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A RAMAN SPECTROSCOPIC STUDY OF THE REACTIONS OF HYDRIDOPENTACYANOCOBALTATE(III) WITH 1,3-BUTADIENE

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Summary

Raman spectroscopy has been used to investigate the previously reported organocyanocobalt complexes which are formed from the reaction of hydridopentacyanocobaltate(III) with 1,3-butadiene. These complexes are postulated intermediates in the $Co(CN)_5^{3-}$-catalyzed hydrogenation of butadiene. The Raman spectrum of σ-(2-butenyl)pentacyanocobaltate(III), which is formed in the presence of an excess of CN^-, confirms that both *cis* and *trans* isomers of this intermediate are present in solution. In the presence of a deficiency of CN^-, only one complex, *syn*-π-(1-methylallyl)tetracyanocobaltate(III), is formed, and its Raman spectrum is also reported for the first time. When the initial CN/Co ratio is 5.0, both σ- and π-bonded complexes are present in solution, with the σ complex predominating.

Introduction

An application of Raman spectroscopy to the study of homogeneous catalysis in aqueous solutions is presented in this paper. There is widespread interest in the catalysis of the hydrogenation of unsaturated carbon compounds [1,2] by transition metal complexes in solution. While a number of physical methods, especially ultraviolet, visible and nuclear magnetic resonance spectroscopies, have been used to provide information on the structures of the intermediate organometallic complexes, Raman spectroscopy does not appear to have been used before.

There were two reasons for choosing the hydrogenation of 1,3-butadiene (referred to as butadiene throughout this paper) catalyzed by pentacyanocobaltate(II) as the initial subject of this study. Firstly, the normal solvent for this reaction is water, which is an ideal solvent for Raman spectroscopy. Secondly,

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although the structures of the intermediate complexes were not known when this work was started, the reaction had been studied in considerable detail [3-5].

Our aims were to obtain the Raman spectra of the intermediates and to deduce their structures. Our conclusions agree with those of a recent proton magnetic resonance study of the same system [6]. We also comment on the implications of these conclusions to the debate on the mechanism of the hydrogenation.

Experimental

Aqueous solutions of $Co(CN)_5^{3-}$ were prepared by dissolving 0.005 mol of reagent grade cobalt(II) chloride and potassium cyanide in 100 ml of distilled water which had been deoxygenated by purging with nitrogen. The initial CN/Co ratio, R, was varied from 4.8 to 10.0. Solutions of $HCo(CN)_5^{3-}$ were prepared by hydrogenation of corresponding solutions of $Co(CN)_5^{3-}$ according to eqn. 1. After the hydrogen-absorption procedure was complete, the hydrogen flow was replaced by butadiene. The Raman spectra of the solutions were recorded when all bands due to $HCo(CN)_5^{3-}$ had completely disappeared [7]. This normally required about 10 min.

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

Reactions between $K_3Co(CN)_5$ (100 ml, 0.05 M cobalt, R = 10.0) and crotyl bromide were carried out immediately after potassium cyanide had been added to the cobalt chloride solution. An excess of freshly distilled crotyl bromide was injected by syringe into the olive-green solution of $K_3Co(CN)_5$. The mixture became orange within 5 min.

All Raman spectra were recorded on a Coderg PHO Raman spectrometer using a Coherent Radiation Model 52 argon-krypton ion laser (approximately 120 mW at 568.2 nm) and the standard 0.3 cm^3 cells.

Results and discussion

Raman Spectra

Both σ- and π-butenyl cobalt complexes have been proposed as intermediates in the pentacyanocobaltate(II) catalysed hydrogenation of butadiene [4, 5]. There are few detailed vibrational studies of complexes containing butenyl ligands, but several have been carried out on the similar but simpler σ- and π-allyl ligands. These are the subject of part of a recent review [8]. The key differences in the vibrational spectra of σ- and π-allyl complexes are in the carbon skeleton stretching vibrations. The σ-complexes show a band above 1600 cm^{-1} characteristic of a localized C=C, which is strong in the Raman, while π-complexes show a strong band between 1015 and 1040 cm^{-1}, attributable to the symmetric C—C—C stretch of the π-allyl system. Both unsubstituted and methyl substituted π-allyls fall into this range. The corresponding C—C—C antisymmetric stretch has been variously assigned from 1390 to 1590 cm^{-1} [8] and is probably mixed with $—CH_2^-$ bending modes [9]. Since the spectra of the organocobalt intermediates we have obtained are far from complete we have not attempted a detailed analysis but concentrated our attentions on these diagnostic bands. The C≡N stretching region was not found useful, since the small shifts observed cannot be directly related to the organic ligand and the region is complicated by the presence of the chemically inert $Co(CN)_6^{3-}$ ion [7]. We have also drawn support for our arguments from a comparison of the spectra reported here with the Raman spectra of σ-(2-butenyl)pentacarbonylmanganese and π-(butenyl)tetracarbonylmanganese, which are isoelectronic with the organocobalt cyanide complexes [10].

