

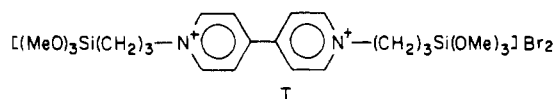
## Potential Dependence of the Stretching Frequency of Carbon Monoxide Bound to the Surface of Platinum Dispersed in an Electrode-Confined Redox Polymer

Jean-Francois André and Mark S. Wrighton\*

Received May 6, 1985

Variation in the electrochemical potential of the electrode results in a change in the stretching frequency of CO bound to elemental Pt dispersed in an electrode-confined redox polymer,  $(PQ^{2+/+})_n$ , derived from an  $N,N'$ -dialkyl-4,4'-bipyridinium monomer. The stretching frequency of the CO, about  $2000\text{ cm}^{-1}$ , can be monitored by transmission infrared spectroscopy using a Fourier transform infrared (FTIR) spectrometer and moves to lower values with movement of the potential to more negative values. Spectroelectrochemical studies were conducted by using an IR-transparent n-Si/ $[(PQ^{2+/+}\cdot Pt(CO)_x)_n]$  electrode assembly in an electrochemical cell with the derivatized surface exposed to the electrolyte solution. Experiments have been carried out with both natural-abundance and 99%  $^{13}\text{C}$ -enriched CO, and the potential dependence is the same, about  $20\text{ cm}^{-1}\text{ V}^{-1}$ , over the potential range studied, approximately 0.0 to  $-1.4\text{ V}$  vs.  $\text{Ag}^+/\text{Ag}$  in  $\text{CH}_3\text{CN}/2\text{ M LiClO}_4$ . The stretching frequency of natural-abundance CO in the same assembly has been studied in  $\text{H}_2\text{O}/3\text{ M LiCl}$  and shows a slightly larger potential dependence, about  $35\text{ cm}^{-1}\text{ V}^{-1}$ , in the range  $-0.2$  to  $-1.0\text{ V}$  vs.  $\text{AgCl}/\text{Ag}$ . The data for the CO bound to the Pt dispersed in the polymer is in accord with similar data obtained for CO bound to smooth Pt electrode surfaces.

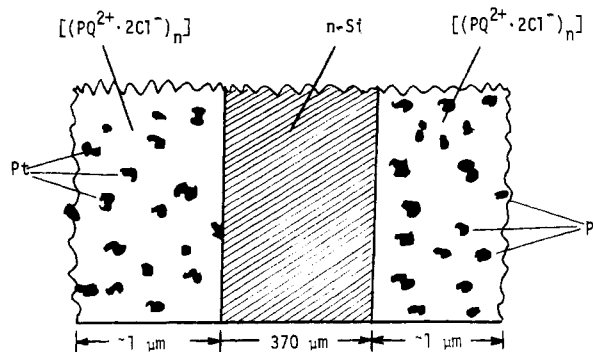
We wish to report the potential dependence of the CO stretching frequency of CO bound to elemental Pt dispersed in an electrode-confined redox polymer. The potential regime considered is one in which the redox polymer undergoes redox reaction and is therefore in charge-transfer equilibrium with the electrode to which the polymer is attached. The system studied in this work is represented by Scheme I, where the  $(PQ^{2+/+})_n$  redox polymer is that derived from hydrolysis of I to form a polysiloxane.<sup>1</sup>



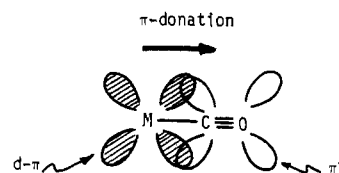
Preparation of such an assembly has been previously described in connection with the use of such electrodes in the electrochemical and photoelectrochemical reduction of  $\text{H}_2\text{O}$ .<sup>2-4</sup> In this paper we show that CO can be bound persistently to the elemental Pt dispersed in the polymer and report the dependence of the CO stretching frequency on the electrode potential.

