A Raman Spectroscopic Study of the Hydrogenation of Aqueous Pentacyanocobaltate(II)

By **Howard J. Clase,* Andrew J. Cleland,** and **Michael J. Newlands,** Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada

Raman spectroscopy has been used to investigate the complexes formed during the hydrogenation of aqueous pentacyanocobaltate(II). The Raman spectra of hydridopentacyanocobaltate(III), the main species present in solution, and of its deuteriated analogue, are reported for the first time. The study also shows that in the presence of excess of CN^- the hydrogenation may be accompanied by the formation of some hexacyanocobaltate(III). The reaction between pentacyanocobaltate(II) and borohydride was also studied.

DILUTE aqueous solutions of pentacyanocobaltate(II) are known to react rapidly and reversibly with molecular hydrogen to form hydridopentacyanocobaltate(III) according to equation (1).[1] In more concentrated solutions, however, reaction (1) is accompanied by the

$$2Co(CN)_5^{3-} + H_2 \rightleftharpoons 2HCo(CN)_5^{3-} \qquad (1)$$

$$2Co(CN)_5^{3-} + 2H_2O \longrightarrow Co(CN)_5(H_2O)^{2-} + HCo(CN)_5^{3-} + OH^- \qquad (2)$$

decomposition (2), which is often referred to as the ageing reaction.[2-4] The first product of the ageing reaction is sometimes formulated[3] as its conjugate base, $Co(CN)_5OH^{3-}$.

Banks and Pratt[5] have recently reported the isolation and i.r. spectra of salts of $HCo(CN)_5^{3-}$ and have presented evidence that several additional cyanocobalt species may be formed during the hydrogenation of $Co(CN)_5^{3-}$ solutions. The latter claim, however, has been disputed by Halpern and Pribanić[6] who studied reaction (1) over a wide range of H_2 partial pressures and $Co(CN)_5^{3-}$ concentrations. They concluded that equation (1) accurately represents the stoicheiometry of the reaction of $Co(CN)_5^{3-}$ with H_2.

The main technique used for studying reaction (1) has been u.v. and visible spectroscopy since it enables one to observe individual complexes in solution. Great care must be taken, however, in interpreting the spectral changes involved.[1] Traces of oxygen can result in the formation of complexes which absorb at 310 nm, very near the characteristic 305 nm band of $HCo(CN)_5^{3-}$. In concentrated solutions, the ageing reaction results in the ultimate formation of $Co(CN)_6^{3-}$, which also absorbs at 310 nm.[1,3] Even under ideal conditions (dilute solutions, rigorous exclusion of oxygen) the 305 nm band of $HCo(CN)_5^{3-}$ is overlapped by the 316 nm band of $Co(CN)_5^{3-}$. For these reasons, reaction (1) has normally been followed by monitoring the disappearance of the 970 nm band of $Co(CN)_5^{3-}$ rather than the appearance of any band associated with the product.[3,5,6]

The present work was undertaken to show that Raman spectroscopy can provide valuable additional information about the products formed during the hydrogenation of aqueous $Co(CN)_5^{3-}$ solutions. Raman has the advantage over u.v. spectroscopy in that its bands are much sharper, thus enabling the simultaneous presence of several similar species to be established. The chief drawback of the technique is that relatively concentrated solutions are required in order to obtain satisfactory spectra and, as mentioned, reaction (2) becomes important under these conditions. The Raman spectrum of $Co(CN)_5^{3-}$ has been reported by Griffith and Lane.[7]

EXPERIMENTAL

Reagents.—Aqueous solutions containing the hydridopentacyanocobaltate(III) ion were prepared by methods previously described.[8-10] Hydrated cobalt(II) chloride, potassium cyanide, and sodium borohydride were AnalaR, used without further purification; D_2O was from Stohler Isotope Chemicals and contained less than 0·2% H_2O.

Excellent Raman spectra could be obtained from an initial cobalt concentration of 0·05M. All experiments were carried out with a CN : Co ratio of 10.

Spectra.—U.v. spectra were observed in 1 cm cells with a Unicam SP 800D spectrophotometer. Raman spectra were recorded on a Coderg PHO Raman spectrometer by use of a Coherent Radiation Model 52 argon–krypton ion laser (120 mW at 568·2 nm) with the standard 0·3 ml cells and 6—8 passes of the laser beam.

RESULTS AND DISCUSSION

An aqueous solution of $Co(CN)_5^{3-}$ (CN : Co = 10) absorbed hydrogen smoothly at room temperature. During this absorption the colour of the solution gradually changed from olive-green to yellow, which is the typical colour of aqueous $HCo(CN)_5^{3-}$. After 30 min, the u.v. and Raman spectra of the solution were checked to ensure that no $Co(CN)_5^{3-}$ remained. The

---

[1] N. K. King and M. E. Winfield, *J. Amer. Chem. Soc.*, 1961, **83**, 3366.

[2] B. De Vries, *J. Catalysis*, 1962, **1**, 489.

[3] M. G. Burnett, P. J. Connolly, and C. Kemball, *J. Chem. Soc.* (*A*), 1967, 800.

