a five-coordinate one, when the complex is located in the boundary layer of surfactant molecules. The complex is surrounded by the rigid structures of surfactant molecules so that there is not enough room for the formation of a spacious five-coordinate intermediate. Second, the substituting ligand in the present studies is a negatively charged ion, not the neutral one as in the previous papers. Thus, an entering ligand should overcome the electrostatic repulsion, if an associative five-coordinate intermediate is formed. On the other hand, when a three-coordinate intermediate is formed, the leaving ligand acquires electrostatic energy. At the present stage it is not certain which of the above two possibilities is the more

predominant factor for the appearance of the three-coordinate intermediate. We are now intending to perform the kinetic study of ligand substitution of CoX_4^{2-} type complexes in inert solvents.

Evaluation of Rate Constants for Redox Self-Exchange Reactions from Electrochemical Measurements with Rotating-Disk Electrodes Coated with Polyelectrolytes

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A procedure is described for estimating rates of electron self-exchange between multiply charged redox reactants by simple electrochemical measurements with rotating-disk electrodes coated with polyelectrolyte films that spontaneously incorporate the redox reactants by electrostatic attraction. Self-exchange rate constants for the $IrCl_6^{2-/3-}$ and $Fe(CN)_6^{3-/4-}$ couples were evaluated with the new technique to demonstrate its capabilities. The limitations of the method are also described.

Recently we described the versatility of polymer and polyelectrolyte coatings in fashioning electrode surfaces that spontaneously bind large quantities of metal complexes.[1-4] Redox catalysts may be incorporated in such coatings and used to catalyze or mediate electron transfer between the electrode surface and reactants present in the solution.[3] Another possible application of such coated electrodes exists when the species incorporated in the coating is also present in the solution being studied. Under appropriate conditions, the current flowing at such electrodes is limited by the rate of the electron-exchange reaction between the solution-phase reactant and its oxidized (or reduced) counterpart confined within the polyelectrolyte film at the electrode surface. In this paper we describe measurements of such self-exchange rates with two anionic redox couples bound electrostatically to polycationic coatings on graphite electrodes. Related studies have been described recently in which electron-transfer mediators were bound to other kinds of electrode surfaces by nonelectrostatic bonding procedures.[5,6]

Experimental Section

Materials. Pyrolytic graphite electrode were obtained, prepared, and mounted for use as rotating disks as previously described.[1,3] Poly(4-vinylpyridine), PVP, precipitated from methanol–ether, had an average molecular weight of 7.4×10^5. K_2IrCl_6 (RIC) and $K_3Fe(CN)_6$ (Mallinckrodt) were used as received. Supporting electrolytes were prepared from CF_3COOH and CF_3COONa. PVP coatings were prepared as previously described[3] by evaporation of measured aliquots of methanolic solutions of the polymer on the surface of freshly cleaved electrodes. The quantities of the anionic reactants,

$IrCl_6^{2-}$ or $Fe(CN)_6^{3-}$, incorporated by protonated PVP films were determined by transferring the electrodes to solutions of pure acidic supporting electrolyte and immediately integrating the current–time curves obtained when the electrode potential was stepped to values well beyond the voltammetric peak potential for reduction of the incorporated reactant. The integration was continued until the current had decreased to background levels. Repetition of the integration procedure showed that only a few percent of the incorporated reactant was lost from the coating during the integration.