Inorganic chemists have long known that systematic variation in the electron density on a metal to which CO is bound will result in systematic variation in the position of the IR absorption(s) associated with the C-O stretch.<sup>5</sup> In general, greater electron density on the metal reduces the CO stretching frequency due to the increase in back-bonding, (Scheme II), thereby decreasing the C-O bond order. Substantial shifts are found in a series of isoelectronic, isostructural species such as  $\text{Ni}(\text{CO})_4$ ,  $\text{Co}(\text{CO})_4^-$ , and  $\text{Fe}(\text{CO})_4^{2-}$  having a single IR absorption in the CO stretching region at  $2060$ ,  $1890$ , and  $1790\text{ cm}^{-1}$ , respectively.<sup>6</sup> Additionally, electron-withdrawing and electron-releasing groups in a ligand can have substantial, systematic effects on the positions of the CO absorptions; the series  $(\eta^6\text{-C}_6\text{H}_5\text{F})\text{Cr}(\text{CO})_3$  ( $1996$ ,  $1930\text{ cm}^{-1}$ ),  $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$  ( $1987$ ,  $1917\text{ cm}^{-1}$ ), and  $(\eta^6\text{-C}_6\text{Me}_6)\text{Cr}(\text{CO})_3$  ( $1962$ ,  $1888\text{ cm}^{-1}$ ) illustrates the magnitude of the effects.<sup>7</sup> Of

Scheme I. IR-Transparent Electrode/Polymer/Pt Assembly Used To Determine Potential Dependence of the IR Stretching Frequency of CO Bound to Pt



Scheme II. Back-Bonding from a Transition Metal to Coordinated CO



more direct relevance to the present work is the finding that a change in oxidation level of a given complex results in a substantial change in the CO stretching frequency; the complex  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})]_4$  exists in the  $+1$ ,  $0$ , and  $-1$  redox levels with a single CO absorption in each at  $1696$ ,  $1623$ , and  $1575\text{ cm}^{-1}$ , respectively.<sup>8</sup> It has long been known that the stretching frequency of CO bound to Pt dispersed on supports depends on the support and additives that may interact with the Pt.<sup>9-12</sup> Interestingly, arguments concerning the trends in the CO stretching frequency on high-surface-area Pt parallel those for discrete metal complexes.

Recently, there have been several reports of the demonstration of a potential dependence of  $\text{CO}^{13,14}$  or  $\text{CN}^{-15,16}$  stretching fre-

- (1) Bookbinder, D. C.; Wrighton, M. S. *J. Electrochem. Soc.* **1983**, *130*, 1080.
- (2) Bookbinder, D. C.; Bruce, J. A.; Dominey, R. N.; Lewis, N. S.; Wrighton, M. S. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 6280.
- (3) Dominey, R. N.; Lewis, N. S.; Bruce, J. A.; Bookbinder, D. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 467.
- (4) Bruce, J. A.; Murahashi, T.; Wrighton, M. S. *J. Phys. Chem.* **1982**, *86*, 1552.
- (5) (a) Braterman, P. S. "Metal Carbonyl Spectra"; Academic Press: New York, 1975. (b) Braterman, P. S. *Struct. Bonding (Berlin)* **1976**, *26*, 1. (c) Kettle, S. F. A. *Top. Curr. Chem.* **1977**, *71*, 111. (d) Wender, I., Pino, P., Eds. "Organic Synthesis via Metal Carbonyls"; Interscience: New York, 1968; Vol. 1.
- (6) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 2nd ed.; Interscience: New York, 1966; p 731.
- (7) Fischer, R. D. *Chem. Ber.* **1960**, *93*, 165.

- (8) Ferguson, J. A.; Meyer, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 3409.
- (9) Blyholder, G. *J. Phys. Chem.* **1964**, *68*, 2772.
- (10) Primet, M.; Basset, J. M.; Mathieu, M. V.; Prettre, M. *J. Catal.* **1973**, *29*, 213.
- (11) Queau, R.; Labroue, D.; Poilblanc, R. *J. Catal.* **1981**, *69*, 249.
- (12) Bartok, M.; Sarkany, J.; Sitkei, A. *J. Catal.* **1981**, *72*, 236.
- (13) (a) Kunimatsu, K. *J. Phys. Chem.* **1984**, *88*, 2195. (b) Kunimatsu, K. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *145*, 219.
- (14) (a) Beden, B.; Bewick, A.; Lamy, C. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *148*, 147. (b) Bewick, A. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *150*, 481.

quencies for CO or CN<sup>-</sup> bound to the surface of an electrode. The general notion is that the metallic electrode is enriched in electron density at negative potentials (negative of the point of zero charge)<sup>17</sup> and the stretching frequency of the coordinated molecule can be tuned smoothly by potential variation. A theoretical treatment has been performed that shows that a linear variation in frequency with variation in potential can be expected.<sup>18</sup> In this sense smooth variation of electronic properties of a given metal can be achieved without the usual variation in the steric properties of the ligands.