[4] J. H. Espenson and J. R. Pipal, *Inorg. Chem.*, 1968, **7**, 1463.

[5] R. G. S. Banks and J. M. Pratt, *J. Chem. Soc.* (*A*), 1968, 854.

[6] J. Halpern and M. Pribanić, *Inorg. Chem.*, 1970, **9**, 2616.

[7] W. P. Griffith and J. R. Lane, *J.C.S. Dalton*, 1972, 158.

[8] W. P. Griffith and G. Wilkinson, *J. Chem. Soc.*, 1959, 2757.

[9] J. M. Bayston, R. N. Beale, N. K. King, and M. E. Winfield, *Austral. J. Chem.*, 1963, **16**, 954.

[10] J. Kwiatek, I. L. Mador, and J. K. Seyler, *Adv. Chem. Ser.*, 1963, **37**, 201.

presence of a strong broad band at 305 nm in the u.v. spectrum confirmed the presence of $HCo(CN)_5^{3-}$. The Raman spectrum of the freshly prepared $HCo(CN)_5^{3-}$ solution was then recorded from 250—2250 cm^{-1}. The Table lists those Raman bands which can be attributed to the hydride as well as the previously reported [11] ν(CN) i.r. bands of aqueous $HCo(CN)_5^{3-}$.

Vibrational spectra of $HCo(CN)_5^{3-}$ and $DCo(CN)_5^{3-}$ ions in solution

$HCo(CN)_5^{3-}$		$DCo(CN)_5^{3-}$
Raman	I.r. [a]	Raman
2127s(p)	2125w	2127s(p)
2110m(p)	—	2109m(p)
2100sh	2097s	2100sh
1890s(p)	—	1369s(p)
782w	—	616w

[a] Ref. 11. Frequencies in cm^{-1}.

In the cyanide stretching region four Raman bands were normally observed at 2151, 2127, 2110, and *ca.* 2100(sh) cm^{-1}; the free CN^- stretch at 2080 cm^{-1} was also of course observed. The relatively intensity of the strongly polarized 2151 cm^{-1} peak was not reproducible, however, and in those experiments where it was strong, a fifth weaker depolarized ν(CN) band was also observed at 2136 cm^{-1}. We have assigned the two peaks at 2151 and 2136 cm^{-1} to the $Co(CN)_6^{3-}$ ion which we believe to be present in solution (see below).[12] This then leaves the three ν(CN) bands at 2127, 2110, and *ca.* 2100 cm^{-1} which must be associated with $HCo(CN)_5^{3-}$ since, from the u.v. spectrum, this ion is the major species present in solution.

Assuming C_{4v} symmetry for $HCo(CN)_5^{3-}$ in solution, we would expect to observe four Raman-active CN stretches ($2A_1 + B_1 + E$) with only the two A_1 modes polarized. The strong, polarized band at 2127 cm^{-1}, can be assigned to the symmetric stretch of the four equatorial cyanide ligands ($A_1^{(2)}$) while the weaker polarized band at 2110 cm^{-1} is presumably the $A_1^{(1)}$ mode for the single axial ligand. The former mode is expected to be stronger since it involves the simultaneous stretching of four ligands; in the i.r. spectrum this mode appears as a weak broad absorption at 2125 cm^{-1}. The poorly resolved weak shoulder at *ca.* 2100 cm^{-1} in the Raman spectrum must be the asymmetric CN stretch (E) since there is a strong i.r. counterpart at 2097 cm^{-1}. The fourth expected Raman-active band (B_1) was not observed and may well be obscured by one or more of the other modes.

In the 700—2000 cm^{-1} region of the spectrum only two Raman bands were observed at 1890 and 782 cm^{-1}, and these are clearly the cobalt–hydrogen stretching and bending modes respectively of $HCo(CN)_5^{3-}$. On deuteriation these two bands shifted to 1369 and 616 cm^{-1}, this confirming the assignment.

In the low-frequency region (250—700 cm^{-1}) we would expect to observe the Co–CN stretching and Co–C–N bending modes of any species present in solution. The spectrum obtained, however, was very simple and showed only two peaks at 332 and 411 cm^{-1}, though a weak band at 456 cm^{-1} was sometimes observed as a shoulder on the 411 cm^{-1} peak. Assignments of these bands are necessarily tentative but some general comments are possible. The very intense 411 cm^{-1} peak was significantly polarized and is likely due mainly to the A_{1g} Co–CN stretching mode [12] of $Co(CN)_6^{3-}$. The weaker 332 cm^{-1} band is rather low for a Co–CN stretch and we believe it to be the Co–O stretch of $Co(CN)_5(H_2O)^{2-}$, one of the products of the ageing reaction. Support for this assignment was obtained from the spectrum of $DCo(CN)_5^{3-}$ in D_2O where it was observed that the 332 cm^{-1} band had shifted to 322 cm^{-1}. This would be expected for the ν(Co–O) mode since in D_2O the ageing reaction would of course lead to $Co(CN)_5(D_2O)^{2-}$. The weak shoulder at 456 cm^{-1} is most likely a Co–CN stretching mode rather than a bending mode [13] but at present it is impossible to associate this peak with any particular species in solution. It is doubtful, however, that the 456 cm^{-1} band is due to the hexacyanide.[12] No band was observed in the Raman spectrum which corresponded to the 535 cm^{-1} peak observed by Banks and Pratt [5] in the i.r. spectra of solid salts of $HCo(CN)_5^{3-}$.

