

Fourier Transform Infrared Studies of the Irreversible Oxidation of Cyanide at Platinum Electrodes

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The behaviour of cyanide on platinum electrodes at anodic potentials has been studied by voltammetric and Fourier transform infrared reflectance spectroscopic techniques. The voltammetry shows that cyanide adsorbs on platinum at potentials more negative than -0.8 V (SCE). Potential-sensitive infrared absorptions appearing between 2200 and 2250 cm^{-1} are tentatively assigned to strongly adsorbed cyanide species. Another band at 2074.5 cm^{-1} shows no change in wavenumber with potential and is thought to be associated with cyanide in the double-layer region. An absorption at 2169 cm^{-1} , which appears with significant intensity at anodic potentials, has been attributed to bulk cyanate. Other features at 2093 and 2343 cm^{-1} are assigned to aqueous hydrogen cyanide and carbon dioxide, respectively, possibly formed as a result of changes in interfacial pH associated with electro-oxidation.

Advances in Fourier transform infrared spectrometry¹ have permitted the study of interfacial processes in thin-layer electrochemical cells.^{2–8} The sensitivity and high-energy throughput of the interferometric instruments¹ permit the detection of weak absorptions arising from the interfacial region, even in the presence of an aqueous electrolyte thin layer which absorbs extensively in the infrared region.

In proposing band assignments to specific species in the sampling zone the following possibilities should be considered: molecules either chemisorbed or in a state of contact adsorption on the metal surface; molecules associated with corrosion (*e.g.* oxide) films on the metal surface; molecules within the double-layer region (which may be subject to modified inter-ion or solvent-restructuring effects); solution products of electrochemical reactions, which may or may not incorporate a metal ion; and species in the electrolyte thin layer which are merely changing concentration.

The recent infrared studies of carbon monoxide adsorption on platinum electrodes^{2, 3} are important in the context of future applications to electrosorption because the interfacial reactive chemistry is relatively simple (and therefore several of the possibilities listed above may be discarded) and because the infrared spectroscopy of CO adsorbed on platinum surfaces is extremely well documented.⁹ It was decided in the present study to investigate interfacial processes in the system, Pt/0.1 mol dm⁻³ NaCN, because cyanide is isoelectronic with carbon monoxide and so constituted an interesting comparative case with Pt/CO and because the vibrational spectroscopy of cyanide is also well established.¹⁰ However, the well documented tendency of cyanide to react with metal oxides to form soluble stable cyanates^{11, 12} raises the possibility of more complex interfacial processes (see table 1) than exist for the Pt/CO case.

Table 1. Survey of candidate species for the infrared region 2000–2400 cm^{-1}

$\nu(\text{CN})/\text{cm}^{-1}$	species
2052	CNO^- , fulminate ^a
2080.2	CN^- in 2.5 mol dm^{-3} NaCN ^b
2080	CN^- in 0.1 mol dm^{-3} NaCN ^b
2097	$\text{HCN}(\text{g})^c$
2133.4	$[\text{Pt}(\text{CN})_4]^{2-}$ (E_u mode) ^a
2157	$(\text{CN})_2(\text{g})$, cyanogen ^d
2169	NCO^- , cyanate ^b
2274	$\text{HNO}(\text{g})^a$
2294	$\text{HO}(\text{CN})$ (matrix) ^a
2000–2200	coordinated cyanide ^a
2110–2200	coordinated fulminate ^a
2160–2290	coordinated isocyanate ^a

^a See ref. (10). ^b This study. ^c See ref. (14). ^d See ref. (19).