In order to check that none of the observed Raman bands were due to dissolved free organic species we recorded the Raman spectra of aqueous KCN (0.50 *M*) solution saturated with butadiene, *trans*-2-butene, *cis*-2-butene, and 1-butene respectively. Only the butadiene solution showed bands attributable to the organic species, which is not unexpected since butadiene has a much higher partition coefficient under these conditions than the butenes [4]. This spectrum is given in Table 1 along with the assignments of Panchenco et al. [11]. Solutions free from the bands of butadiene, without changing other features of the spectrum, could be obtained by stirring the solution vigorously for 0.5 h. However, since these bands did not interfere with those of the organic complexes the spectra were generally recorded immediately.

The left hand column of Table 2 shows the Raman peaks observed from the clear yellow solution obtained by saturating a solution of $HCo(CN)_5^{3-}$ (0.05 *M* in Co, $R = 10$) with butadiene. A similar spectrum was obtained from the reaction of crotyl bromide with pentacyanocobaltate(II) except that the peaks due to the hexacyanocobaltate(III) ion were more intense. The presence of two strong bands at 1624 and 1639 cm^{-1}, attributable to isolated C=C stretching, suggests that the *cis* and *trans* isomers of σ-(2-butenyl)pentacyanocobaltate(III) are both present in appreciable amounts. This is in agreement with the NMR evidence of Funabiki and coworkers [6], and σ-(2-butenyl)pentacarbonylmanganese has also been shown to be a mixture of *cis* and *trans* isomers [10,12]. A prominent but puzzling feature of the spectrum is the strong band at 1067 cm^{-1} in the region assigned to C—H deformations since they are rarely so intense [8]. However, a similar band at 1068 cm^{-1} is observed in the spectrum of σ-(2-butenyl)-pentacarbonylmanganese [10]. The greater amount of hexacyanocobaltate(III) ion and absence of detectable amounts of bromopentacyanocobaltate(III) in the solution produced from crotyl bromide and pentacyanocobaltate can be explained by displacement of bromide ion from the bromo complex by cyanide ion. Although this process is normally slow, it has been shown to be catalysed by one of the primary reactants, the pentacyanocobaltate(III) ion [13].

Solutions prepared by passing butadiene into a prehydrogenated solution

TABLE 1

RAMAN SPECTRUM OF 1,3-BUTADIENE SATURATED IN 0.50 *M* POTASSIUM CYANIDE SOLUTION

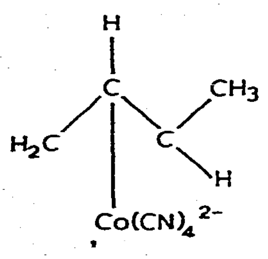
Absorption (cm^{-1})	Assignment
513 m	δ(C=C—C)
1203 m	ν(C—C)
1283 m	
1303 w	
1404 m	δ($=CH_2$)
1638 s	ν(C=C)

TABLE 2

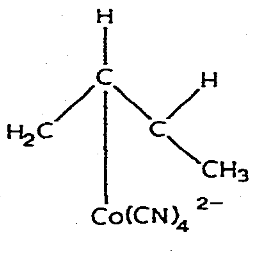
RAMAN SPECTRA OF BUTENYLCYANOCOBALTATES(III) IN AQUEOUS SOLUTION (ALL FREQUENCIES IN cm^{-1})

CN/Co = 10.0		CN/Co = 4.8	
352 s		323	
384 w		360	
412	$Co(CN)_6^{3-}$	412	$Co(CN)_6^{3-}$
449 w			
474 s		467 (br)	
499 m			
534 w(br)		516 s	
550 m		566 s	
979 w			
1006 m		1034 m	$\nu_s(C\text{---}C\text{---}C)$
1067 vs		1066 w	
1166 m		1125 (br)	
1254 w		1215 (br)	
1301 w		1247 m	
1364 w		1309 w	
1379 w		1381 m	
1399 w		1397 w	
1452 w		1441 m	
1624 s	$\nu(C=C)$	1525 m	
1639 s	$\nu(C=C)$		
2078	CN^-	2095 m(sh)	
2097 m	$\nu(CN)$	2100 m(sh)	
2119 s	$\nu(CN)$	2108	$Co(CN)_5^{3-}$
2138	$Co(CN)_6^{3-}$	2119 s	
2150	$Co(CN)_6^{3-}$	2150	$Co(CN)_6^{3-}$

