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Quantum Mechanical Description of Electrode Reactions. I. Extended Huckel Molecular Orbital Treatment of the Halide-Bridged Electrode Reactions of Platinum Complexes

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The extended Huckel molecular orbital method has been employed to calculate the activation energies of the halide bridged electrochemical interconversion of typical Pt(IV) and Pt(II) complexes. Conventional spectroscopic values of the mo parameters were employed. When combined with the theory of absolute rates for adiabatic reactions, the calculated activation energies led to theoretical rates in qualitative agreement with experimental values based upon the Tafel equation and the Gouy–Chapman–Stern theory of electrode processes. Covalent interaction between the reactants and the electrode surface, although important in establishing the reaction pathway, was neglected in these calculations and will be introduced at a later stage. The procedure described here appears to allow unequivocal identification of the electronic states primarily responsible for electron-transfer between typical electrodes and reactants and thus may be of considerable practical interest for correlating, interpreting, or predicting the courses of electrode reactions.

Introduction

Electrochemical interconversion of Pt(II) and Pt(IV) is facilitated by halide ions and halogen ligands.[1-5] It appears that in each instance the halogen acts as a bridging group between the Pt ion of the complex and the electrode surface. Comparison of trends in electrode rate[2-5] with spectral energy levels and the results of semiempirical molecular orbital calculations[6] suggests that electron transfer proceeds between an $a_{1g}(\sigma^*)[5d_{z^2}]$ level of the Pt complex and certain appropriate levels of the electrode surface by way of the bridging halide ion or ligand.[5]

Electrolysis results in addition or removal of two ligands along one trans axis (eq 1) (here denoted the z axis). According to the Franck–Condon principle the X–Pt–Z internuclear distances must decrease upon approaching the transition state for oxidation of Pt(II) and, conversely, must increase prior to reduction of Pt(IV). Energies of the highest occupied, lowest unoccupied, and nearby orbitals of hexachloroplatinum(II), -(III), and -(IV) calculated by means of the extended Huckel method in terms of this "z-axis" internuclear distance, r_z, appear in Figure 1. From Figure 1 it can be seen that the energy of $a_{1g}(\sigma^*)[5d_{z^2}]$ increases sharply as the Pt–Cl distance is decreased while the energies of other orbitals are relatively unaffected, indicating that this is the orbital which is occupied in $Pt^{II}L_4$, unoccupied in *trans*-$Pt^{IV}L_4X_2$, and most strongly involved in the interconversion process.

$$Pt^{II}L_4 + X^- + Z \rightleftharpoons trans\text{-}Pt^{IV}L_4XZ + 2e^- \qquad (1)$$

$$(X^- = Cl^-, Br^-, I^-; Z = X^-, H_2O; L = X^-, Z, NO_2^-, R_3N)$$

Pt(IV)–Pt(II) couples for which L = NR_3 or H_2O are invariably more reactive than those for which L = Cl^-, Br^-, I^-, NO_2^-, CN^-, or SCN^-.[2,5] Coulombic attraction facilitates coordination of $Pt(NR_3)_4{}^{2+}$ with the adsorbed-halide bridge, X^-, and the trans group, Z, prior to oxidation. This attraction, of course, gives way to repulsion as neutral ligands are replaced by anionic ones. The potential energy surface for $X\cdots[Pt(NR_3)_4]^{2+}\cdots Z$ involves smaller values of the z-axis Pt–X internuclear distance, r_z, when Z is a neutral species than when Y is an anion. The variation of potential energy with r_z is less dependent upon the identity of the in-plane ligands, L, for Pt(IV) than for Pt(II) because substantial delocalization of charge over the X–Pt–Z axis occurs. Graphs of free molecule potential energy *vs.* z-axis Pt–X internuclear distance for various Pt complexes, calculated by means of the extended Huckel method, appear in Figure 2.

Interactions involving the electrode were not considered in making the calculations displayed in Figure 2. However, a full treatment of the potential energy surface for a model which includes atoms of the electrode will be reported in the near future; the problems of selecting models to represent the metal crystal surface in contact with electrolyte will be described separately.[7]

Factors leading to the ability of various species, notably halides and unsaturated organic compounds, to act as ligand bridges in the homogeneous electron-transfer reactions of transition metal complexes[8] have been discussed qualitatively by Halpern and Orgel.[9] It appears that the homogeneous and heterogeneous cases are analogous,[10] with the electrode