Apparatus and Procedures. Cyclic voltammograms were obtained with PAR Model 173 and 175 instruments (EG & G Instrument Co., Princeton, NJ) and a Houston Instruments X–Y recorder. Rotating-disk current–potential curves were measured with a Pine Instrument Co. (Grove City, PA) electrode rotator and control potentiostat. As noted previously,[3] inclined rather than flat current plateaus were encountered at rotation rates above about 1000 rpm because of inevitable failures in mounting the electrode surfaces exactly perpendicular to their axis of rotation and because the surfaces were not polished. In such cases, limiting currents were taken to be the intersection of lines drawn tangent to the steeply rising portion of the current–potential curve and to the inclined current plateau. Rotating-disk current–potential curves were recorded by scanning the electrode potential at 30 mV s^{-1}. This scan rate produced current peaks in the initial portion of the current–potential curves at low rates of rotation arising from the reduction of the incorporated reactant (e.g., Figure 3). However, as expected, there was no dependence of the steady-state limiting currents on the rate of potential scan. All measurements were conducted at ambient temperature (22 ± 2 °C) in solutions freed of oxygen by bubbling with prepurified argon. Potentials were measured and are reported with respect to a sodium chloride saturated calomel electrode, SSCE.

Results and Discussion

Figure 1A shows a set of cyclic voltammograms recorded successively at a graphite electrode coated with poly(4-vinylpyridine), PVP, in a 2-mM solution of $IrCl_6^{2-}$ at pH 1. The pyridine groups in the polymer coating are protonated at this pH[7] so that the electrode is covered with a polycationic film that spontaneously incorporates multiply charged anions by ion exchange.[2] The incorporation of $IrCl_6^{2-}$ anions by the

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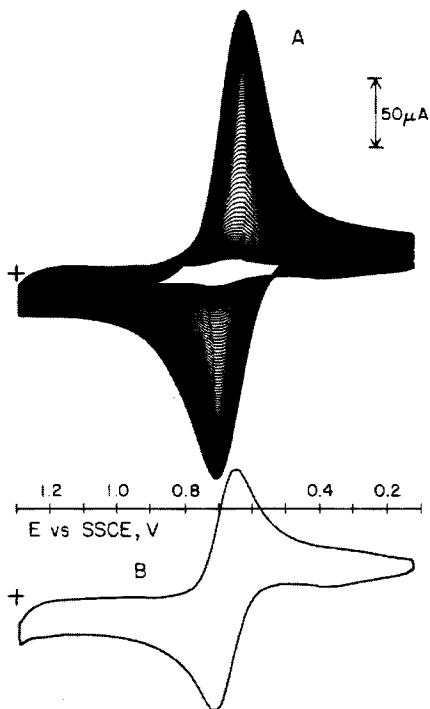(7) Nishikawa, H.; Tsuchida, E. *J. Phys. Chem.* **1975**, *79*, 2072.

Figure 1. (A) Cyclic voltammograms recorded successively in a 2-mM solution of $IrCl_6^{2-}$ at pH 1 with a pyrolytic graphite electrode coated with 4×10^{-7} mol cm^{-2} of pyridine as PVP (scan rate 500 mV s^{-1}; supporting electrolyte 0.1 M CF_3COOH + 0.1 M CF_3COONa). (B) Cyclic voltammogram for the same solution with an uncoated electrode.

Figure 2. Schematic representation of electron conduction between an electrode and reactants in solution when the two are separated by a polyelectrolyte coating in which the hexachloro complexes of Ir(III) and Ir(IV) are incorporated. The Levich layers are hydrodynamic layers formed at the polymer–electrolyte interface when the coated electrode is used as a rotating disk.[8] The thickness of the Levich layer is inversely proportional to the square root of the rate of rotation of the electrode.

electrode coating in Figure 1A is evident from the steady increases in peak current. It is noteworthy that the first few scans produce very small peak currents and only after about 10 or 20 scans do the peak currents become as large as that obtained in the same solution before the electrode was coated (Figure 1B). This demonstrates that the polycationic coating prevents the reduction of $IrCl_6^{2-}$ from proceeding at the electrode until a sufficient quantity of the reactant is incorporated into the coating to provide a pathway for the conduction of electrons from the graphite to the electrolyte via the polymer film.

Figure 2 depicts schematically the mechanism of electron transport across the polyelectrolyte coating that we envision under conditions where the polymer coatings on the electrode surface are uniform and thick enough to prevent solution-phase reactants from reaching the graphite surface. When the rate of electron exchange between pairs of the bound complexes is sufficiently high, the observed currents are limited by the rate of electron transfer between reactant bound at the polymer/electrolyte interface and solution-phase reactant that arrives there. This provides a simple and convenient means for measuring the rate of this self-exchange reaction.

