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Technical Report No. 102

An in situ Surface Fourier Transform Study of Complexes of Lithium, Magnesium
Potassium, and Lanthanum Ferrocyanide at Platinum and Gold Electrodes

by

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Prepared for publication in J. Electroanal. Chem.

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July 15, 1988

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4. PERFORMING ORGANIZATION REPORT NUMBER(S) ONR Technical Report No. 102			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION University of Utah		6b. OFFICE SYMBOL (if applicable)		7a. NAME OF MONITORING ORGANIZATION	
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry Henry Eyring Building Salt Lake City, UT 84112				7b. ADDRESS (City, State, and ZIP Code)	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (if applicable)		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-83-K-0470-P00003	
8c. ADDRESS (City, State, and ZIP Code) Chemistry Program, Code 1113 800 N. Quincy Street Arlington, VA 22217				10. SOURCE OF FUNDING NUMBERS	
				PROGRAM ELEMENT NO.	PROJECT NO.
11. TITLE (Include Security Classification) An in situ Surface Fourier Transform Study of Complexes of Lithium, Magnesium Potassium, and Lanthanum Ferrocyanide at Platinum and Gold Electrodes					
12. PERSONAL AUTHOR(S) D.J. Blackwood and S. Pons					
13a. TYPE OF REPORT Technical		13b. TIME COVERED FROM 9/87 TO 7/88		14. DATE OF REPORT, 1988, Month, Day July 25, 1988	
15. PAGE COUNT 24					
16. SUPPLEMENTARY NOTATION					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) infrared spectroelectrochemistry, platinum		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Attached.					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT ☒ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ OTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified		
22a. NAME OF RESPONSIBLE INDIVIDUAL Stanley Pons			22b. TELEPHONE (Include Area Code) (801) 581-4760		22c. OFFICE

Short communication

AN IN SITU SURFACE FOURIER TRANSFORM INFRARED STUDY
OF COMPLEXES OF LITHIUM, MAGNESIUM, POTASSIUM AND
LANTHANUM FERROCYANIDE AT PLATINUM AND GOLD ELECTRODES

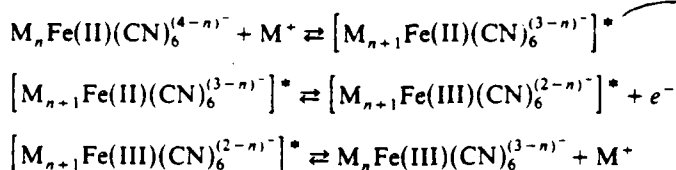
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(Received 6th October 1987; in revised form 15th December 1987)

INTRODUCTION

The $\text{Fe}(\text{CN})_6^{4-/3-}$ redox couple has been the subject of a great deal of research [1-9], with special attention being paid to its non-ideal heterogeneous charge transfer mechanism. Peter et al. (5) have shown that the rate of electron transfer is first order in concentration of the alkali metal cation and increases in the order $\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Cs}^+$. This has led to the proposition of the existence of an activated complex formed between the cation and the complex anion which is already paired to at least one other cation. A three step mechanism for the electron transfer event has then been suggested [7]:



If this mechanism is correct, one would expect that the infrared spectra of the ferrocyanide and ferricyanide species will change as the cation involved is varied. This has indeed been observed for the case of adsorbed hexacyanoferrate species at electrode surfaces and solution cations [1]; the result has been treated theoretically [2]. Weak interactions, such as those between totally solvated cations and anions generally do not give rise to vibrational changes in one ion when the counterion is changed. It is the purpose of this paper to provide direct infrared spectroelectrochemical data concerning the nature of the $\text{M}_n \text{Fe}(x)(\text{CN})_6^{(x-n)-}$ complexes.

* To whom correspondence should be addressed.

[5]

EXPERIMENTAL

The working electrode was either a platinum or gold disk (1 cm diameter), which had been polished to a mirror finish using progressively smaller diameters of alumina down to 0.05 μm . The disk was mounted on the end of a glass syringe barrel designed to fit the infrared cell. The cell construction was of the thin layer type and has been described previously [9].

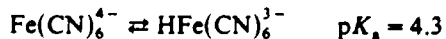
All reagents were of AnalaR grade quality and all solutions were prepared using triply distilled water and deoxygenated with argon. The glassware was thoroughly cleaned by soaking in a $\text{HNO}_3 + \text{H}_2\text{SO}_4$ solution, followed by rinsing with triply distilled water and finally steamed (triply distilled water) for 30 min. The working electrode was cleaned, after polishing, by cycling between -0.2 V and $+0.8 \text{ V}$ vs. SCE, at 50 mV s^{-1} for 15 min in $0.5 \text{ mol dm}^{-3} \text{ KNO}_3$. A platinum wire quasi-reference electrode was used throughout these experiments. The spectrometer employed was a vacuum bench Bruker-IBM model IR/98 FTIR on which subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS [9]) could be performed. In SNIFTIRS difference spectra, the data are displayed so that bands extending to positive (upwards) values of relative reflectance are due to species at the base reference potential ("reactants" in the unperturbed system), while negative bands denote species formed when the potential is stepped to a new value (the "products" of the electrochemical reaction).

