit, O., and Flemming, Ind. Eng. Chem. 37, 485 (1945).
- Smith, A. I., Ph.D. Thesis, Western Reserve University, June 1943.
- Priester, R., Fette, Seifen, Anstrichmittel 63, 361 (1961).
- Bolley, D. S., JAOCS 30, 396 (1953).

# Deuterium Tracer Studies of the Mechanism of Homogeneous Catalytic Hydrogenation of Sorbic Acid with Pentacyanocobaltate II<sup>1</sup>

A. F. MABROUK, E. SELKE, W. K. ROHWEDDER and H. J. DUTTON,  
Northern Regional Research Laboratory,<sup>2</sup> Peoria, Illinois

## 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<sub>2</sub> and H<sub>2</sub>O, H<sub>2</sub>-D<sub>2</sub>O exchange, and D<sub>2</sub>-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<sub>2</sub>O were compared with those reduced in H<sub>2</sub>O 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)<sub>5</sub>]<sup>3-</sup> 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<sup>III</sup>(CN)<sub>5</sub>]<sup>3-</sup> in reduced aqueous pentacyanocobaltate solutions (7). Visible and ultraviolet studies indicate that [Co(CN)<sub>5</sub>]<sup>3-</sup> reacts reversibly with H<sub>2</sub> 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<sub>2</sub>, 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)<sub>5</sub>]<sup>3-</sup> was prepared in D<sub>2</sub>O from anhydrous salts, no proton resonance appeared in the high field region even after H<sub>2</sub> had been passed through the solution for 1 hr. Since resonance is found when solutions in H<sub>2</sub>O are prepared under nitrogen, these observations can only be interpreted to mean that the [HCo(CN)<sub>5</sub>]<sup>3-</sup> ion must be formed by interaction of pentacyanocobaltate II ions with water (7). Mills, Weller, and

TABLE I  
Effect of Pentacyanocobaltate II<sup>a</sup> Concentration and Anions in Aqueous Solutions on Deuterium Absorption

Co, concn mM/liter	Anion	Observed D <sub>2</sub> absorbed mM	D <sub>2</sub> 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

<sup>1</sup> Presented at the AOCs meeting, Minneapolis, 1963.

<sup>2</sup> A laboratory of the No. Utiliz. Res. and Dev. Div., ARS, USDA.

<sup>a</sup> Ratio of CN ions to Co ions was 6:1; 25C.

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: stoichiometric 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  $\mu$ l) are required to obtain a satisfactory mass spectrum, it was decided to separate reduced sorbate samples to their components by gas-liquid chromatography (GLC) with a single injection rather than in a preparative column. A column (8 ft,  $\frac{1}{4}$  in.) packed with 25% diethylene glycol succinate on Chromosorb W 60-80 mesh was used. Up to 30  $\mu$ l 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 reser-

TABLE II  
Effect of Temperature on Deuterium Absorption by Pentacyanocobaltate II<sup>a</sup> 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

<sup>a</sup> 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.

voir 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.

### 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  $Co^{II} \rightarrow Co^I$  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<sup>a</sup> 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

<sup>a</sup> Ratio of CN ions to Co ions was 6:1; chloride anions are present in solutions.

TABLE IV  
 Isotopic Exchange,<sup>a</sup> 25C

Co, concn mM/liter	Anion	Sorbate mM/liter	Sample taken after sec	Volume, %		
				H <sub>2</sub>	HD	D <sub>2</sub>
<b>Deuterium-H<sub>2</sub>O</b>						
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
<b>Hydrogen-D<sub>2</sub>O</b>						
86.40	Chloride	.....	3600	60.31	0.92	38.77
85.30	Chloride	12.34	8400	59.87	1.10	39.03

<sup>a</sup> 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)<sub>5</sub>]<sup>3-</sup> 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<sub>2</sub>-H<sub>2</sub>O exchange. Acetate ions increase the hydrogen content in the gas phase but do not change the H<sub>2</sub>/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<sub>2</sub> and MeOH is undetected by mass spectrometric analysis (Table V).

On using ACS grade methanol containing 0.04 to 0.06% H<sub>2</sub>O, the solubility of pentacyanocobaltate II can be increased to 4.5 mM/liter and a slight D<sub>2</sub>-MeOH exchange occurs. D<sub>2</sub>-MeOH exchange experiments show a much lower H<sub>2</sub>/HD ratio than in either D<sub>2</sub>-H<sub>2</sub>O exchange or H<sub>2</sub>-D<sub>2</sub>O exchange.