The experiments are facilitated by employing the coated electrodes as rotating-disk electrodes in order to control the rate of supply of reactant from the solution to the electrode surface.[8] The thickness of the unstirred layer of solution next to the electrode surface that the reactants must traverse in such experiments is controlled by the rate at which the disk electrode is rotated according to hydrodynamic relationships derived by Levich.[8] Figure 3 shows a typical set of current–potential curves for the reduction of $IrCl_6^{2-}$ in an acidic supporting electrolyte at a rotating pyrolytic graphite disk coated with a rather heavy coating of PVP. The current responses on the rising portion of the current–potential curves include contri-
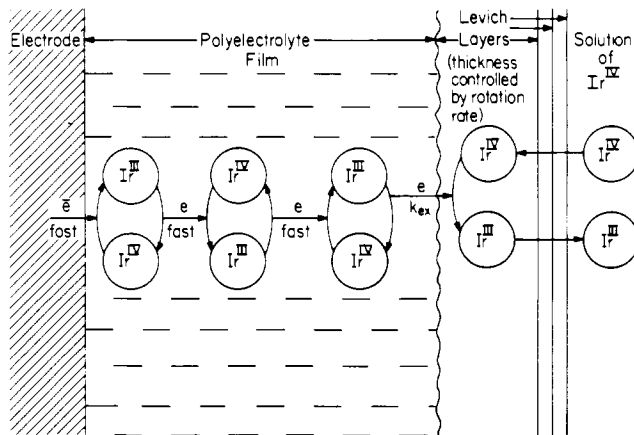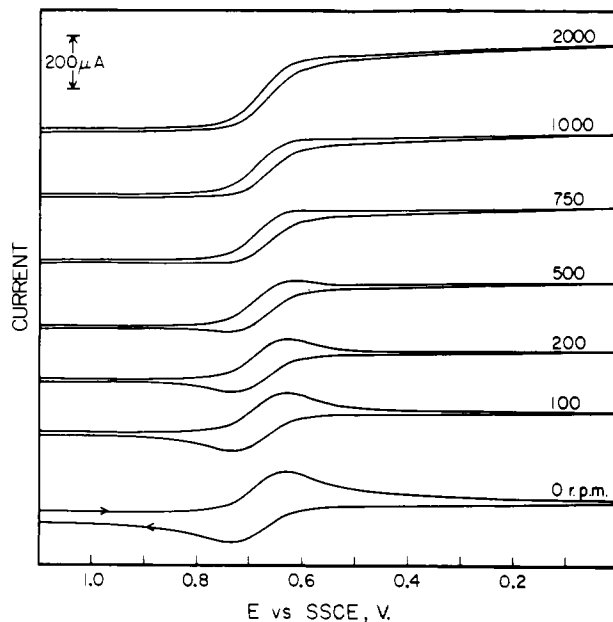

Figure 3. Current–potential responses at a pyrolytic graphite rotating-disk electrode coated with 4×10^{-7} mol cm^{-2} of pyridine as PVP in a 2-mM solution of $IrCl_6^{2-}$ (electrode area 0.2 cm^2; supporting electrolyte 0.1 M CF_3COOH + 0.1 M CF_3COONa). The disk rotation rate is indicated on each curve. The potential of the disk was scanned at 30 mV s^{-1}.

butions from the incorporated reactant, and that is the reason that a peaked current response appears at low rotation rates. However, at potentials on the limiting current plateaus the incorporated reactant is fully reduced so that it does not contribute to the measured limiting currents. Nevertheless, $IrCl_6^{3-}$ held within the polyelectrolyte may mediate electron transfer between the electrode and the $IrCl_6^{2-}$ ions in solutions as depicted in Figure 2.