RESULTS AND DISCUSSION

We point out first that all spectra recorded in this work are solution spectra; no attempt was made to record the spectra of adsorbed species at the interface. Perturbations in the electrode potential were for the purpose of changing the concentrations (by migration) of the bulk ferro- and ferricyanides in the relatively (to surface spectral techniques) thick layer of solution between the electrode and the cell window.

The pH dependence of the CN stretching region of the vibrational spectra of the ferri-ferrocyanide species was determined first. In neutral solutions ferrocyanide and ferricyanide were observed to absorb at 2040 cm^{-1} and 2116 cm^{-1} respectively as reported previously [7] (Fig. 1).

The addition of $0.01 \text{ mol dm}^{-3} \text{ HClO}_4$ to a solution of $0.01 \text{ mol dm}^{-3} \text{ K}_4\text{Fe}(\text{CN})_6 \cdot 3 \text{ H}_2\text{O}$ and $\text{K}_3\text{Fe}(\text{CN})_6$ resulted in the splitting of the ferrocyanide band into the original 2040 cm^{-1} band and a new feature at 2054 cm^{-1} (Fig. 2). This new band is characteristic of a protonated ferrocyanide species, the characteristics of which have been reported previously [10]:



On increasing the HClO_4 concentration to 0.1 mol dm^{-3} , the 2040 cm^{-1} band disappears and is replaced by a band at 2067 cm^{-1} (Fig. 3). At the same time the

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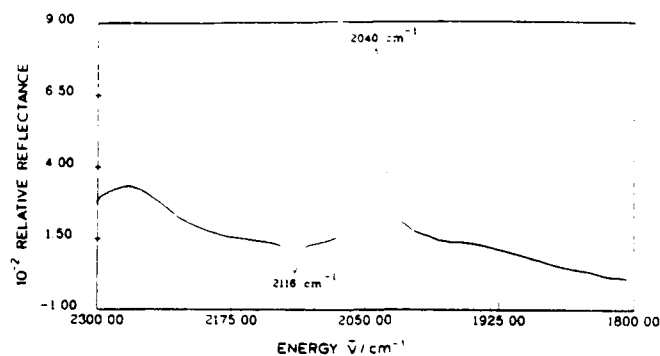


Fig. 1. SNIFTIRS spectra for a platinum electrode in contact with $0.01 \text{ mol dm}^{-3} \text{ K}_4\text{Fe(CN)}_6 \cdot 3 \text{ H}_2\text{O}$, $0.01 \text{ mol dm}^{-3} \text{ K}_3\text{Fe(CN)}_6$, $0.5 \text{ mol dm}^{-3} \text{ KNO}_3$. Reference potential = 0.0 mV , sample potential = $+180 \text{ mV}$ vs. Pt wire.

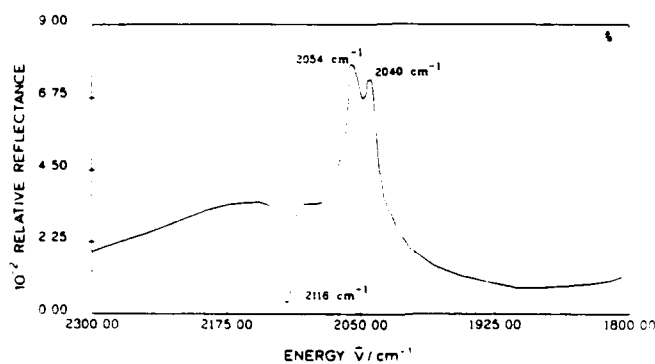


Fig. 2. As Fig. 1, with the addition of $0.01 \text{ mol dm}^{-3} \text{ HClO}_4$ to the solution.

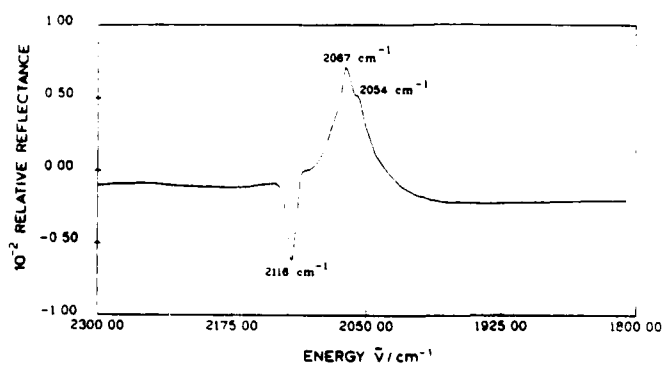


Fig. 3. As Fig. 1, with the addition of $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$ to the solution.