Experimental

The infrared spectra were recorded using a Nicolet 8000 Fourier transform spectrometer incorporating an indium antimonide detector (held at 77 K). The incident beam was p-polarized using a gold wire grid polarizer (Cambridge Physical Sciences) to improve the signal-to-noise ratio for species within 500 nm of the electrode surface. Spectra were recorded at 8 cm^{-1} resolution and each spectrum was the result of the deconvolution of the average of 512 double-sided interferograms. The electrochemical equipment used for the i.r. studies consisted of a Princeton Applied Research model 173 potentiostat and model 175 waveform-generator. The thin-layer spectroelectrochemical cell employed a calcium fluoride window and incorporated a 7 mm diameter platinum disc working electrode in conjunction with Pt wire counter and saturated calomel (SCE) reference electrodes. The cell configuration was similar to that employed by Pons.⁸ Potential control was accomplished with a PAR model 173 potentiostat and model 175 waveform-generator. The Pt mirror working electrode was polished on 0.5 μm alumina prior to each experiment. The main body of the spectrometer was evacuated during the experiments and the sample compartment purged with N_2 .

Sodium cyanide, potassium hydrogen phosphate, and sodium hydroxide (Fisher ACS) were employed in the preparation of the electrolyte solutions. Doubly distilled water was used throughout.

All the species detected (see Results and Discussion) were formed in electrochemically irreversible processes. Attempts to reduce these species at cathodic potentials (-0.7 V for 60 s) resulted in relatively slow change in peak intensities. For this reason potential-modulation experiments were not attempted. The sequence of experiments in each case would start with the cell at cathodic potentials (usually -0.70 V *vs.* SCE) and the potential would then be stepped in an anodic direction, with spectra being collected at each step. Absorbance spectra were then obtained by using the initial (cathodic) spectrum as a reference.

Voltammetric experiments employed the same working electrode and SCE reference electrodes used in the infrared studies, but the cell was of a design allowing for bulk diffusion of species to the electrode surface. Potential control in this case was achieved

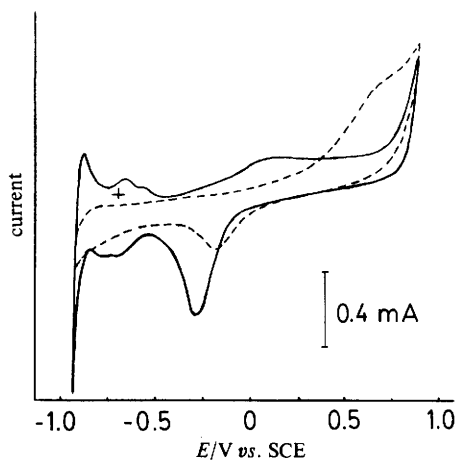


Fig. 1. Repetitive sweep cyclic voltammetry of a Pt electrode in 0.1 mol dm^{-3} phosphate buffer (pH 12) before (—) and after (---) addition of 0.1 mol dm^{-3} NaCN. Sweep rate = 200 mV s^{-1} .

with a Hi-TEK model DT 2101 potentiostat operating in conjunction with a Hi-TEK model PPR1 waveform-generator. A Pt wire helix served as the counter electrode. Voltammetric traces were recorded with a Linseis model 1700 x - y - t recorder.

Results and Discussion

Cyclic Voltammetry

The solid line in fig. 1 illustrates the voltammetric behaviour observed for the Pt mirror electrode in 0.1 mol dm^{-3} phosphate buffer (pH 12) on repetitive cycling of the potential between the hydrogen and oxygen evolution regions. The voltammetry is analogous to that previously characterized by other workers¹³ for Pt electrodes in alkaline media. The broad, featureless anodic wave extending from *ca.* -0.5 V up to the onset of oxygen evolution represents the formation of various hydroxide/oxide surface layers on the Pt substrate. The sharp cathodic peak at -0.25 V is due to reduction of the oxide surface phase. The small cathodic and coupled anodic peaks at potentials just positive of the hydrogen evolution region are due to hydrogen adsorption/desorption.