Similar curves resulted with thinner coatings of PVP, but coatings containing more than ca. 4×10^{-7} mol cm^{-2} of pyridine units proved less stable on rotating electrodes and were therefore avoided.

Figure 4 summarizes the results of a series of rotating-disk experiments in the form of Levich plots[8] of the limiting reduction currents vs. the square root of the electrode rotation rate which is inversely proportional to the thickness of the

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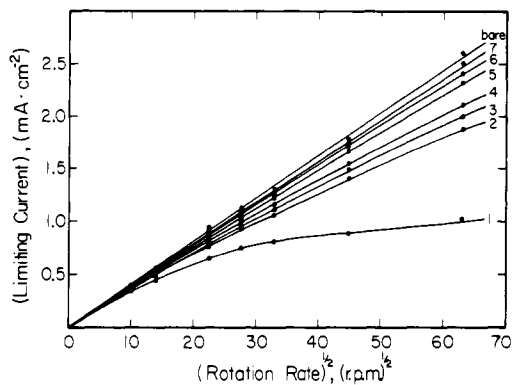
Figure 4. Levich plots for the reduction of 4 mM $IrCl_6^{2-}$ at a rotating-disk graphite electrode coated with increasing quantities of PVP. The uppermost line is for an uncoated electrode. The PVP coatings for the remaining curves contained (1) 400, (2) 81, (3) 40, (4) 16.2, (5) 8.1, (6) 4.0, and (7) 1.6×10^{-9} mol cm^{-2} of pyridine units. Other conditions are as in Figure 3.
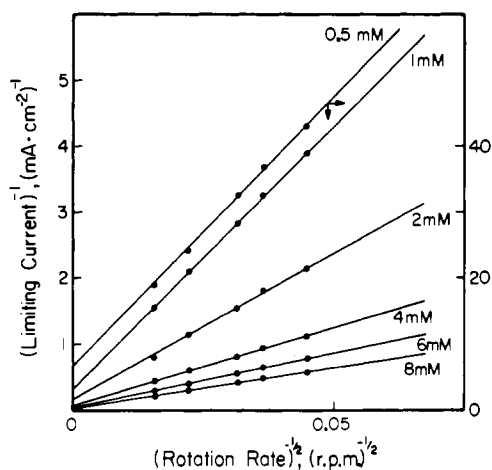

Figure 5. Koutecky–Levich plots for the reduction of $IrCl_6^{2-}$ at a rotating-disk graphite electrode coated with 4×10^{-9} mol cm^{-2} of pyridine as PVP. The concentration of $IrCl_6^{2-}$ is indicated on each plot. Other conditions are as in Figure 3.

Levich layer (Figure 2). The expected linearity is obtained at an uncoated electrode, but increasing deviations appear as the quantity of polyelectrolyte in the electrode coating is increased. For each thickness of the polyelectrolyte coating, data such as those in Figure 4 may be analyzed by means of Koutecky–Levich reciprocal plots[9] as shown in Figure 5. The slopes of these straight lines are (inversely) proportional to the bulk concentration of the reactant, and their finite intercepts give the (reciprocal of the) current that passes when the supply of reactant is so great that its concentration is not decreased at the electrode surface despite the current flow. (At uncoated electrodes this current is unlimited so the corresponding Koutecky–Levich plot passes through the origin). Under conditions where the rate of penetration of the polymer coating by the reactant is negligible the current may be limited by the rate of the electron-transfer reaction between incorporated and solution-phase reactant. This was the case for the $IrCl_6^{2-/3-}$ couple. (The current could be limited, instead, by the rate of electron conduction through the polyelectrolyte layer. In this case, however, the intercepts of the Koutecky–Levich plots would show a dependence on changes in the concentration of reactant in the solution phase only to the extent that these produced changes in the quantity of reactant incorporated by

Table I. Dependence of Rate Constants for Electron Exchange between $IrCl_6^{2-}$ in Solution and $IrCl_6^{3-}$ Incorporated in a Polyelectrolyte Coating on the Concentration of $IrCl_6^{2-}$