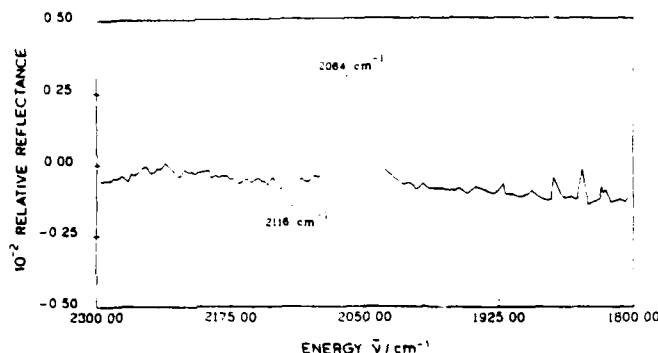
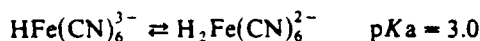


Fig. 4. As Fig. 1, with the addition of $0.5 \text{ mol dm}^{-3} \text{ LaCl}_3$. Reference potential at 0.0 mV, sample potential at +120 mV vs. Pt wire.

color of the solution was observed to change to green. This new band is assigned to the diprotonated ferrocyanide species [10]:



Next, the dependence of the vibrational spectra of the ferrocyanide species on the cation type was investigated. The experiment was performed by adding the various cations to a neutral solution containing $0.01 \text{ mol dm}^{-3} \text{ K}_4\text{Fe(CN)}_6 \cdot 3 \text{ H}_2\text{O}$ and $0.01 \text{ mol dm}^{-3} \text{ K}_3\text{Fe(CN)}_6$ and recording the reflectance infrared spectra at various potentials. It was found that the addition of $0.5 \text{ mol dm}^{-3} \text{ Li}^+$ had no detectable effect on the spectra, whereas $0.2 \text{ mol dm}^{-3} \text{ Mg}^{2+}$ shifted the ferrocyanide absorption band by 2 cm^{-1} to 2038 cm^{-1} . A more dramatic change, however, was observed on the addition of $0.5 \text{ mol dm}^{-3} \text{ La}^{3+}$. This cation caused the solution to turn to a fluorescent yellow, while simultaneously precipitating a pale yellow compound. The CN stretch of the ferrocyanide species was now found to absorb at 2064 cm^{-1} , while the ferricyanide species CN stretch mode remained unchanged at 2116 cm^{-1} (Fig. 4).

In fact, the ferricyanide species was found to absorb always at 2116 cm^{-1} regardless of the type or concentration of cation presents, suggesting that it exists simply as octahedral Fe(CN)_6^{3-} . On the other hand, the absorption of infrared radiation by the ferrocyanide species is shown to be quite dependent on both pH and the nature of the cations in the solution. This suggests that the ferrocyanide species exists as a species which is complexed to at least one cation. Although, as only one infrared active band was observed for each species the average symmetry of the complex must still be octahedral, suggesting that the cation is labile, being entropically coordinated through all six nitrogen atoms.

Evidence for the activated complexes has been limited to some observations of transient and rather weak bands at high initial concentrations of the reactants.

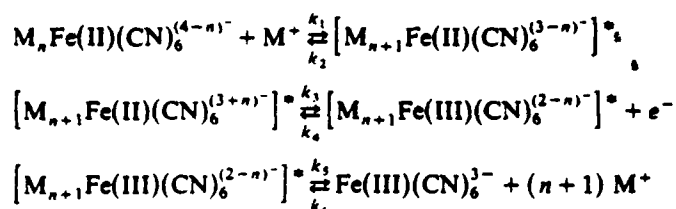
TABLE 1

CN stretch vibrational frequencies for various complexes of the ferrocyanide anion

Complex	Wavenumber $\bar{\nu}/\text{cm}^{-1}$
$\text{Fe(III)(CN)}_6^{3-}$	2116
$\text{K}_n\text{Fe(II)(CN)}_6^{(4-n)-}$	2040
$\text{K}_n\text{HFe(II)(CN)}_6^{(3-n)-}$	2054
$\text{K}_n\text{H}_2\text{Fe(II)(CN)}_6^{(2-n)-}$	2067
$\text{K}_n\text{Li}_m\text{Fe(II)(CN)}_6^{(4-n-m)-}$	2040
$\text{K}_n\text{Mg}_m\text{Fe(II)(CN)}_6^{(4-n-2m)-}$	2038
$\text{K}_n\text{La}_m\text{Fe(II)(CN)}_6^{(4-n-3m)-}$	2064

Efforts at low temperatures are continuing in an effort to isolate any activated complex that may be formed in the reaction.

A likely mechanism is therefore:



with $k_1 \ll k_2$ and $k_5 \ll k_6$. Table 1 lists the various complex species and the observed CN stretching frequencies.

ACKNOWLEDGEMENT

We thank the Office of Naval Research for support of this work.

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