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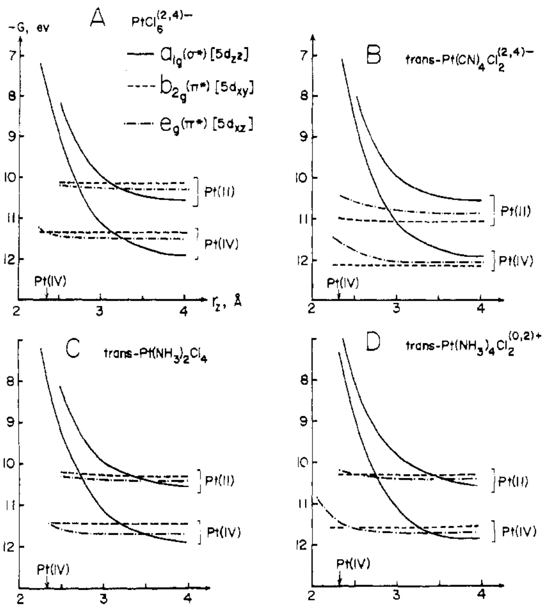

Figure 1. Molecular orbital energy levels *vs.* z-axis internuclear distance for complexes of Pt(II) and Pt(IV).

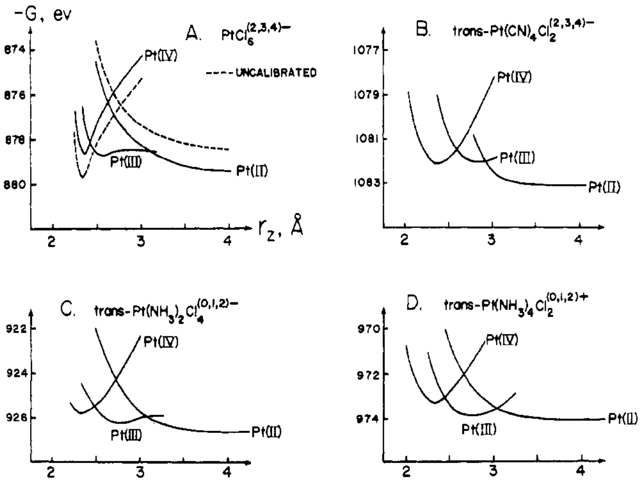

Figure 2. Total energy of valence electrons as a function of internuclear distance along one axis for typical Pt complexes.

Table I. Molecular Orbital Overlaps Calculated for $PtCl_6^{(2,3,4)-}$ at Various Internuclear Distances by Means of the Extended Huckel Molecular Orbital Method

Valence of Pt	r_z,[a] Å	Energy of $a_{1g}(\sigma^*)[5d_{z^2}]$ orbital, eV	Overlap matrix elements $5d_{z^2}$-3s	$5d_{z^2}$-3p	$5d_{z^2}$-4s
IV	2.33	−8.15	0.0924	0.1387	0.0037
IV	2.41	−8.67	0.0805	0.1277	0.0014
III	2.41	−8.36	0.0805	0.1277	0.0014
III	3.1	−10.93	0.0194	0.0462	0.0132
II	3.1	−10.18	0.00194	0.0462	0.0132
II	4.0	−10.56	0.0019	0.0073	0.0152

[a] r_z is the z-axis Pt–Cl internuclear distance; r_z = 2.33 Å represents the Pt(IV) ground state, 2.41 Å the Pt(IV)–Pt(III) transition state, 3.10 Å the Pt(II)–Pt(III) transition state, and 4.0 Å the approximate distance of closest approach of Cl^- to Pt(II) in the ground state.

and double layer occupying the role of the one of the "homogeneous" reactants. The effectiveness of the electrodic electron-transfer bridges depends upon (a) the electronic energy levels of the bridging species, of the reactant and of the electrode (particularly the higher occupied and lower unoccupied levels), (b) the stability of bonds formed between the bridge and the electrode and reactant, that is, the extent of specific adsorption of the bridging species and the stability of its metal complexes, and (c) the distance between the electrode surface and the reactant in the bridged state. Of the numerous possibilities[8] which have been investigated, only Cl^-, Br^-, I^-, and SCN^- have been shown to serve as bridges in the electrode reactions of Pt complexes.[1-5] Each of these ions has vacant s and d orbitals of reasonably low energy (for instance the Cl 4s VSIP is −4.30 eV) which overlap appreciably with the orbitals of principal importance to the electron-transfer process at internuclear distances characteristic of the transition state. Some numerical examples, calculated as described below, appear in Table I. I^- and SCN^- are easily oxidizable and accordingly it is very probable that atom transfer as well as bridging accounts for their accelerating influence in some cases. The ability of these ions to adsorb at Pt electrodes[11] varies in the same order as their ability to coordinate with Pt^{2+} and Pt^{4+} [12] and to accelerate the electrode reactions of Pt complexes.[13] Indeed, indirect experimental estimates[14] place the Pt-Pt internuclear distance in the Pt-Cl-Pt (II or IV) bridged state at about 3.1 Å, a value comparable to the minimum figure computed from typical bond angles and covalent radii, suggesting that the molecular dimensions of the preferred transition states allow very little leeway for bulky or lengthy bridges. In the context of molecular orbital calculations this is equivalent to saying that only those atoms directly bonded to Pt have sizable overlap integrals with Pt, whether in a complex or at an electrode surface. Calculated electronic characteristics of plausible bridged transition states are described, and compared with rate data, below.