at $R = 4.8$ (0.05 M in Co) were slightly cloudy, and gave poorer spectra than those with a higher proportion of cyanide. Raman bands recorded from such a solution are listed in the right hand column of Table 2. The medium intensity band at 1034 cm^{-1} is assigned as the symmetric C—C—C stretching vibration of a π-allyl group. The corresponding asymmetric stretch with CH_2 deformations would be in the complex of bands from 1381 to 1525 cm^{-1} [8]. There is no band in the region just above 1600 cm^{-1} indicating the absence of any isolated carbon—carbon double bond. This spectrum is therefore in agreement with the NMR evidence of Funabiki and coworkers [6] that the *syn*-π-complex predominates in these conditions. The C≡N stretching region of the spectrum shows the



syn-π



anti-π

expected presence of the hexacyanocobaltate(III) ion and a band at 2108 cm^{-1} which we have assigned as the A_1 mode of the pentacyanocobaltate(II) ion, which has been reported at 2115 cm^{-1} in aqueous methanol [14]. This assignment is supported by the following observations: *(i)* the 2018 cm^{-1} band is present in the spectra of $HCo(CN)_5^{3-}$ solutions at $R = 4.8$ before butadiene is introduced and cannot therefore be due to any organocobalt species, and *(ii)* it disappears rapidly when more cyanide is added. Reaction 1 is known to be dependent on cyanide ion concentration [15]. Spectra recorded at $R = 5.0$ and $R = 5.1$ showed bands from both columns in Table 2 and are therefore due to a mixture of the σ- and π-species with the σ-complex predominating, even at $R = 5.0$. We observed no changes in these spectra which could be due to conversion of the σ-complexes to the *syn*-π-complex, so presumably the equilibrium is established rapidly. This conversion is known to occur rapidly on addition of cobalt(II) chloride [6] and we did observe that when more cyanide was added the solution became clear and showed only the Raman bands of the σ-complexes. The formation of π-(allyl)tetracyanocobaltate(III) from σ-(allyl)pentacyanocobaltate(III) is known to be slow [5].

To summarize, our Raman spectra showed that the only detectable* organocobalt species present were *cis*- and *trans*-σ-2-(butenyl)pentacyanocobaltate(III) at high cyanide to cobalt ratios ($R = 10$), and a π-(butenyl)tetracyanocobaltate(III) at $R = 4.8$. When R was in the range 5.0-5.1 all three species were in equilibrium, with the σ-isomers predominating. Hexacyanocobaltate(III) was always present as an inert byproduct [1] and some pentacyanocobaltate(II) was detected at $R = 4.8$.

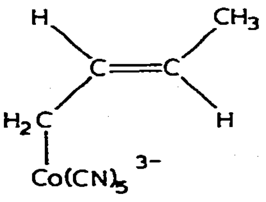
These results shed further light on the mechanism of the hydrogenation of butadiene catalyzed [1] by pentacyanocobaltate. All reports agree that at high values of R the principal product is 1-butene while at low values of R the main product is *trans*-2-butene [3-5]. Kwiatek and Seyler [3] established that the following three steps occurred:

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

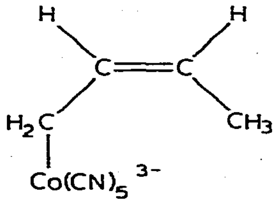
$$HCo(CN)_5^{3-} + C_4H_6 \rightleftharpoons \underset{(I)}{(C_4H_7)Co(CN)_5^{3-}} \tag{2}$$

$$(C_4H_7)Co(CN)_5^{3-} + HCo(CN)_5^{3-} \rightleftharpoons C_4H_8 + 2\,Co(CN)_5^{3-} \tag{3}$$

Argument centers around the structure of I and the changes in structure with changes in R. Kwiatek and Seyler [3] postulated that I was the product of



trans-σ_1



cis-σ_1

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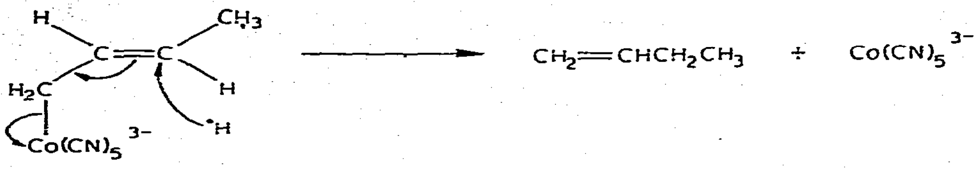
* Species involving less than about 10% total cobalt could be overlooked by this method.