#### Mass Spectrometric Analysis of Reduced Sorbate.

The mass spectrometric analyses for deuterium 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)<sub>5</sub>]<sup>3-</sup> 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<sup>a</sup>

Co, concn mM/liter	Temp, C	H <sub>2</sub> O % in methanol	Sorbate mM/liter	Sample taken after, sec	Volume, %		
					H <sub>2</sub>	HD	D <sub>2</sub>
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

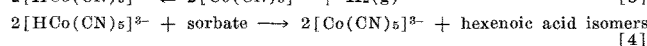
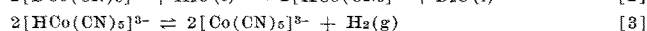
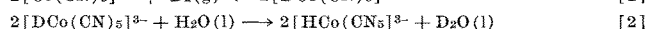
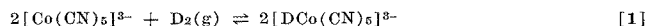
<sup>a</sup> Ratio of CN ions to Co ions was 6:1.

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

System	Temp C	2-Hexenoate, %			3-Hexenoate, %		
		d <sub>0</sub> <sup>a</sup>	d <sub>2</sub>	d <sub>3</sub>	d <sub>0</sub>	d <sub>2</sub>	d <sub>3</sub>
D <sub>2</sub> -D <sub>2</sub> O	29	0	16	84	0	26	74
D <sub>2</sub> -D <sub>2</sub> O	10	0	13	87	.....	.....	.....
D <sub>2</sub> -H <sub>2</sub> O	25	100	0	0	100	0	0
H <sub>2</sub> -D <sub>2</sub> O	25	0	27	73	0	36	64

<sup>a</sup> d<sub>0</sub>, d<sub>2</sub>, d<sub>3</sub> = 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<sub>2</sub>-H<sub>2</sub>O 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<sub>2</sub> from the gas phase. The chemical equations representing the reactions taking place in D<sub>2</sub>-H<sub>2</sub>O system are:



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<sub>2</sub> (eq. 3) or reduce sorbate (eq. 4), if it is present in solution.

Experimental results show the same explanation is true for H<sub>2</sub>-D<sub>2</sub>O exchange. Of particular significance is the absence of deuterium atoms in reduced sorbate prepared in the D<sub>2</sub>-H<sub>2</sub>O system and the presence of deuterium atoms in reduced sorbate prepared in H<sub>2</sub>-D<sub>2</sub>O (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<sub>2</sub> and carbon-bonded hydrogen under experimental conditions that favor exchange between D<sub>2</sub> and water or D<sub>2</sub> 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<sub>2</sub>O in the presence of heterogeneous catalysts.

#### REFERENCES

1. Adamson, A. W., *J. Am. Chem. Soc.* **73**, 5710-5713 (1951).
2. Bayston, J., N. K. King, and M. E. Winfield, *Advan. Catalysis* **9**, 312-318 (1957).
3. Bitner, E. D., E. Selke and H. J. Dutton, *JAOCS* **41**, 1-3 (1964).
4. De Vries, B., Koninkl. Ned. Akad. Wetenschap. Proc., Ser. B, **63**, No. 4, 443-448 (1960).
5. De Vries, B., *J. Catalysis* **1**, 489-497 (1962).
6. Greenhalgh, R. K., and M. Polanyi, *Trans. Faraday Soc.* **35**, 520-542 (1939).
7. Griffith, W. P., and G. Wilkinson, *J. Chem. Soc.* 2757-2762 (1959).
8. Horrex, C., R. K. Greenhalgh and M. Polanyi, *Trans. Faraday Soc.* **35**, 511-520 (1939).
9. Hume, D. N., and I. M. Kolthoff, *J. Am. Chem. Soc.* **71**, 867-869 (1949).
10. Iguchi, M., *J. Chem. Soc. (Japan)* **63**, 634-643 (1942); *Chem. Abstr.* **41**, 2975 (1947).
11. King, N. K., and M. E. Winfield, *J. Am. Chem. Soc.* **83**, 3366-3373 (1961).
12. Kwaitek, J., I. L. Mador and J. K. Seyler, *Advan. Chem. Ser.* **37**, 201-215 (1963).
13. Mabrouk, A. F., unpublished data.
14. Mabrouk, A. F., H. J. Dutton and J. C. Cowan, *JAOCS* **41**, 153-158 (1964).
15. Mills, G. A., S. Weller and A. Wheeler, *J. Phys. Chem.* **63**, 403-410 (1959).
16. Ogg, R. A., Abstract of Papers **24P**, Division of Physical and Inorganic Chemistry, 123rd ACS Meeting, Los Angeles, California, March 1953.
17. Rohwedder, W. K., E. D. Bitner, Helen M. Peters and H. J. Dutton, *JAOCS* **41**, 33-36 (1964).
18. Rohwedder, W. K. A., A. F. Mabrouk and E. Selke. *J. Phys. Chem.* in press.

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