We believe for the following reasons that the minor product formed during hydrogenation is $Co(CN)_6^{3-}$ rather than the first product of the ageing reaction, $Co(CN)_5(H_2O)^{2-}$, which may have a similar Raman spectrum. First, the bands at 2151, 2136, and 411 cm^{-1} correspond exactly to our Raman spectrum of a known solution of $Co(CN)_6^{3-}$. Secondly, while reaction (3) has been shown to be slow and irreversible [1] under

$$Co(CN)_5H_2O^{2-} + CN^- \longrightarrow Co(CN)_6^{3-} + H_2O \quad (3)$$

normal conditions, it is catalysed [14] by $Co(CN)_5^{3-}$ and would be expected to be rapid under the initial conditions of the hydrogenation. $Co(CN)_5(H_2O)^{2-}$ would continue to be converted into the hexacyanide until most of the $Co(CN)_5^{3-}$ had been removed. We have monitored the reaction during several hours by Raman spectroscopy and found that the peaks at 2151 and 411 cm^{-1} were present shortly after the start of hydrogenation and increased in intensity as the reaction continued, when the weaker band at 2136 cm^{-1} also appeared. The band at 332 cm^{-1} attributed to $Co(CN)_5(H_2O)^{2-}$ did not increase, but ultimately vanished, and could not be due to the same species. Finally, Burnett *et al.*,[3] who studied the ageing reaction (2) in the presence of excess of CN^- by u.v. spectroscopy,

---

[11] T. Funabiki, M. Matsumoto, and K. Tarama, *Bull. Chem. Soc. Japan*, 1972, **45**, 2723.

[12] B. I. Swanson and L. H. Jones, *J. Chem. Phys.*, 1970, **53**, 3761.

[13] D. M. Adams, 'Metal-Ligand and Related Vibrations,' Arnold, London, 1967, p. 111.

[14] J. P. Birk and J. Halpern, *J. Amer. Chem. Soc.*, 1968, **90**, 305.

observed that the amount of $Co(CN)_5(H_2O)^{2-}$ formed was often less than the stoicheiometrically expected amount. This was attributed to the formation of $Co(CN)_6{}^{3-}$ by reaction (3). Our u.v. studies confirm these observations but, owing to the problem of overlapping u.v. bands mentioned in the Introduction section, the presence of $Co(CN)_6{}^{3-}$ cannot be confirmed directly by this method.

Several groups have reported that the pentacyanocobaltate(II) ion can be directly and rapidly reduced by borohydride.[1,5,8] We have found, however, that the reaction of $Co(CN)_5{}^{3-}$ with $BH_4{}^-$ is not an efficient method of producing $HCo(CN)_5{}^{3-}$. The reaction is slow, even in the presence of excess of $BH_4{}^-$, and after several hours the Raman spectrum showed that the major species present was $Co(CN)_6{}^{3-}$. Bands associated with $HCo(CN)_5{}^{3-}$ and $BH_4{}^-$ were also observed but the weakness of the former indicated that it was present in relatively low concentration. Hanzlík and Vlček[15] studied the borohydride reduction of $Co(CN)_5{}^{3-}$ in dilute solutions (*ca.* 10^{-3}M) and have shown that under these conditions, where the ageing reaction is not important, the final products are $HCo(CN)_5{}^{3-}$, $BO_2{}^-$, and H_2. They have suggested that the actual reducing species in the reaction may be BH_3OH^- which is the first product of the hydrolysis of $BH_4{}^-$. Jackman *et al.*,[16] however, believe that the hydrogen produced by hydrolysis is the active species in the borohydride reduction.

Conclusions.—The results presented here show that Raman spectroscopy is a simple, yet effective, method of observing the formation of $HCo(CN)_5{}^{3-}$ in aqueous $Co(CN)_5{}^{3-}$ solutions. At the concentrations required, however, decomposition of $Co(CN)_5{}^{3-}$ is important and apparently leads to the formation of $Co(CN)_6{}^{3-}$, a complex which is not easily observed by other spectrophotometric methods. No other hydride species, such as those observed by Banks and Pratt, were observed in the Raman spectra, although it is unlikely that these would be detected if present in small amounts. We are presently investigating the possibility of using Raman spectroscopy to study catalytic hydrogenation reactions which involve $HCo(CN)_5{}^{3-}$.

We thank the National Research Council of Canada and the Memorial University of Newfoundland for financial support.

[3/1157 *Received, 5th June,* 1973]

---

[15] J. Hanzlík and A. A. Vlček, *Coll. Czech. Chem. Comm.*, 1972, **37**, 693.

[16] L. M. Jackman, J. A. Hamilton, and J. M. Lawlor, *J. Amer. Chem. Soc.*, 1968, **90**, 1914.