Electrode Rate Equations

Electrochemical interconversion of complexes of Pt(II) and Pt(IV) appears[1,2,14] to involve the steps

$$Pt^{II}L_4 + Z \overset{K_{eq}}{\rightleftharpoons} Pt^{II}L_4Z \qquad (2)$$

$$(\text{Pt electrode}) + X^- \overset{{}_1a_{X^-}}{\rightleftharpoons} (\text{Pt electrode})X^- \qquad (3)$$

$$Pt^{II}L_4Z + (\text{Pt electrode})X^- \rightleftharpoons (\text{Pt electrode})XPt^{II}L_4Z \qquad (4)$$

$$(\text{Pt electrode})XPt^{II}L_4Z \overset{{}_{2,3}k_Z}{\rightleftharpoons} (\text{Pt electrode})XPt^{III}L_4Z + e^- \qquad (5)$$

$$(\text{Pt electrode})XPt^{III}L_4Z \underset{{}_{4,3}k_Z}{\rightleftharpoons} (\text{Pt electrode})XPt^{IV}L_4Z + e^- \qquad (6)$$

$$\text{Pt(electrode)}XPt^{IV}Z \rightleftharpoons (\text{Pt electrode}) + trans\text{-}XPt^{IV}L_4Z \qquad (7)$$

where L = Cl^-, Br^-, I^-, SCN^-, CN^-, NO_2^-, NH_3, NR_3, or H_2O, in any combination, X^- = Cl^-, Br^-, or I^-, Z = L or X^-, and K_{eq} is defined by

$$K_{eq} = (a_{Pt^{II}L_4Z})/(a_{Pt^{II}L_4})(a_Z) \qquad (8)$$

That is, Pt(II) associates at equilibrium with each potential ligand present in the solution (eq 2, 8) even in cases of seemingly unfavorable electrostatic interaction such as that of $Pt(NO_2)_4^{2-}$ with Cl^-.[2] The species $Pt^{II}L_4Z$ then associates with a specifically adsorbed bridging group, X^- (eq 4). Transfer of one electron from the bridged intermediate (Pt

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electrode)$XPt^{II}L_4Z$ to the electrode (eq 5) is the rate-limiting step in the oxidation process and is followed immediately by the transfer of a second electron (eq 6). Desorption of the product, *trans*-$Pt^{IV}L_4XZ$, completes the sequence (eq 7). Reduction of Pt(IV) complexes retraces eq 2-7 in reverse order.

The electrode current for Pt(II)-Pt(IV) interconversion is the sum of cathodic and anodic components

$$i = i_c - i_a \qquad (9)$$

where the cathodic component, i_c, is given by eq 10.[2-4,14]

$$i_c = nFA({}_{4,3}k^\circ)({}_2a_{Pt(IV)}) \times \exp\left[\frac{(-\alpha_{4,3})F}{RT}\left(E - E^\circ{}_{4,2} - {}_2\phi_{Pt(IV)}\right)\right] \qquad (10)$$

k° is the standard electrochemical rate constant and α is the charge-transfer coefficient; semiempirical calculation of ${}_{4,3}k^\circ$ will be described below. ${}_2a_{Pt(IV)}$ is the activity of Pt(IV) at the reactant plane of closest approach (eq 11), and $a_{Pt(IV)}$

$${}_2a_{Pt(IV)} = a_{Pt(IV)} \exp\left[-\frac{Z_{Pt(IV)}F}{RT}({}_2\phi_{Pt(IV)})\right] \qquad (11)$$

is the activity of the Pt(IV) complex in the solution outside of the reach of electrical double-layer effects. E_Z is the zero-charge potential of the electrode under the specific conditions of the experiment. ${}_2\phi_{Pt(IV)}$ is the average potential of the reactant plane of closest approach relative to the bulk of the solution. $Z_{Pt(IV)}$ is the ionic charge of the Pt(IV) complex. Other symbols are conventional (please refer to the List of Symbols at the end of the article). Terms containing ${}_2\phi_{Pt(IV)}$ describe the influence of the electrical double layer on the apparent reactant activity and electrode potential and, accordingly, are not unique to Pt complexes.[15] The anodic current component is given by eq 12. ${}_1a_{X^-}$ is the surface activity of the bridging group, X^-, in specifically adsorbed form.