$10^6 \times$ $C^b_{Ir(IV)}$, mol cm^{-3}	$10^{10} \times$ $\Gamma_{Ir(III)}$,[a] mol cm^{-2}	$10^3 \times$ $(i_L)_\infty$,[b] A cm^{-2}	$10^{-4} \times$ $(k_{ex})_{app}$,[c] M^{-1} s^{-1}
8	10.2	48	5.9
6	9.2	34	5.9
4	7.0	19	5.9
2	5.9	6.6	5.7
1	4.5	2.6	6.1
0.5	2.6	0.76	5.8

[a] Γ_{PVP} was fixed at 4.0×10^{-9} mol cm^{-2} of pyridine units. [b] Obtained from the intercepts of plots such as those in Figure 5. [c] $(k_{ex})_{app} = 10^{-3}(i_L)_\infty [FC^b_{Ir(IV)}\Gamma_{Ir(III)}]^{-1}$; see text.
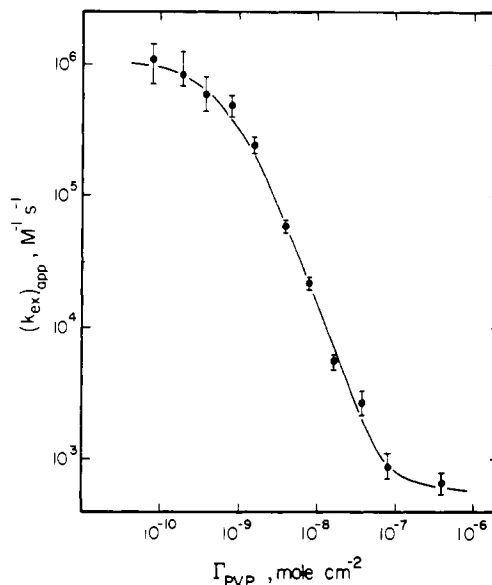

Figure 6. Apparent rate constants for electron exchange between Ir(III) confined within a polyelectrolyte film and Ir(IV) in solution as a function of the quantity of PVP used to form the film. The range of experimental values for the rate constants at each value of Γ_{PVP} is indicated by the bars on each data point.

the polyelectrolyte layer.[3] Linear Koutecky–Levich plots with intercepts that remain proportional to the product of the reactant concentrations in the solution and polyelectrolyte phases (Table I) essentially rule out the possibility that the current is limited by conduction of electrons through the polyelectrolyte layer.) The intercepts of the Koutecky–Levich plots in Figure 5 were therefore identified with the values of the limiting current density, $(i_L)_\infty$, given by eq 1, where F is

$$(i_L)_\infty = F(k_{ex})_{app}\Gamma_{Ir(III)}C^b_{Ir(IV)} \qquad (1)$$

the Faraday, $(k_{ex})_{app}$ is the apparent second-order rate constant for the reaction between the $IrCl_6^{3-}$ incorporated by the polyelectrolyte coating (to the extent of $\Gamma_{Ir(III)}$ mol cm^{-2}) and the $IrCl_6^{2-}$ present in the solution (at concentration $C^b_{Ir(IV)}$ mol cm^{-3}). (The units of $(k_{ex})_{app}$ in eq 1 are mol^{-1} cm^3 s^{-1} so that the measured values need to be multiplied by 10^{-3} for comparison with the usual homogeneous self-exchange constants that are typically reported in units of mol^{-1} L s^{-1}.)