1,4-addition of hydridopentacyanocobaltate to butadiene, i.e., it was a mixture of *cis*- and *trans*-σ_1. These authors suggested that *trans*-σ_1 was more stable than *cis*-σ_1 and was the larger component. α-Hydrogen attack on σ_1 would then give 1-butene and pentacyanocobaltate.



(4)

Kwiatek and Seyler [3] also suggested that there was an equilibrium between σ_1- and π-complexes at low values of R:

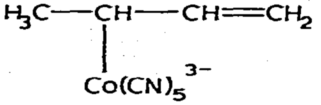
$$(\sigma\text{-}C_4H_7)Co(CN)_5^{3-} \rightleftharpoons (\pi\text{-}C_4H_7)Co(CN)_4^{2-} + CN^- \quad (5)$$

with the π-complex primarily in the *syn*-configuration. Hydrogen attack on the latter then gave *trans*-2-butene. These authors prepared impure σ_1 from the reaction:

$$CH_3CH{=}CHCH_2Br + 2Co(CN)_5^{3-} \rightarrow CH_3CH{=}CHCH_2Co(CN)_5^{3-} + BrCo(CN)_5^{3-}$$

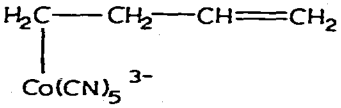
and showed that it slowly lost CN^- to give the π-complex. The process was rapidly reversed in the presence of an excess of cyanide ion.

Burnett, Conolly and Kemball [4] carried out a detailed kinetic study of the reaction and analyzed the results in terms of a very complex mechanism consisting of three equilibria and six displacement reactions. These authors



$H_3C{-}CH(Co(CN)_5^{3-}){-}CH{=}CH_2$

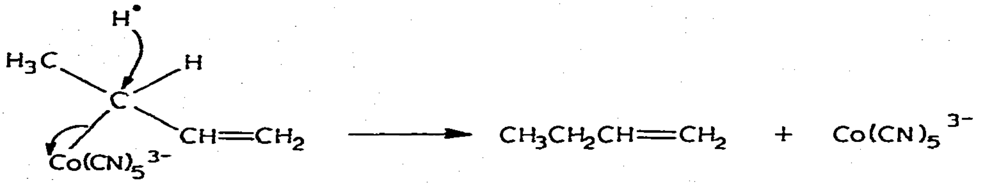
σ_2



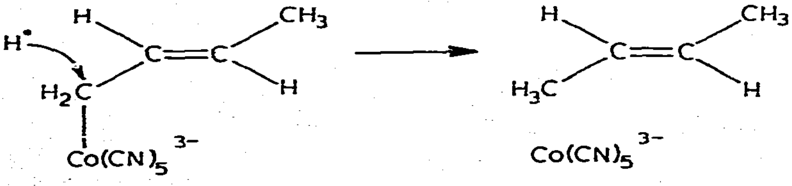
$H_2C(Co(CN)_5^{3-}){-}CH_2{-}CH{=}CH_2$

σ_3

suggested that the initial product at high R was σ_2. Hydrogen attack at the carbon α to cobalt then gave 1-butene:



σ_2 was also in equilibrium with *cis*- and *trans*-σ_1, hydrogen attack on which gave the small amounts of *cis*- and *trans*-2-butene, e.g.,



The mechanism proposed by Burnett, Connolly and Kemball for low values of R was essentially the same as that of Kwiatek and Seyler, except that it was suggested that some *anti*-π-complex might also be present.

Our work and the recent, elegant NMR studies of Funabiki, Matsumoto and Tarama [6] show quite clearly that the initial product of the reaction of butadiene and hydridopentacyanocobaltate at high values of R is a mixture of approximately equal amounts of *cis*- and *trans*-σ_1. Equally, both studies show that at low values of R the only organocobalt compound present is the *syn*-π-complex which is rapidly converted to σ_1 in the presence of an excess of cyanide ion. Our Raman work and Funabiki et al.'s NMR study therefore provide strong evidence for the Kwiatek and Seyler analysis of the butadiene/hydridopentacyanocobaltate reaction and against the Burnett, Connolly, and Kemball mechanism.

The present study shows that Raman spectroscopy is a powerful tool for the investigation of reaction intermediates especially under conditions less favourable for other physical methods, for example for reactions carried out in aqueous solution.

Acknowledgement

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