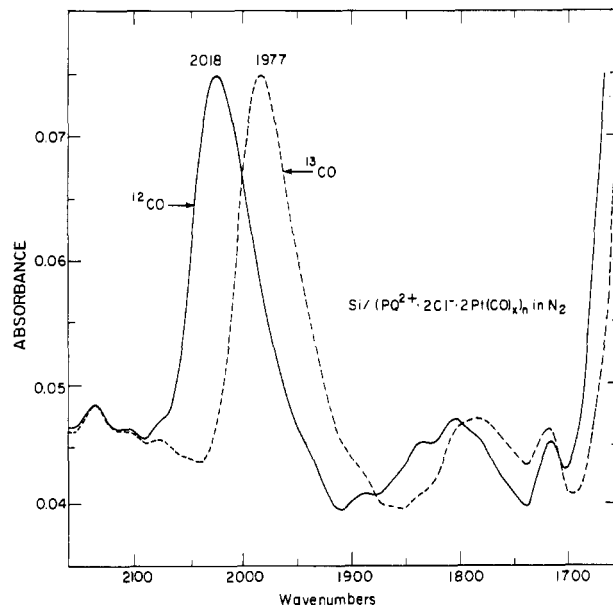
It is known that the reactivity of nucleophiles toward coordinated CO can be correlated with the position of the CO stretching frequency.<sup>19</sup> Our work was undertaken with the aim of demonstrating the use of variation in electrochemical potential to modulate the properties of CO bound to a high-surface-area form of a transition metal. The ultimate hope is to be able to sufficiently modify properties that variation in stoichiometric or catalytic reaction rates can be achieved by variation in electrode potential. We now wish to report our findings concerning the potential dependence of the stretching frequency of CO bound to the high-surface-area Pt dispersed in the redox polymer derived from I.

### Experimental Section

**Electrodes and Surface Derivatization with Reagent I.** Single-crystal n-type Si wafers (P-doped, resistivity 3–7 Ω/cm) with the (111) face exposed were obtained from Monsanto Co., Electronics Division, Palo Alto, CA. The 0.37 mm thick wafers are sufficiently transparent in the IR region that such material can be useful in fabricating IR-transparent electrode assemblies. Electrodes were fashioned from wafers cut into pieces of rough squares of about 1.5 cm<sup>2</sup> exposed area on each side. The top portion of one side of the n-type Si electrode was coated with a Ga–In eutectic to provide an ohmic contact with a Cu wire. The Cu was attached by using Ag epoxy. The Cu-wire lead was encased in a glass tube. The tube was attached with ordinary epoxy, and all exposed surfaces except Si were covered with ordinary epoxy for insulation. The completed IR-transparent electrode provided about 1 cm<sup>2</sup> of electrode area on both sides. The IR beam passed through a portion of the electrode of about 0.3 cm<sup>2</sup>.

The synthesis of reagent I and its use as a derivatizing reagent for Si electrodes have been described previously.<sup>1–4</sup> The n-type Si was pretreated by first etching with HF to remove the insulating air-grown oxide and then washing with H<sub>2</sub>O. The electrode was then dipped into aqueous base for about 10 s, rinsed immediately thereafter with a generous portion of H<sub>2</sub>O followed by a rinse with EtOH, and dried. The derivatization with I was effected by using the electrochemically assisted polymerization procedure previously reported.<sup>1</sup> The coverage of monomer units was determined by an integration of a cyclic voltammogram associated with the interconversion of (PQ<sup>2+</sup>)<sub>n</sub> and (PQ<sup>+</sup>)<sub>n</sub>. The coverage typically employed in the experiments described herein was in the range (2–10) × 10<sup>-3</sup> mol/cm<sup>2</sup>.