The dashed line in fig. 1 illustrates the voltammetry observed after the addition of 0.1 mol dm^{-3} NaCN to the phosphate buffer electrolyte. When the NaCN was added, the potential was initially held at -0.8 V (*i.e.* intermediate between H_2 adsorption and evolution) before making any anodic excursion. On the first anodic scan the peaks due to H_2 desorption were completely absent. This observation indicates that cyanide adsorbs at potentials less than -0.8 V , resulting in a surface blocking effect. That surface oxide formation is suppressed by cyanide adsorption is indicated by the absence of any significant anodic current for anodic sweep limits $\leq +0.4 \text{ V}$. Similarly, no peak ascribable to oxide reduction is observed on the reverse cathodic scan unless potentials greater than $+0.4 \text{ V}$ have been reached on the forward scan. A broad anodic wave beginning at $+0.4 \text{ V}$ and extending into the oxygen evolution region is assumed to result both from surface oxide formation, as suggested by the appearance of a reduction-desorption peak at -0.2 V during the cathodic sweep and from the oxidation of cyanide to cyanate, as indicated in the literature.¹²

Table 2. Infrared data^a from the thin-layer electrochemical system Pt/0.1 mol dm⁻³ NaCN

band /cm ⁻¹	E_{app}/V	
	buffered pH 12	buffered pH 7
2074.5 ± 0.3	-0.5 V (A)	+0.25 V (D)
2093 ± 1	*	+0.30 V (D)
2135 ± 2	-0.25 V (A)	*
2169 ± 1	+0.15 V (A)	+0.30 V (A)
2200 ± 1	complex spectra formed from the overlap of potential-dependent appearance and disappearance bands	
2250 ± 1		
2343 ± 1	+0.15 V (A)	+0.25 V (A)

^a E_{app} is the potential at which the band is first observed; (A), appearance or positive (increased) absorption; (D), disappearance or negative (decreased) absorption; *, not detected.

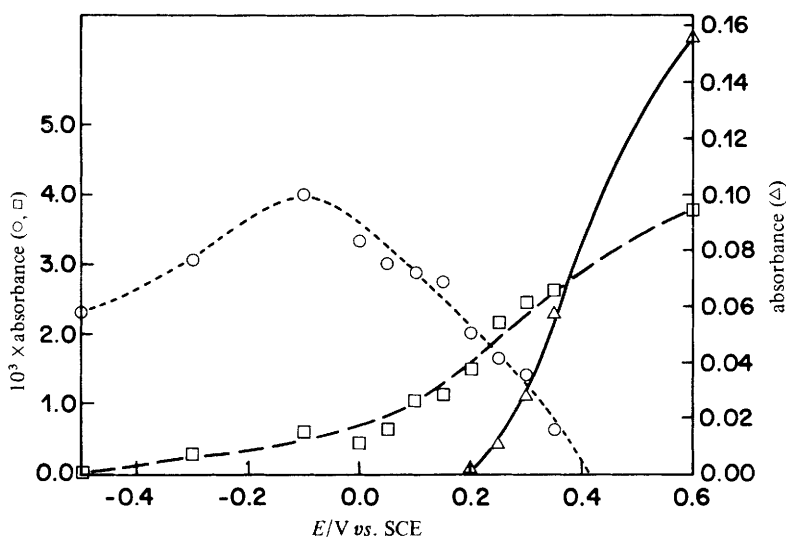


Fig. 2. Variation in intensity of absorbance at (○) 2075, (△) 2169 and (□) 2343 cm⁻¹ for the buffered pH 12 electrolyte. Note that the ordinate for the 2343 and 2075 cm⁻¹ bands employs a different scale from that for the 2169 cm⁻¹ band.

Infrared Spectroscopy

Infrared reflectance spectra recorded with p-polarized light for the system Pt/0.1 mol dm⁻³ NaCN in 0.1 mol dm⁻³ phosphate buffer (pH 12 or pH 7) reveal evidence for a series of weak but reproducible absorbance changes in the region 2050–2350 cm⁻¹ as the potential is stepped anodically. These are indicated in table 2. In the pH 12 system, the base potential at which the reference spectrum was obtained was -0.7 V. In the pH 7 system, this value was increased to -0.5 V to avoid the evolution of substantial quantities of hydrogen gas within the thin-layer cell.