At each fixed thickness of the PVP coatings the intercepts of plots such as those in Figure 5 correspond to a consistent value of $(k_{ex})_{app}$. A representative set of data is shown in Table I. However, the resulting values of $(k_{ex})_{app}$ are affected strongly by changes in the thickness of the polyelectrolyte coatings as would be expected if only a fraction of the $IrCl_6^{3-}$ in the polyelectrolyte film is accessible for reactions with the $IrCl_6^{2-}$ that arrives at the polymer solution interface.[3] Figure

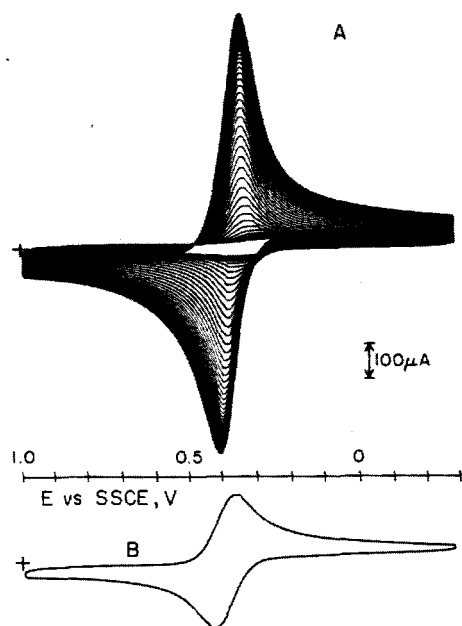(9) Koutecky, J.; Levich, V. G. *Zh. Fiz. Khim.* **1956**, *32*, 1565 and ref 8, p 345–57.

Figure 7. (A) Successively recorded cyclic voltammograms for the reduction of 2 mM $Fe(CN)_6^{3-}$ at a graphite electrode coated with 4×10^{-7} mol cm^{-2} of pyridine as PVP (scan rate 500 mV s^{-1}; supporting electrolyte 0.2 M CF_3COONa–0.1 M CF_3COOH). (B) Cyclic voltammogram for the same solution with an uncoated electrode.

6 shows a set of apparent rate constants evaluated at a fixed concentration of $IrCl_6^{2-}$ but with differing quantities of polyelectrolyte applied to the electrode surface. As the thickness of the polyelectrolyte coating is decreased, the apparent rate constants level off at a value slightly larger than that measured in homogeneous solutions of $IrCl_6^{2-}$ and $IrCl_6^{3-}$, namely, 2.5 $\times 10^5$ M^{-1} s^{-1}.[10] This suggests that incorporation of one of the reacting anions by the polyelectrolyte film does not diminish its redox reactivity and may even enhance it slightly.

The smallest apparent rate constant plotted in Figure 6 was obtained at an electrode to which a very thick PVP coating had been applied. Polyelectrolyte is gradually lost from such thick coatings as the electrode is rotated, and we suspect that the apparent rate constant obtained in this case actually corresponded to a lower value of Γ_{PVP} than indicated in the figure. Thus, the indication of a lower limiting value in the apparent rate constant is probably illusory.

The same procedure also proved successful in measuring a self-exchange rate for the $Fe(CN)_6^{3-}$–$Fe(CN)_6^{4-}$ couple. Figure 7A shows the cyclic voltammetric responses obtained at a PVP-coated electrode in acidic solutions of $Fe(CN)_6^{3-}$, and Figure 7B is for an uncoated electrode. As with the $IrCl_6^{2-}$ system, the polyelectrolyte coating initially inhibits the reduction of $Fe(CN)_6^{3-}$ until its incorporation by the coating provides an electron conduction pathway. The almost equal values of the peak potentials and the approximately 90 mV width at half-height of the current-potential curves show that rather high rates of electron transfer prevail with the fully developed waves.