$$i_a = nFA({}_{2,3}k^\circ)K_{eq}({}_1a_{X^-})a_{Pt(II)} \times \exp\left[\frac{1 - \alpha_{2,3}F}{RT}\left(E - E^\circ{}_{4,2} - {}_2\phi_{Pt(III)}\right) - \frac{Z_{Pt(II)}F}{RT}({}_2\phi_{Pt(II)}\right] \qquad (12)$$

Evaluation of ${}_{4,3}k^\circ$, $\alpha_{4,3}$, ${}_{2,3}k^\circ$, and $\alpha_{2,3}$ from current-potential data requires ${}_2\phi_{Pt(IV)}$ and ${}_2\phi_{Pt(II)}$ be estimated from interfacial data. Since the data required for direct calculation of diffuse-layer potentials are not available, an indirect approach is employed which leads to values suitable for use in comparison of the rates of reaction of various reactants at the same electrode, as follows.[3,4,14] If, in regard to the variation of ${}_2\phi_{Pt(II)}$ or ${}_2\phi_{Pt(IV)}$ with electrode potential, over a narrow range, the electrical double layer is modeled after a series pair of ideal capacitors, then the potential at the reactant plane of closest approach is given by eq 13.

$${}_2\phi_R = \frac{C}{C_d}(E - E_Z) \qquad (13)$$

C or C_d are the differential capacitances of the double layer or the diffuse component of the double layer, respectively. The value $C/C_d = 0.03$ appears to give consistent results over a wide variety of Pt complexes and will be employed here. The zero-charge potential, E_Z, for Pt electrodes in 1 *M* ClO_4^- solutions will be taken as −0.01 V *vs.* sce, in line with various estimates published by Frumkin[16] and values indicated rather definitely by our experiments involving the orientation of charged, chemisorbed olefins at Pt surfaces.[17] For 1 *M* Cl^- solution, E_Z will be taken as −0.19 V *vs.* sce.[16]

Current-potential data from which to calculate electrode rate parameters α and k° were taken from ref 2-5 and 14 or were obtained by means of thin-layer electrochemical techniques, as described in ref 5.

Semiempirical Calculation of Electrode Rates

Starting from the theory of reaction rates, first described by Eyring[18] and adapted to electrode reactions by Marcus,[19] the current for reduction of Pt(IV) and oxidation of Pt(II) will be represented by

$$i_c = nFA\left[\frac{RT}{2\pi M_{Pt(IV)}}\right]^{1/2}({}_2a_{Pt(IV)}) \exp\left[\frac{-\Delta G_{4,3}(r_z{}^\ddagger, \phi)}{RT}\right] \qquad (14)$$

$$i_a = nFA\left[\frac{RT}{2\pi M_{Pt(II)}}\right]^{1/2} K_{eq}({}_1a_{X^-})\frac{{}_2a_{Pt(II)}}{\gamma^\ddagger} \times \exp\left[\frac{-\Delta G_{2,3}(r_z{}^\ddagger, \phi)}{RT}\right] \qquad (15)$$

in which $M_{Pt(IV)}$ and $M_{Pt(II)}$ are the molecular weights of the Pt(IV) and Pt(II) reactants; $\Delta G_{4,3}(r_z{}^\ddagger, \phi)$ and $\Delta G_{2,3}(r_z{}^\ddagger, \phi)$ are the Gibbs free energies of activation for transfer of the first electron to Pt(IV) and from Pt(II), respectively, where r_z is the *z*-axis internuclear distance and ϕ is the potential from the reactant plane of closest approach to the inside of the metal, $\phi = E - E^\circ - {}_2\phi_j$ [$j \equiv$ Pt(IV) or Pt(II)], relative to the standard potential; and $\gamma^\ddagger$ is the activity coefficient of the activated complex, equated for simplicity to that of the reactant. The following simplications seem appropriate when applying eq 14 and 15 to the subject reactions, eq 1: (i) motion of the nuclei is described by classical mechanics, and electronic phenomena are treated by quantum mechanics;[18] (ii) thermal equilibrium among all reactive configurations is assumed; (iii) electron transfer is treated as an "adiabatic" process;[20] *i.e.*, the probability for reaction per passage through the intersection region of the potential energy curve is unity; this hypothesis is in keeping with the apparently substantial electrode-reactant electronic interaction in bridged states and the correspondingly large splitting of the higher and lower potential energy surfaces in the intersection region; this assumption is prompted by the absence of evidence to the contrary and the unlikelihood that appreciable errors will result; (iv) electron tunneling is neglected, once again based upon the apparently large splitting between upper and lower