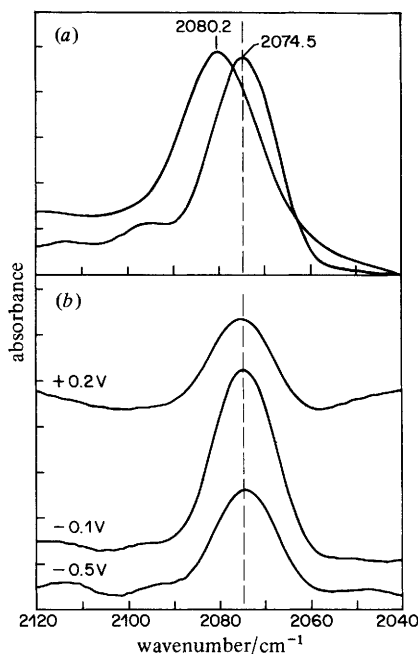


Fig. 3. The cyanide i.r. band under different conditions. (a) A comparison of the absorbance spectrum of free CN^- in aqueous solution (no electrode involved, band at 2080.2 cm^{-1}) and the p-polarized f.t.i.r. spectrum of CN^- (unbuffered, 0.1 mol dm^{-3} NaCN, band at 2074.5 cm^{-1}) in the presence of a Pt electrode held at $+0.60\text{ V vs. SCE}$. These two spectra are not on the same absorbance scale; the spectrum of CN^-/Pt has been expanded to facilitate comparison of the positions of the two bands. (b) The reflectance-absorbance spectra of 0.1 mol dm^{-3} KCN (buffered to pH 12) showing the change of intensity but the virtual invariance of position of the 2074.5 cm^{-1} band with electrode potential. The potentials shown are *vs. SCE*. These three spectra are on the same absorbance scale. The dashed vertical line is drawn at 2074.5 cm^{-1} .

Assignments

The Band at 2075 cm^{-1}

In pH 12 phosphate buffer, a positive absorbance at 2075 cm^{-1} is observed as the electrode potential is increased anodically from the -0.7 V base potential (fig. 2). The band centre position is displaced by a small but consistent increment from that observed for free cyanide (2080.2 cm^{-1} , fig. 3) and is independent of electrode potential. Its intensity increases to a maximum at a potential of -0.2 V and then decreases with further increases in potential, eventually becoming a strong negative absorbance in the spectrum obtained at $+0.6\text{ V}$. The negative absorbance observed at the most positive potentials indicates that the species giving rise to the 2075 cm^{-1} band was already present in significant quantity at the -0.7 V base potential.

In an *in situ* f.t.i.r. study of a platinum electrode in sulphate solutions containing cyanide, Bewick and Pons⁷ reported the observation of a negative absorbance at 2071 cm^{-1} . They ascribed this feature to the displacement of adsorbed cyanide from the electrode surface by the more highly charged sulphate ion as the potential was made more positive. Similarly, displacement of interfacial cyanide by phosphate ion is a possible explanation for the decrease in absorbance at 2075 cm^{-1} observed in this study. When the spectra are recorded in 0.1 mol dm^{-3} NaCN at its natural pH (=11), the

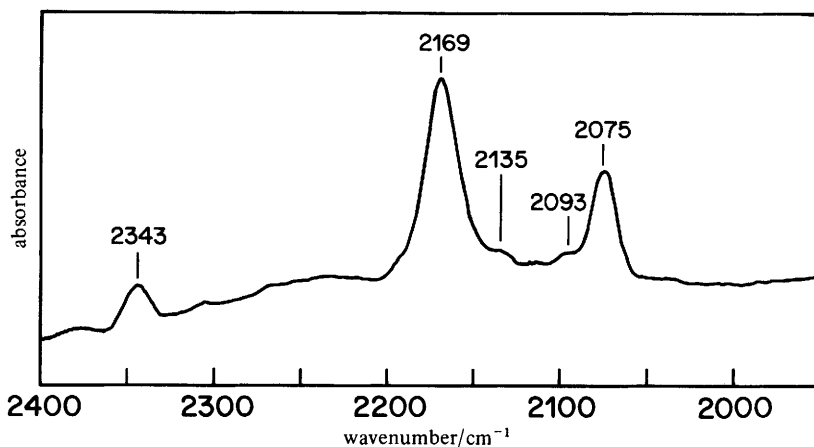


Fig. 4. F.t.i.r. spectrum of unbuffered $0.10 \text{ mol dm}^{-3} \text{ CN}^-$ in contact with a Pt electrode, which is held at 0.60 V vs. SCE .

phosphate buffer being omitted, no decrease in intensity of the 2075 cm^{-1} band is observed up to potentials of 0.6 V , supporting this suggestion.