**Introduction of Elemental Pt into the Electrode-Confined Redox Polymer.** The Pt was introduced into the redox polymer by exchanging the charge-compensating halides of the polymer for PtCl<sub>4</sub><sup>2-</sup> followed by electrochemical reduction.<sup>2–4</sup> The ion exchange was effected by dipping the n-Si/[(PQ<sup>2+</sup>·2X<sup>-</sup>)<sub>n</sub>] assembly into an aqueous solution of 3 mM K<sub>2</sub>PtCl<sub>4</sub> for 20 min. Electrochemical reduction of the Pt(II) to Pt(0) was effected by cycling the potential of the electrode between -0.2 and -0.85 V vs. SCE at 1 mV/s in aqueous 0.1 M KCl. The complete procedure was repeated once. Thus, each electrode is prepared in such a way as to introduce two Pt atoms per monomer unit of the polymer. It has been established by electron microscopy that such procedures result in the introduction of Pt particles having a dimension of the order of 5 nm<sup>20</sup> that



**Figure 1.** Comparison of the FTIR transmission spectra for n-Si/[(PQ<sup>2+</sup>·2Pt·2Cl<sup>-</sup>)<sub>n</sub>] reacted with <sup>12</sup>CO and <sup>13</sup>CO, illustrating the strong absorption associated with a terminal CO bound to the dispersed Pt. These spectra are recorded for the assembly in a N<sub>2</sub> atmosphere.

are distributed throughout the polymer.

**Carbonylation of Pt Dispersed in the Redox Polymer.** Reaction of a freshly platinized polymer with CO was effected by first placing the derivatized electrodes under vacuum (about 10<sup>-2</sup> torr) at room temperature for 40 min followed by exposure to 2 atm of natural-abundance CO (Matheson) or 99% <sup>13</sup>C-enriched CO (Cambridge Isotopes Lab, Cambridge, MA) for 15 h at room temperature. The electrodes were then pumped under vacuum (10<sup>-2</sup> torr) for 30 min at room temperature to eliminate any weakly bound CO, transferred in a glovebag purged with N<sub>2</sub>, and placed in a thin-layer spectroelectrochemical cell.

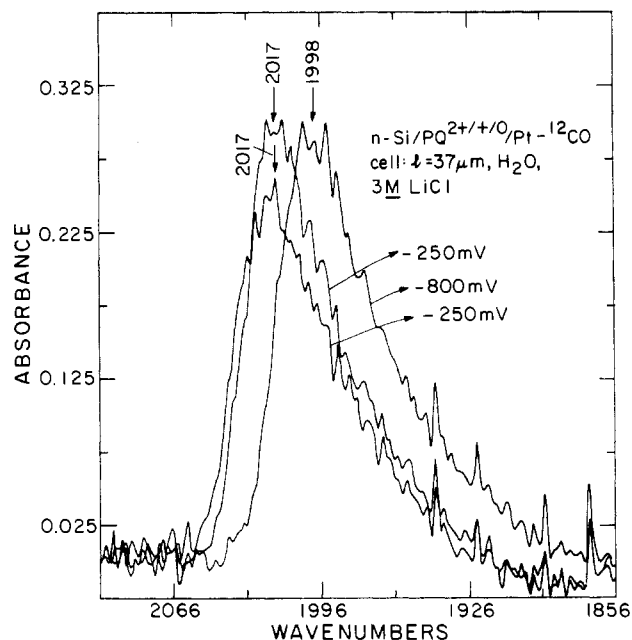
**IR Thin-Layer Spectroelectrochemical Cell.** A thin-layer spectroelectrochemical cell was designed to record transmission IR spectra of electrode assemblies. Cells having a path length of less than 50 μm are necessary to measure spectral changes in aqueous electrolytes. The cell consisted of two CaF<sub>2</sub> windows, one of them drilled as in common IR cells. The two plates were glued together on three sides with a resulting space of 0.407 mm between so that the polished 0.370 mm thick IR-transparent Si electrode could be placed between them. The cell path was measured for an empty cell by the interference pattern found when the FTIR spectrum of the cell was recorded. An optical path length of 37 μm was thus created and contained the electrolyte solution.

A 0.250 mm thick Pt gauze (1 cm<sup>2</sup> geometrical area) was used as the counter electrode and placed in the lower portion of the cell. The Pt counter electrode was contacted with a Pt wire passing through the epoxy to the outside of the cell. The entire assembly was mounted on a conventional solution IR cell holder. The filling holes of the cell were tightly sealed with rubber septa. A conventional Ag<sup>+</sup>/Ag or AgCl/Ag, wire-shaped reference electrode was used and introduced through the septum of one of the filling holes. While held in a vertical position, the cell was filled (with all electrodes in place) under N<sub>2</sub> in a glovebag.