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potential energy surfaces, as in (iii);[20] (v) the reaction coordinate is identified with the "z-axis" internuclear distance, r_z; calculation of the electron-transfer rate is based upon the use of $r_z^{\ddagger}$, the z-axis internuclear distance at the intersection of the potential energy surfaces, for each assigned value of the electrode potential; (vi) vibrational excited states other than those involving r_z are neglected; (vii) multiplicity of electronic states is included in calculation of the electronic properties of the reactant and transition state, but the potential energy surfaces corresponding to the highest occupied or lowest unoccupied state are employed for numerical evaluation of $\Delta G(r^{\ddagger}, 0)$; that is, the electron-transfer path of lowest energy is taken to be indicative of the expected electrode reaction rate; (viii) numerous concepts introduced into other theories[21] to represent various features of the electron-transfer process are included within the extended Huckel molecular orbital method, or others, in use for calculation of the potential energy surfaces; these include reactant-electrode overlap, "inner-sphere reorganization" of nuclear positions in complexes, "electronic polarization" within the reactant, solvent or electrode, the Franck-Condon restriction, and electron-spin selection rules; (ix) reversible work involved with bringing the reactants from the bulk solution to the reactant plane of closest approach, w_r, will be treated by means of the Gouy-Chapman-Stern theory of the electrical double layer,[15] as embodied in eq 11; it should be noted that the expression, eq 16, employed by Marcus[19] to represent the effect of this

$$\exp[-w_r/kT] \tag{16}$$

reversible work on the concentration of the activated complex, is identical with the expression in the Gouy-Chapman-Stern theory, eq 11, when w_r/kT is calculated, as is usual, by means of eq 17.

$$w_r/kT = Z_jF({}_2\phi_j)/RT \qquad \text{(for species } j\text{)} \tag{17}$$

Equating the value of i_c dictated by the electrode rate law, eq 10, to that expected on theoretical grounds, eq 14, for the case in which $\phi \equiv E - E^\circ - {}_{2\phi j} \equiv 0$, leads to an expression for ${}_{j,k}k^\circ$, the standard electrochemical rate constant, in terms of properties of the potential energy surface

$${}_{j,k}k^\circ = \left[\frac{RT}{2\pi M_j}\right]^{1/2} \exp\left[\frac{-\Delta G_{j,k}(r_z^{\ddagger}, 0)}{RT}\right] \tag{18}$$

where "j,k" refers to the reaction, Pt(j) + e$^-$ → Pt(k). Further, combining eq 18 for ${}_{j,k}k^\circ$ with eq 10 and 11 and comparing the result with eq 14 and 15 yield expressions for the charge-transfer coefficients in terms of the potential energy surface

$${}_{4,3}\alpha = \frac{\Delta G_{4,3}(r_z^{\ddagger}, \phi) - \Delta G_{4,3}(r_z^{\ddagger}, 0)}{F\phi} \tag{19}$$

$$1 - {}_{2,3}\alpha = \frac{\Delta G_{2,3}(r_z^{\ddagger}, \phi) - \Delta G_{2,3}(r_z^{\ddagger}, 0)}{F\phi} \tag{20}$$

As can be seen from eq 18, the electrode potential does not enter explicitly into the calculation of ${}_{j,k}k^\circ$, although it does so in the equations for ${}_{j,k}\alpha$, and accordingly it is feasible to calculate values of ${}_{j,k}k^\circ$ for the X-PtL$_4$-Z transition state with neglect of specific interaction with the electrode surface (provided that it is similar for all bridging ligands, X), in order to determine the extent to which the predicted trends in reactivity result from the properties of Pt complexes rather than of the electrode or compact layer.