Figure 8 shows a set of Koutecky–Levich plots prepared from rotating-disk data for the $Fe(CN)_6^{3-}$–$Fe(CN)_6^{4-}$ system, and Figure 9 presents the values of apparent self-exchange constants calculated from the intercepts of lines such as those in Figure 8. The value of the apparent self-exchange constant measured with the thinnest PVP coating approaches 10^7 M^{-1} which is considerably larger than the values reported in experiments with homogeneous solutions of the reactants.[11,12]
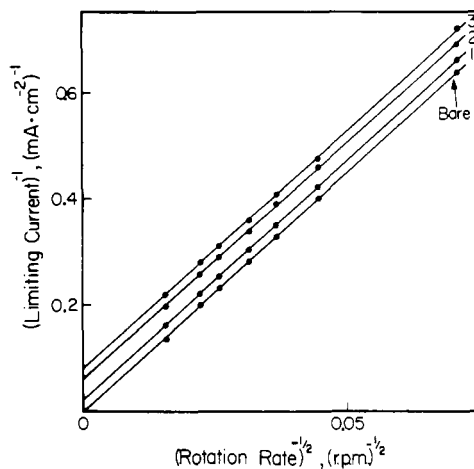

Figure 8. Koutecky–Levich plots for the reduction of 10 mM $Fe(CN)_6^{3-}$ at rotating-disk electrodes coated with increasing quantities of protonated PVP containing electrostatically bound $Fe(CN)_6^{4-}$. The PVP coatings contained (1) 0.4, (2) 2, and (3) 4×10^{-7} mol cm^{-2} of pyridine units (supporting electrolyte 0.2 M CF_3COONa–0.1 M CF_3COOH).

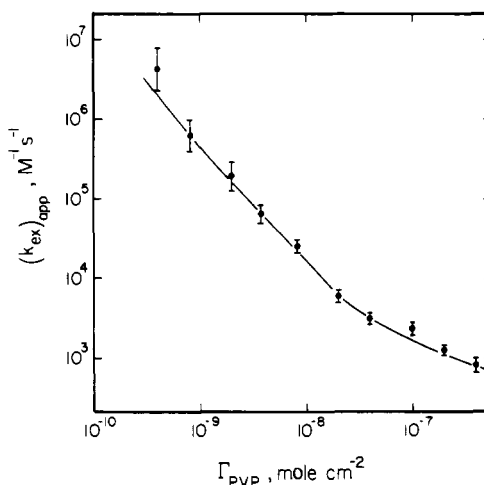**Figure 9.** Apparent rate constants for electron exchange between $Fe(CN)_6^{4-}$ confined within a polyelectrolyte film and $Fe(CN)_6^{3-}$ in solution as a function of the quantity of PVP used to form the film.

However, the self-exchange rate in homogeneous solutions is exceedingly sensitive to the nature and concentration of supporting electrolytes present: a rate constant of 2×10^2 M^{-1} s^{-1} was estimated at zero ionic strength[12] while values near 10^5 M^{-1} s^{-1} result at high ionic strength.[11] The ionic strength dependence is believed to reflect an enhanced reactivity of the reactants when their mutual coulombic repulsion is diminished by the formation of ion pairs with cations from the supporting electrolyte.[12] Pronounced enhancement of the self-exchange between multiply charged can also be produced by the addition of soluble polyelectrolytes.[13] Thus, the unusually large self-exchange rates observed for the $Fe(CN)_6^{3-/4-}$ couple when one of the coreactants is confined within thin polycationic films are a reflection of the significant suppression of the coulombic repulsion between the reactants.[14] For example, the contribution of coulombic repulsion to the free energy of activation for the homogeneous self-exchange reaction has been estimated to be 5.7 kcal[12] which corresponds to a factor of $\sim 10^4$ in the

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rate constant for self-exchange. The absence of a similar effect with the $IrCl_6^{2-/3-}$ couple is in line with the lower sensitivity of the self-exchange rate for this couple to the nature and concentration of cations present.[10] This difference presumably reflects the greater diameter and lower charges of the reactants involved in $IrCl_6^{2-/3-}$ self-exchange.

Conclusions

The relative ease and simplicity of the method described here for estimating self-exchange rates are among its most attractive features. In principle the method would seem to offer rather general applicability to multiply charged reactants. However, attempts to apply the method to cationic reactants by confining them in polyanionic coatings have thus far proved less suc-

cessful because of difficulties in preparing sufficiently long-lived coatings with polyanionic polymers. In addition, the current–potential responses observed for several cationic reactants confined within polyanionic films were less well-behaved than those obtained with anionic reactants in poly-cationic films. Nevertheless, we expect the present obstacles to more general application of the procedure described to be surmounted as more experience and practice with techniques for preparing polyelectrolyte-coated electrodes are acquired.