**Electrochemistry.** The three-electrode thin-layer spectroelectrochemical assembly was driven by a PAR Model 173 potentiostat with a Model 175 programmer. A Houston Instruments Model 2000 X-Y recorder was used to record current–potential scans. The AgCl/Ag reference electrode used in aqueous electrolytes was measured to be at -0.04 V vs. SCE in aqueous 1 M KCl at 298 K, and the Ag<sup>+</sup>/Ag electrode was measured to be at +0.35 V vs. SCE in CH<sub>3</sub>CN/0.1 M [*n*-Bu<sub>4</sub>N]BF<sub>4</sub>. Solvents used were HPLC grade, obtained commercially and used after deoxygenation by purging with prepurified N<sub>2</sub> for 20 min. The electrolytes used are commercially available and were used as received. The cell had a large resistance, and current–potential scans were typically recorded at a scan rate of 1 mV/s to ensure proper potential control.

**FTIR Spectroscopy.** Transmission IR spectra were recorded on a Nicolet Model 7199 or 60 SX Fourier transform spectrometer. The optical bench and sample chamber were continuously purged with N<sub>2</sub> to minimize CO oxidation on the Pt and to remove H<sub>2</sub>O and CO<sub>2</sub> from the instrument. Typically, 256 or 512 interferograms were collected at 1 cm<sup>-1</sup> resolution and at a gain value higher than 32. Correction of the interferograms from problems associated with differences in the refractive indices of the cell and N<sub>2</sub> was made prior to transforming. When mea-

- (15) Kunimatsu, K.; Seki, H.; Golden, W. G. *Chem. Phys. Lett.* **1984**, *108*, 195.
- (16) (a) Anderson, A. B.; Kotz, R.; Yeager, E. *Chem. Phys. Lett.* **1981**, *82*, 130. (b) Kotz, R.; Yeager, E. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *123*, 335.
- (17) Bard, A. J.; Faulkner, L. R. "Electrochemical Methods"; Wiley: New York, 1980; Chapter 12.
- (18) Holloway, S.; Nørskov, J. K. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *161*, 193.
- (19) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 299–303.
- (20) Daube, K. A.; Harrison, D. J.; Mallouk, T. E.; Ricco, A. J.; Hendrickson, W. A.; Drube, A. J.; Chao, S.; Wrighton, M. S. *J. Photochem.* **1985**, *29*, 71.



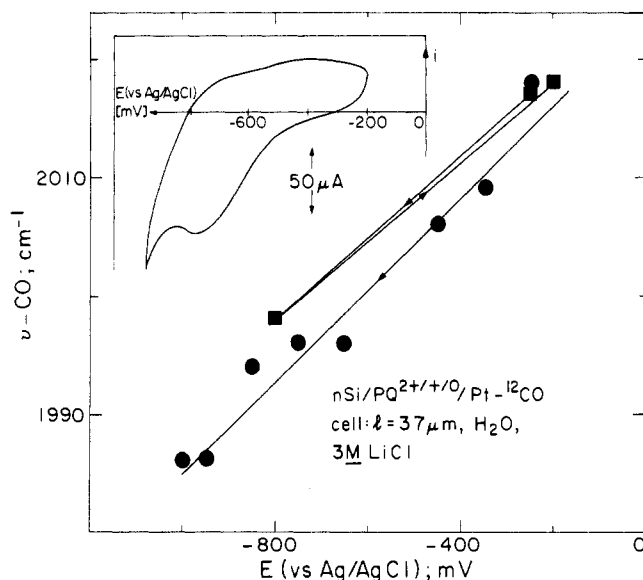
**Figure 2.** Transmission FTIR spectra of  $n\text{-Si}/[(\text{PQ}^{2+/+}/2\text{Pt}(\text{CO})_x)_n]$  at two different potentials in an aqueous electrolyte. The first spectrum was recorded at  $-0.25$  V and the second at  $-0.85$  V; then the potential was returned to  $-0.25$  V and the spectrum recorded to ensure that the shift in the CO stretching frequency is reversible.

Measurements of the CO frequency vs. potential were made, the potential was held constant at the desired potential for a period of 2 min prior to recording the IR spectrum. The reference spectrum in all cases is a polymer-derivatized  $n\text{-Si}$  electrode treated in an identical fashion, including exposure to CO, but not platinized.