Semiempirical calculation of potential energy surfaces from which to predict $\Delta G_{j,k}(r_z, 0)$ was based upon the extended Huckel molecular orbital methods developed recently for organic compounds by Hoffmann[22] and for transition metal complexes by Cotton and Harris[23] and by Zumdahl and Drago.[24] As is characteristic of molecular orbital methods, the extended Huckel approach is inexact. However, of the available methods it appears to be the most practical for the problem at hand: all overlap integrals are included, yet the program requires only moderate computation time to treat models having 50 or more atoms; errors incurred because calculation of the overlap integrals is not carried to self-consistency in charge are about 5% for Pt(II) complexes[24] and are probably smaller for electrode models because they consist of a preponderance of nearly neutral atoms; further, the overlaps are not recalculated for each simulated electrode potential, greatly reducing the outlay of computer time. Calculations by means of this method of the electronic structure of Pt complexes are reportedly in good agreement with resonance spectroscopic measurements of electron density distribution in Pt(II) and Pt(IV)[23] and with ligand-substitution rates of Pt(II) complexes.[24]

Pt-L interatomic distances obtained from X-ray diffraction data are employed in the calculations when available[25] and sums of typical covalent radii (in parentheses), otherwise: Pt-Cl = 2.33 Å; Pt-N = 2.00 Å and N-H = 1.01 Å for NH_3; Pt-N = 2.02 Å and N-O = 1.22 Å for NO_2^-; Pt-C = 1.93 Å and C-N = 1.16 Å for CN$^-$; Pt-O = 2.10 Å and O-H = 0.96 Å for H_2O. With reference to eq 1-8, in mapping out the potential energy surfaces along the reaction coordinate, the Pt-X and Pt-Z distances, r_z and r_z', are varied by proportionate fractions of their equilibrium values in Pt(IV) complexes, ${}_0r_z$ and ${}_0r_z'$; that is, $r_z/{}_0r_z = r_z'/{}_0r_z'$. The suitability of this procedure is supported by the fact that in each instance the distances r_z and r_z' at which the potential energy minimum occurred corresponded closely to the crystallographically determined distances.

Numerical values of the valence-state ionization potentials (VSIP) employed in the calculation as estimates of the diagonal elements of the Hamiltonian matrix are as follows:[23,26] 3s, −24.02 eV, 3p, −15.03 eV, for Cl$^-$; 2s, −26.92 eV, 2p, −14.42 eV for N; 1s, −13.60 eV, for H; 2s, −21.01 eV, 2p, −11.26 eV, for C; 2s, −36.07 eV, 2p, −18.53 eV, for O; 6s, −9.80 eV, 6p, −5.35 eV, 5d, −10.61 eV, for Pt(II); 6s, −11.16 eV, 6p, −6.71 eV, 5d, −11.97 eV, for Pt(IV). Spectroscopic VSIP values are not available for Pt(III); the numbers employed here are intermediate between those for Pt(II) and Pt(IV). The values were obtained empirically for the $PtCl_6^{2-}$-$PtCl_4^{2-}$ couple; values for other Pt couples were then obtained from eq 21 which consists of the spectroscopic

$$\text{VSIP[Pt(III)]} = \frac{\text{VSIP[Pt(IV)]} + \text{VSIP[Pt(II)]}}{2} - 0.16\frac{{}_0\bar{r}_z - r_z^{\ddagger}}{{}_0\bar{r}_z - r_z^{\ddagger}[\mathrm{PtCl}_6{}^{z-}]} \tag{21}$$

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$$\overline{{}_0r_z} \equiv \frac{{}_0r_z[\mathrm{Pt(IV)}] + {}_0r_z[\mathrm{Pt(II)}]}{2}$$

values for Pt(II) and Pt(IV), weighted to reflect the degree of similarity (of interatomic distances) between the transition-state species and the adjoining ground states. The results are as follows: 6s, −10.64 eV, 6p, −6.19 eV, 5d, −11.45 eV, for all Pt(III) species except $\mathrm{Pt(CN)_4Cl_2}^{3-}$ (6s, −10.59 eV, 6p, −6.14 eV, 5d, −11.40 eV).

The VSIP values were adjusted to the extent of only 1 eV per atomic unit of final net charge, as discussed by Cotton and Harris,[23] except Pt for which no adjustment was made at all. Off-diagonal elements of the Hamiltonian matrix are estimated by means of the Mulliken-Wolfsberg-Helmholz approximation with the proportionality constant equal to 1.8. Atomic orbital basis sets for Pt and z-axis Cl are constructed from Slater orbitals.[23] The numerical values of the shielding parameters are as follows:[23,27] 3s, 2.245 eV, 3p, 1.850 eV, for z-axis Cl; 3s, 1.60 eV, 3p, 1.36 eV, for Cl; 2s, 1.88 eV, 2p, 1.06 eV, for N; 1s, 1.20 eV, for H; 2s, 1.57 eV, 2p, 0.88 eV, for C; 2s, 2.19 eV, 2p, 1.22 eV, for O; the values employed for Pt were those of Basch and Gray.[28]