If the 2075 cm^{-1} band were to be assigned to cyanide adsorbed on the platinum electrode, then its behaviour differs from that observed by *in situ* f.t.i.r. for CO adsorbed on platinum³ and for CN^- adsorbed on silver.⁵ In these cases, the vibrational frequencies of the adsorbed species shift positively by *ca.* $30 \text{ cm}^{-1} \text{ V}^{-1}$ as the potential is increased, possibly reflecting a change in the extent of π back-bonding between metal and adsorbate.^{3, 5} In contrast, the small 5 cm^{-1} shift of the 2075 cm^{-1} band from the vibrational frequency of solution cyanide suggests that the forces responsible for the shift are weak. This appears to be inconsistent with an assignment of the 2075 cm^{-1} band to the cyanide adsorbed on the inner Helmholtz plane, which displaces strongly adsorbed hydrogen (see above). Therefore, it is suggested that the species giving rise to the 2075 cm^{-1} absorbance is cyanide either at or beyond the outer Helmholtz plane. The small 5 cm^{-1} displacement with respect to bulk solution cyanide may reflect modified inter-ion and/or solvation interactions in the double-layer region. The frequency shift does not appear to be a concentration effect as no change in the vibrational frequency of solution cyanide is observed on varying its concentration from 0.1 to 2.5 mol dm^{-3} in phosphate buffer.

The Band at 2093 cm^{-1}

This band is observed as a weak appearance feature in the unbuffered pH 11 system (fig. 4). In the buffered pH 7 system (fig. 5) it is seen as a strong disappearance feature at more anodic potentials. It is not seen for the system buffered at pH 12. The band is adjacent to the reported $\nu(\text{CN})$ of gas-phase HCN (2097 cm^{-1})^{10, 14} and coincides with a band ascribed to aqueous HCN in an infrared study of cyanide adsorption on Ag electrodes.⁵ This feature is accordingly assigned to aqueous HCN in the present case.

The 2093 cm^{-1} band first appears at approximately the same potential as a more intense feature at 2169 cm^{-1} , assigned (below) to solution cyanate. Cyanide is known to be oxidized to cyanate at Pt electrodes¹² as follows:



In the unbuffered pH 11 system, then, the increased absorbance at 2093 cm^{-1} may reflect an increase in the concentration of HCN due to the lowering of the interfacial pH

resulting from the reaction above. This is consistent with the absence of any 2093 cm^{-1} feature in the system buffered at pH 12. The decrease in absorbance at 2093 cm^{-1} observed in the buffered pH 7 solution, where the cyanide would exist almost completely as HCN, indicates a net oxidative depletion of bulk electrolyte cyanide.

The Band at 2169 cm^{-1}

At anodic potentials, this band is generally the most intense feature in the spectrum (*cf.* fig. 4). The position of the band coincides with the $\nu(\text{CN})$ stretching frequency observed for an aqueous potassium cyanate solution (table 1) and is accordingly attributed to cyanate produced by the oxidation of cyanide species as noted above. The 2169 cm^{-1} absorbance first appears at $+0.15\text{ V}$ in pH 12 solution, but is not observed until $+0.3\text{ V}$ in neutral solution.