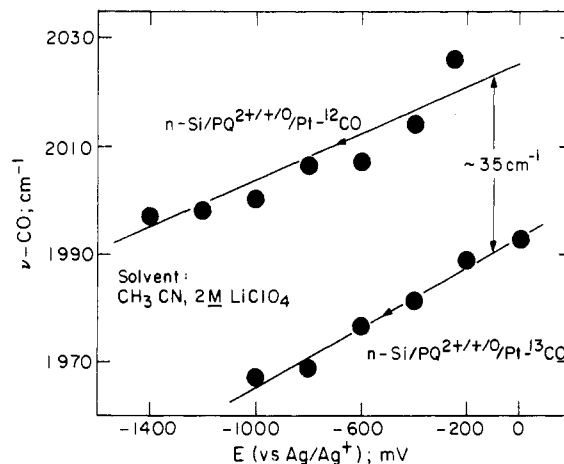
### Results and Discussion

The electrode assembly represented by Scheme 1 reacts essentially irreversibly with gas-phase CO to yield  $\text{Pt-CO}$  species as evidenced by the IR spectral changes that occur upon exposure of the  $n\text{-Si}/[(\text{PQ}^{2+}/2\text{Pt})_n]$  assembly to 2 atm of CO at 298 K. Figure 1 illustrates the IR spectral changes associated with the reaction of the electrode assembly with CO, showing the important feature at about  $2018\text{ cm}^{-1}$  due to a terminal CO absorption. Exposure of a nonplatinized  $n\text{-Si}/\text{polymer}$  assembly to gas-phase CO results in no measurable IR spectral changes in the polymer, allowing the unambiguous conclusion that the Pt dispersed in  $(\text{PQ}^{2+})_n$  is responsible for the strong absorption at  $2018\text{ cm}^{-1}$ . A comparison of the spectral changes when 99%  $^{13}\text{C}$ -enriched CO is used instead of natural-abundance CO is included in Figure 1. The shift in the position of the main absorption of about  $40\text{ cm}^{-1}$  is in accord with the expected mass effect on the absorption. The position of the main absorption is somewhat lower than the position of terminal CO absorption on smooth Pt electrodes.<sup>13,14</sup> A lower frequency terminal CO absorption is in accord with the fact that the environment of the Pt is quite different from that for smooth Pt. The polymer that surrounds the Pt and the charge-compensating anions are likely responsible for the shift to lower frequency. Substantial shifts of the CO frequency have been found depending on the nature of the environment of the bound CO and the coverage of the CO.<sup>9-12</sup> The FTIR spectra, and especially the comparison of the  $^{12}\text{CO}$  and  $^{13}\text{CO}$  data, show weaker absorption at lower frequencies that can be attributed to bridging CO species.<sup>13,14</sup> In the discussion that follows, attention is directed to the dominant absorption at about  $2018\text{ cm}^{-1}$ , since the features due to the bridging CO species are too weak to follow quantitatively upon reduction of the redox polymer.

Figure 2 shows FTIR spectra of the  $n\text{-Si}/[(\text{PQ}^{2+/+}/2\text{Pt}(\text{CO})_x)_n]$  assembly in an aqueous electrolyte at two different potentials. The formal potential of the  $(\text{PQ}^{2+/+})_n$  polymer in aqueous solution is approximately  $-0.55$  V vs. SCE.<sup>1-4</sup> Accordingly, the redox polymer undergoes redox change in moving the electrode potential



**Figure 3.** Plot of the CO stretching frequency as a function of the electrode potential for the  $n\text{-Si}/[(\text{PQ}^{2+/+}/2\text{Pt}(\text{CO})_x)_n]$  assembly in an aqueous electrolyte. The inset shows a slow,  $1\text{ mV/s}$ , linear-sweep voltammogram of the modified electrode showing the reduction of the surface-bound polymer.



