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

A. F. MABROUK, E. SELKE, W. K. ROHWEDDER and H. J. DUTTON, Northern Regional Research Laboratory, 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 D₂ and H₂O, H₂-D₂O exchange, and D₂-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 D₂O were compared with those reduced in H₂O 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 [DCo(CN₅)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 8-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(CN)₅]₃⁻ in reduced aqueous pentacyanocobaltate solutions (7). Visible and ultraviolet studies indicate that [Co(CN)₅]₃⁻ reacts reversibly with H₂ to form the hydrido complex ion (11). Furthermore, the aging process involves the homolytic scission of water to yield hydrido and hydrazo complex ions (4,11).

In 1953, Ogg (16) reported that when an acidified pentacyanocobaltate II solution liberated hydrogen in the presence of D₂, 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 D₂O from anhydrous salts, no proton resonance appeared in the high field region even after HD had been passed through the solution for 1 hr. Since resonance is found when solutions in H₂O 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...
Wheeler (15) reported that reduced solutions and aged nonreduced solutions of pentacyanocobaltate II catalyze D$_2$-H$_2$O 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 diduero-buta- dienes.

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$_2$O, H$_2$-D$_2$O, 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$_2$O and methanolic solutions. Clear solutions were used throughout, and each determination was made at least in triplicate.

**Materials.** Deuterium gas and D$_2$O of 99.7% isotopic purity were obtained from General Dynamics Corp.

Hydrogen deuteride used for mass spectrometer calibration was prepared by reducing D$_2$O with LiAlH$_4$.

Deuterated hexenoates were prepared for mass spectrometer calibration by reducing D$_2$O with LiAlH$_4$.

**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 bottle, 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 70ev.

**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-liquid chromatography (GLC) with a single injection rather than in a preparative column. A column (8 ft, ½ 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 reser-

| TABLE I
<p>| Effect of Temperature on Deuterium Absorption by Pentacyanocobaltate II Prepared in Deuterium Oxide |</p>
<table>
<thead>
<tr>
<th>Temp</th>
<th>Observed D$_2$ absorbed mM</th>
<th>D$_2$ absorbed %</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>53.40</td>
<td>72.28</td>
</tr>
<tr>
<td>18</td>
<td>59.20</td>
<td>80.00</td>
</tr>
<tr>
<td>10</td>
<td>65.20</td>
<td>92.00</td>
</tr>
</tbody>
</table>

*Ratio of CN ions to Co ions was 6:1; pentacyanocobaltate II 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$_2$O and D$_2$O.** When [Co(CN)$_5$]$^{3-}$ was prepared in D$_2$O, 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$_2$O, the amount of reduced cobalt corresponded to 81% of the theoretical value. This increase might be caused by the difference of hydrogen gas solubility in H$_2$O and D$_2$O (14,15). Lack of complete correspondence between H$_2$ uptake and Co$^{3-}\rightarrow$Co$^{2-}$ 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$_2$O, D$_2$O, and MeOH are given in Tables I, II, and III. D$_2$ uptake measurements show that the amount of reduced [Co(CN)$_5$]$^{3-}$ is much greater in methanol than in H$_2$O and D$_2$O. This increase might be attributed to the greater solubility of D$_2$ in methanol. Using methanol containing 0.06% H$_2$O 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 hydrido 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 amount 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$_2$O and H$_2$-D$_2$O exchange. In contrast to homogeneous catalysts,