Although the mechanism by which cyanide is oxidized to cyanate has not been clearly established, it has been postulated to involve initial formation of a surface oxide species, *e.g.* PtHO_2 , which then reacts with cyanide to produce cyanate and a reduced form of the oxide.¹² It has also been suggested that the reaction could involve initial oxidation of cyanide to cyanogen, $(\text{CN})_2$, which is known to hydrolyse rapidly to cyanate in basic solution.¹⁵ Although the data presented here do not provide any direct insight into the possible involvement of surface oxide in the reaction, in no case has any absorption band ascribable to aqueous cyanogen been observed.

On occasion, a weak shoulder on the 2169 cm^{-1} band is observed at 2135 cm^{-1} . While the data in this case are not clear-cut, the 2135 cm^{-1} shoulder is adjacent to characteristic frequencies for a number of products (table 2), including $\text{Pt}(\text{CN})_4^{2-}$ (D_{4h} , E_u : 2133.4 cm^{-1})¹⁰ and adsorbed/coordinated fulminate (CNO^- : $2110\text{--}2200\text{ cm}^{-1}$).¹⁰ Fulminate (CNO^-) represents an alternative, albeit less stable, product of cyanide oxidation than cyanate (NCO^-).

The Bands in the $2200\text{--}2250\text{ cm}^{-1}$ Region

All solutions tested exhibited potential-dependent vibrational bands in the region between 2200 and 2250 cm^{-1} , as shown in fig. 5 for the pH 7 system. As can be seen, disappearance features are evident at *ca.* 2207 and 2247 cm^{-1} at -0.30 V ; at -0.10 V some appearance features are seen, and another disappearance feature at *ca.* 2197 cm^{-1} is found. At all potentials more anodic than this, one feature is consistently present: an appearance band at 2245 cm^{-1} . However, the spectrum between 2200 and 2225 cm^{-1} continues to show changes with potential up to $+1.00\text{ V}$, the anodic limit of the series of experiments.

At potentials above *ca.* $+0.30\text{ V}$, bulk cyanate is forming (the 2169 cm^{-1} band appears) and it is possible that one of the bands in this region at such potentials arises from adsorbed/coordinated cyanate, which would be anticipated to appear in this region. $\text{Ge}(\text{NCO})_4$, for example, displays CN stretching vibrations at 2247 cm^{-1} .¹⁰ However, cyanate is unlikely to be responsible for the disappearance features seen at the more cathodic potentials. Such disappearance features must arise from vibrational frequencies of species which are already adsorbed on the electrode surface at the base potential of -0.50 V used in the pH 7 experiments.

Because of the close overlap of these appearance and disappearance features these spectra are difficult to interpret. It appears, however, that at least two potential-dependent bands are present between *ca.* 2200 and 2250 cm^{-1} . Because of their potential dependence, it would appear that the species responsible for these bands are more closely associated with the electrode surface than the potential-independent band at 2075 cm^{-1} . The voltammetric data indicate that surface coverage of the electrode by cyanide is extensive in the potential region -0.7 V to $+0.4\text{ V}$. Therefore, adsorbed cyanide may be

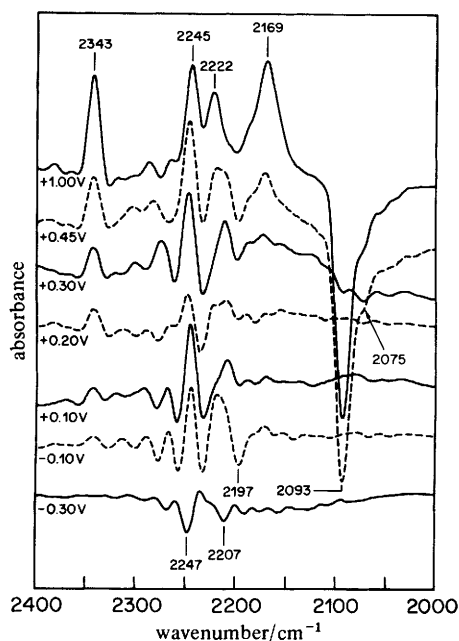


Fig. 5. F.t.i.r. spectra of $0.10 \text{ mol dm}^{-3} \text{ CN}^-$ in contact with a Pt electrode. The solution is buffered to pH 7. The electrode potentials (*vs.* S.C.E.) are shown for each spectrum; the spectrum obtained at $-0.5 \text{ V vs. S.C.E.}$ was used as a reference spectrum to obtain these absorbance spectra.