In view of the approximate nature of total energy calculations employing molecular orbital theory, it is necessary to calculate the standard potentials for Pt(IV)-Pt(II) couples, $E^\circ_{4,2}$, from the difference between the calculated potential energy minima, $(H^\circ_4 - H^\circ_2)$, for ϕ equal to $E^\circ - E_\mathrm{Z} - {}_2\phi_j$ (neglecting the net contribution due to free energy of solvation which is small and not readily available) and to equate the calculated results with the experimental values. Further, the calculated potential energy surface yields the energy of the reactants, H, whereas the quantity required by the rate equation is the Gibbs free energy, G; for the present purpose it will be sufficient to neglect the entropy of activation, on the assumption that its contribution is small and similar for all Pt couples. These approximations are summarized by eq 22. The total ground-state energy, H°_i, the solvation energy, ${}_sG^\circ_j$, and the correction for inaccuracy in calculation of the absolute energy of the reactants can be combined in a single, empirical step by adjusting H°_4 and H°_2 equally so as to bring the adjusted values, denoted G°_4 and G°_2 into correspondence with the measured standard potentials (eq 23).

$$E^\circ_{4,2} = (H^\circ_4 - H^\circ_2 - H^\circ_\mathrm{X} - H^\circ_\mathrm{Z})/2 \qquad (22)$$

$$\Delta G^\circ_{4,2} \equiv G^\circ_2 + G^\circ_\mathrm{X} + G_\mathrm{Z} - G^\circ_4 = -2E^\circ_{4,2} \qquad (23)$$

That is, $G^\circ_4 \equiv H^\circ_4$ + constant, $G^\circ_3 \equiv H^\circ_3$, $G^\circ_2 \equiv H^\circ_2$ − constant, $G^\circ_\mathrm{X} \equiv H^\circ_\mathrm{X}$ and $G^\circ_\mathrm{Z} \equiv H^\circ_\mathrm{Z}$; *i.e.*, the positions of the Pt(IV) and Pt(II) curves were adjusted by equal and opposite amounts in accordance with $E^\circ_{4,2}$, while those for Pt(III) were not changed. The effect of this procedure is to make the calculated activation parameters dependent only on the shape and relative (rather than absolute) energy coordinates of the potential energy surface. Typical results are displayed in Figure 2. Figure 2A illustrates the process of adjusting the ground-state energies for the $\mathrm{PtCl_6}^{2-}$-$\mathrm{PtCl_4}^{2-}$ couple. Smooth curves are constructed by interconnecting the calculated points with a polynomial in r_z. As can be seen from the figure, adjustment of the ground-state energy influences $r_z^\ddagger$, although the values obtained seem reasonable in either instance. Theoretical and experimental activation energies, displayed in Figure 3 and Table II, demonstrate the expected qualitative agreement, indicating that molecular characteristics of the complex establish the qualitative features of Pt(II)-Pt(IV) interconversion, while the structure of the electrode surface apparently affects the choice of reaction path but influences the reactants nonspecifically within the confines of that path. In keeping with the experimental indications, it is the intersection of the Pt(III) potential energy curve with that for Pt(II) and Pt(IV) which most correctly represents the activation energy. The structure and properties of Pt(III) are unknown and therefore it may be of interest to note that the present calculations yield the best agreement with experiment when it is assumed that Pt(III) has structural characteristics consistently intermediate between those of Pt(II) and Pt(IV).

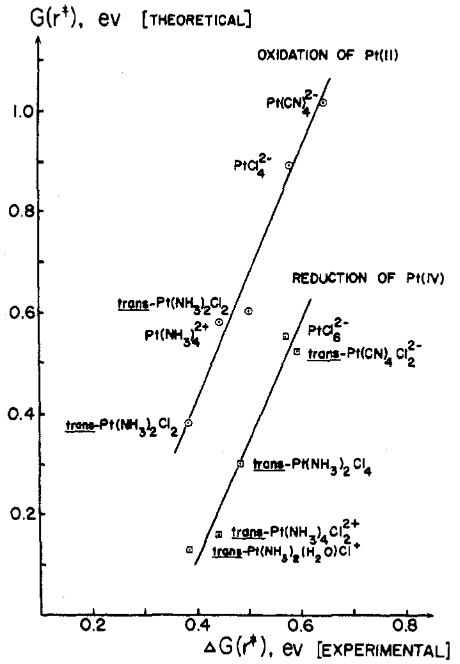

Figure 3. Theoretical and experimental values of the activation energy for halide-bridged Pt(II)-Pt(IV) interconversion.