**Figure 4.** Potential dependence of the CO stretching frequency for the  $n\text{-Si}/[(\text{PQ}^{2+/+}/2\text{Pt}(\text{CO})_x)_n]$  assembly in a nonaqueous electrolyte solution. Data are shown for both  $^{12}\text{CO}$  and  $^{13}\text{CO}$ .

from one extreme to the other. Figure 3 illustrates a slow-sweep current-potential curve for such a system and gives a plot of the absorption maximum for the bound CO as a function of electrode potential. As can be seen, the position of the CO absorption shifts reversibly upon interconversion of the  $(\text{PQ}^{2+})_n$  and  $(\text{PQ}^+)_n$  states of the polymer. The shift in absorption position is linear with a shift in electrode potential. Quantitatively, the shift is  $35\text{ cm}^{-1}\text{ V}^{-1}$ . The redox polymer is not durable in the  $(\text{PQ}^0)_n$  state in aqueous solution;<sup>1</sup> the  $n\text{-Si}$  is not durable at potentials more positive than about  $-0.2$  V vs. SCE in aqueous electrolytes, and oxidation processes require absorption of band gap or greater light to create minority carriers.<sup>21</sup> Thus, the potential range that can be examined in aqueous electrolyte is limited to approximately that shown in Figure 3.

Figure 4 illustrates the data obtained for the  $n\text{-Si}/[(\text{PQ}^{2+/+}/2\text{Pt}(\text{CO})_x)_n]$  assembly in  $\text{CH}_3\text{CN}/2\text{ M LiClO}_4$ . Data are included for an electrode treated with natural-abundance CO and for an electrode treated with 99%  $^{13}\text{C}$ -enriched CO after the platinization step. The potential range examined includes the potential regime where the redox polymer can be varied from the

(21) Bocarsly, A. B.; Walton, E. G.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 3390.

oxidized to the one-electron reduced and to the two-electron reduced states. An approximately linear relationship between electrode potential and the CO stretching frequency is found for both  $^{12}\text{CO}$  and  $^{13}\text{CO}$ , but the variation in the position with potential is somewhat smaller than in the aqueous electrolyte. The shift in the nonaqueous electrolyte is about  $20\text{ cm}^{-1}\text{ V}^{-1}$ . The shift of the stretching frequency upon replacement of  $^{12}\text{C}$  by  $^{13}\text{C}$  is about the same as in the aqueous solution,  $35\text{ cm}^{-1}$ .

The results illustrated in Figures 2-4 are in accord with the conclusion that increased electron density at the Pt surface will result in a lower frequency for CO bound to the surface of the Pt. The magnitude of the shift in frequency is quite similar to that found by other workers<sup>13,14</sup> for CO on smooth Pt in acidic aqueous solution, even though the earlier work was carried out in a different potential regime, generally no more negative than the  $\text{H}_2$  evolution potential. The results presented here elaborate the earlier findings in showing that the electrode potential can be used to effect variations in the properties of coordinated CO in a wide range of media and for situations where the Pt surface area is high. Since the shift in the CO stretching frequency varies with a change in the n-Si electrode potential, it can be concluded that the dispersed Pt is in charge-transfer equilibrium with the Si via the redox polymer. This conclusion has been drawn independently from studies of  $\text{H}_2$  evolution from electrodes like that represented in Scheme I.<sup>2-4</sup>

We have developed the results as if the changes in the CO stretching frequency occur because the Pt is moved more negative in potential and its surface is therefore more electron-rich. It must be noted that the mechanism for achieving the lower stretching frequencies involves reduction of the redox polymer, which changes the environment about the Pt. Not only does the redox polymer change, but the number of anions is also diminished. In one view, the redox polymer can be regarded as a coligand with adjustable electron donor ability to the Pt. This is analogous to being able to adjust the electron donor ability of the arene group in (arene) $\text{M}(\text{CO})_3$ , for example, without changing the steric properties. Another mechanism for affecting the CO stretching frequency of electrode-bound CO is the electric field changes associated with the near-electrode region. The bound CO is certainly in the double-layer region, and it is not clear whether the field can alter the spectral properties to the extent and in the direction found. It is known that there can be consequences on electrode reaction rates associated with species in the double-layer region.<sup>17</sup> But whatever the mechanism, the point is that a large amount of CO

that can be bound to dispersed Pt can be manipulated with respect to important physical and chemical properties to a significant extent when the redox polymer can equilibrate with the Pt and with the conducting substrate onto which the polymer is immobilized.