responsible for the potential-dependent bands between 2200 and 2250 cm^{-1} . These bands are outside the range normally anticipated for adsorbed/coordinated cyanide (2000 – 2200 cm^{-1} , table 1) and far removed from the band near 2100 cm^{-1} assigned to cyanide adsorbed on Ag electrodes.⁵ However, Schardt *et al.*¹⁶ have postulated from LEEDS and Auger spectroscopic studies that at $\text{pH} \leq 9$, cyanide spontaneously adsorbed on Pt(111) single crystals exists largely as neutral hydrogen isocyanide (CNH). Protonation of coordinated cyanide has been found to cause shifts to higher wavenumber of *ca.* 60 cm^{-1} in a number of complexes.¹⁷ $\text{H}_2\text{Pt}(\text{CN})_4$ and $\text{HAu}(\text{CN})_2$, for example, display CN stretching modes at 2203 and 2212 cm^{-1} , respectively.¹⁷ It is therefore possible that the complex behaviour of the bands between 2200 and 2250 cm^{-1} is due to potential-dependent shifts of the vibrations of adsorbed CNH. The appearance of more than one band in this region could be due to the presence of both linearly and bridged CNH, by analogy to the linear and bridged CO detected on polycrystalline Pt surfaces.⁹ Coadsorption of surface oxide, particularly at the positive potentials, could also result in the appearance of more than one band. On silver, cyanide adsorbs in sub-monolayer coverage in which it is '... less likely that the negatively charged cyanide ions maintain densely packed islands...' while on platinum, cyanide spontaneously adsorbs to give a highly ordered densely packed layer.¹⁶ The tendency towards neutralization of this dense ionic layer by protonation would be large, because of the energetically unfavourable nature of a lattice consisting of adjacent, mutually repelling anions.¹⁶ It is possible that for CN^-/Pt , little adsorbed cyanide remains unprotonated.

The Band at 2343 cm^{-1}

This band position agrees with the literature value reported for the asymmetric stretch of aqueous CO_2 (2342.2 cm^{-1}),¹⁸ and is assigned accordingly. At all pH values studied

this band is most evident at potentials corresponding to the oxidation of cyanide to cyanate. These observations suggest that the CO_2 is formed from HCO_3^- as the interfacial pH decreases, while cyanide is oxidized to cyanate. As no special precautions were taken to isolate the basic cyanide solutions from the atmosphere in their preparation and handling, the presence of CO_2 and its ionized forms is assumed to result from the uptake of atmospheric CO_2 . Cyanate is also believed to oxidize to CO_2 and NH_3 ,¹² and this reaction could be partly responsible for the appearance of CO_2 , particularly at the more anodic potentials.

Conclusion

The changes observed in the i.r. spectra of the CN^-/Pt system at different pH and potentials indicate that this system is more complex than either CN^-/Ag or CO/Pt , which were studied previously. It is clear that oxidation of cyanide to cyanate, identified by an i.r. band at 2169 cm^{-1} , is responsible for some of this complexity. In addition, however, the appearance of potential-dependent i.r. bands above 2200 cm^{-1} and the absence of such a band near 2100 cm^{-1} have led us to speculate that cyanide adsorbed on a Pt electrode is to a large extent protonated, as indeed, earlier LEEDS and Auger studies have also suggested.¹⁶ Polarization-modulated FT-IRRAS studies might be helpful in confirming this result. A band at 2075 cm^{-1} has been assigned to CN^- at or beyond the outer Helmholtz plane, based on its small wavenumber shift from solution cyanide and the lack of dependence of its position on electrode potential. This study illustrates the excellent sensitivity of *in situ* f.t.i.r. for the detection of very small quantities of electrochemically generated solution species. Cyanate, for instance, is readily observable at potentials where current flow due to its formation in voltammetric studies is negligible.

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