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Dissociation Energy and Standard Heat of Formation of Gaseous LaPt

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The molecule LaPt was observed in the gas phase above the system Pt–La–graphite, by using the Knudsen effusion mass spectrometric technique in the temperature range of 1959–2466 K. The enthalpy change of the reaction LaPt(g) = La(g) + Pt(g) (or dissociation energy of LaPt(g)) was determined as $\Delta H°_0$ (or $D°_0$) = 496 ± 21 kJ mol^{-1} or 118.5 ± 5.0 kcal mol^{-1}. The corresponding standard heat of formation of LaPt(g) was obtained as $\Delta H_f°_{298}$ = 497 ± 21 kJ mol^{-1} or 118.7 ± 5.0 kcal mol^{-1}. The dissociation energy of gaseous LaPt is discussed in terms of empirical models of bonding.

Introduction

The physical and chemical properties of small transition-metal clusters have been the object of experimental and theoretical investigations in recent years because such clusters appear to play an important role in certain catalytic processes.[1] The knowledge of the bonding energies of diatomic metal molecules is fundamental and provides an important step in bridging the properties when going from metal atoms to small clusters and alloys. We have been engaged in the study of the dissociation energies of strongly bonded intermetallic molecules and in the interpretation of the values obtained in terms of empirical models of bonding. Two such models have been successful. The first is a valence-bond approach for multiply bonded diatomic molecules[2] which has been found applicable to the diatomic platinum metal compounds with the d-electron deficient transition metals of groups 3–5, the lanthanides, or the actinide metals. This model utilizes the electron bonding energies determined by Brewer[3] for the corresponding bulk metals and suitable valence states for the atoms that permit the formation of double bonds, triple bonds, and, to a restricted extent, quadrupole bonds. The sum of the necessary valence-state promotion energies is subtracted from the sum of the electron bonding energies, yielding the calculated dissociation energy. The second model[4] is based on the atomic cell model developed by Miedema and associates for calculating enthalpies of formation of solid or liquid alloys.[5] Both models encounter difficulties when applied to platinum compounds of the more electropositive transition metals. For such mol-

ecules the valence-bond model tends to underestimate the dissociation energy,[6] while the atomic cell model tends to overestimate it.[4]

In the present investigation we have therefore determined the dissociation energy of gaseous LaPt by Knudsen effusion mass spectrometry in order to enlarge the experimental basis to understand the bond energies in platinum metal compounds with group 3 transition metals[7-10] and possibly refine the available empirical models of bonding. A previous estimate for the dissociation energy of LaPt by the valence-bond model yielded 423 kJ mol^{-1},[11] whereas the atomic cell model results in 573 kJ mol^{-1} when the parameters in ref 4 are used.

Experimental Section

The system Pt–La–graphite was studied by using a single-focusing 90° magnetic-sector mass spectrometer (Nuclide 12-90 HT) described previously.[12,13] The graphite-lined tantalum-carbide-coated tantalum Knudsen cell, with a 1.0-mm orifice diameter, was loaded with platinum wire (100 mg), lanthanum sheet (20 mg), graphite powder (50 mg), and, for the pressure calibration, 15 mg of gold.

The cell was heated by a tungsten coil formed from a rod with a diameter of 3.2 mm. The temperature was measured with a Leeds and Northrup optical pyrometer focused on a black-body hole in the bottom of the Kundsen cell. A calibration of the pyrometer was made in a previous run by measuring the vapor pressure of gold at its melting point. For this purpose a 3-g sample of gold (NBS standard for vapor pressure calibration) was placed in a graphite cell with thin walls (ca. 0.5 mm) in order to permit the observation of the temperature plateau during melting and freezing of the gold. The molecular beam was

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