It is interesting to compare the absolute magnitude of the shifts in the CO stretching frequencies with discrete metal complexes like those mentioned in the introduction. The magnitude of the shift that can be observed for the CO bound to the dispersed Pt is of the same order as can be obtained for variation in substituents in ligands like  $\text{C}_6\text{H}_6$  or  $\text{C}_5\text{H}_5^-$ ,<sup>5-7</sup> and interestingly, the variation found here is also of the same order as typically found upon one-electron oxidation or reduction of metal carbonyl species.<sup>8,22</sup> Since there are many situations where large changes in reactivity of coordinated ligands can be effected by changes in the electron density on the metal, the results found here suggest that high-surface-area electrodes based on dispersed metals may prove useful in modulating the reactivity of substrates that coordinate to the metal. A reaction that may illustrate such effects is represented by the exchange of oxygen of  $\text{H}_2\text{O}$  with the oxygen of CO bonded to metals.<sup>23</sup> Work on such exchange chemistry is under way in this laboratory to attempt to demonstrate that electrode potential can be used to modulate the reactivity of coordinated molecules in a manner consistent with changes in the spectroscopy of coordinated ligands. Correlating the potential dependence of spectral changes and reaction rates may allow conclusions regarding the mechanism of effecting the changes in the infrared spectrum of electrode-bound CO.

**Acknowledgment.** We thank the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, for support of this research. J.-F.A. also acknowledges support as a Postdoctoral Fellow from the Swiss National Science Foundation, 1983-1985. We wish to acknowledge the contributions of Drs. Raymond N. Dominey and Alan B. Fischer in the early work on the carbonylation of Pt-impregnated redox polymer, including the spectral results presented in Figure 1.

**Registry No.** I, 74173-49-2;  $\text{LiClO}_4$ , 7791-03-9;  $\text{LiCl}$ , 7447-41-8;  $^{13}\text{CO}$ , 1641-69-6; Si, 7440-21-3; Pt, 7440-06-4.

- (22) Summers, D. P. Ph.D. Thesis, Massachusetts Institute of Technology, 1984.  
 (23) (a) Muetterties, E. L. *Inorg. Chem.* **1965**, *4*, 1841. (b) Darensbourg, D. J.; Froelich, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 4726.

Contribution from the Department of Chemistry,  
 Iowa State University, Ames, Iowa 50011

## Kinetics and Mechanism of the Reaction of $\text{CrO}_2^{2+}$ with Hydrazinium Ions in Aqueous Acidic Solutions

Suzanne L. Bruhn, Andreja Bakac, and James H. Espenson\*

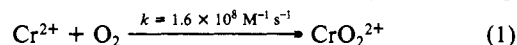
Received August 19, 1985

Hydrazinium ion is oxidized by  $\text{CrO}_2^{2+}$  in aqueous perchloric acid at a rate given by  $-\text{d}[\text{CrO}_2^{2+}]/\text{dt} = (k_0 + k[\text{N}_2\text{H}_5^+][\text{H}^+])[\text{CrO}_2^{2+}]$ , with  $k_0 = 7 \times 10^{-4}\text{ s}^{-1}$  and  $k = 58.1$  ( $\mu = 0.10$ ) and  $50.4$  ( $\mu = 1.0$ )  $\text{M}^{-2}\text{ s}^{-1}$  at  $25.0^\circ\text{C}$ . The rate-limiting step is believed to be formation of the protonated hydrazyl radical cation, which reacts further when  $\text{HCrO}_4^-$  is added but otherwise disproportionates.

### Introduction

In dilute aqueous solutions neither  $\text{N}_2\text{H}_4$  nor  $\text{N}_2\text{H}_5^+$  reacts with  $\text{O}_2$ , although neat hydrazine does react with molecular oxygen. Since  $\text{O}_2$  can be activated by coordination,<sup>1-4</sup> we have investigated

$\text{CrO}_2^{2+}$  (eq 1). It is a species<sup>5,6</sup> that is sufficiently long-lived and well characterized<sup>7</sup> to be studied in the absence of  $\text{Cr}^{2+}$  and  $\text{O}_2$ .



- (1) Endicott, J. F.; Kumar, K. *ACS Symp. Ser.* **1982**, *No. 198*, 425.  
 (2) Spiro, T. G., Ed. "Metal Ion Activation of Dioxigen"; Wiley: New York, 1980.

- (3) Hayaishi, O., Ed. "Molecular Mechanisms of Oxygen Activation"; Academic Press: New York, 1976.  
 (4) Schultz, J.; Cameron, B. F., Eds. "The Molecular Basis for Electron Transport"; Academic Press: New York, 1972.