Summary

Extended Huckel molecular orbital calculations based upon conventional spectroscopic values of the numerical parameters, although expectably inexact, yield orbital energy levels and total molecular energies in qualitative agreement with electrode rate measurements for a series of Pt(IV)-Pt(II) couples involving various charges and ligand types. Electrode reaction activation energies calculated in this way are extremely sensitive to a number of variables and thus provide a rather definite means for deciding among various alternative mechanistic paths. In particular, Pt(III) is indicated to be an intermediate in Pt(IV)-Pt(II) interconversion, and the $a_{1g}(\sigma^*)[5d_{z^2}]$ orbital is shown to be the one primarily involved in the electron-transfer process. Inclusion of electrode-ligand covalent interactions is not necessary to obtain qualitative agreement with experiment so long as electron transfer is assumed to proceed through a halide-bridged intermediate formed by addition or removal of two ligands located along one trans axis of the reactant. Inaccuracy in calculated rates resulting from errors in locating the potential energy surfaces corresponding to different Pt valencies on an absolute energy scale appears to be minimized by adjusting the calculated ground-state energies into correspondence

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Table II. Theoretical and Experimental Values of the Activation Energy for Halide-Bridged Pt(II)–Pt(IV) Interconversion

Reduction of Pt(IV) Complexes

Reactant	Product	$E^{\circ}{}_{4,2}$, V	${}_{4,2}k^{\circ}$, cm sec^{-1}	${}_{4,3}k^{\circ}$, cm sec^{-1}		$\Delta G_{4,3}(r_z{}^{\ddagger})$, eV	
			Theoret	Exptl[a]	Theoret	Exptl	Theoret
$PtCl_6{}^{2-}$	$PtCl_4{}^{2-}$	0.41	9.7×10^{-35}	6.5×10^{-7}	1.5×10^{-6}	0.572	0.55
trans-$Pt(CN)_4Cl_2{}^{2-}$	$Pt(CN)_4{}^{2-}$	0.65	1.1×10^{-21}	2.78×10^{-7}	5.2×10^{-6}	0.595	0.52
trans-$Pt(NH_3)_2Cl_4$	*trans*-$Pt(NH_3)_2Cl_2$	0.35	7.8×10^{-26}	2.23×10^{-5}	2.8×10^{-2}	0.482	0.30
trans-$Pt(NH_3)_4Cl_2{}^{2+}$	$Pt(NH_3)_4{}^{2+}$	0.42	7.8×10^{-23}	$\geqslant 10^{-4}$ [b]	7.4	$\leqslant 0.446$	0.16
trans-$Pt(NH_3)_2Cl_3(H_2O)^+$	*trans*-$Pt(NH_3)_2Cl_2$	0.57	7.0×10^{-18}	$\geqslant 10^{-3}$	20.1	$\leqslant 0.386$	0.13

Oxidation of Pt(II) Complexes

Reactant	Product	$E^{\circ}{}_{4,2}$, V	${}_{2,4}k^{\circ}$, cm sec^{-1}	${}_{2,3}k^{\circ}$, cm sec^{-1}		$\Delta G_{2,3}(r_z{}^{\ddagger})$, eV	
			Theoret	Exptl	Theoret	Exptl	Theoret
$Pt(CN)_4{}^{2-}$	*trans*-$Pt(CN)_4Cl_2{}^{2-}$	0.65	1.9×10^{-49}	6.30×10^{-8}	1.8×10^{-16}	0.636	1.14
$PtCl_4{}^{2-}$	$PtCl_6{}^{2-}$	0.41	9.1×10^{-49}	2.05×10^{-7}	2.9×10^{-12}	0.577	0.89
trans-$Pt(NH_3)_2Cl_2$	*trans*-$Pt(NH_3)_2Cl_4$	0.35	5.9×10^{-37}	1.15×10^{-5}	2.5×10^{-7}	0.502	0.60
$Pt(NH_3)_4{}^{2+}$	*trans*-$Pt(NH_3)_4Cl_2{}^{2+}$	0.42	3.4×10^{-29}	$\geqslant 10^{-4}$ [b]	5.5×10^{-7}	$\leqslant 0.446$	0.58
trans-$Pt(NH_3)_2Cl_2$	*trans*-$Pt(NH_3)_2Cl_3(H_2O)^+$	0.57	5.5×10^{-39}	$\geqslant 10^{-3}$ [b]	1.3×10^{-3}	$\leqslant 0.386$	0.38

[a] Experimental quantities refer to aqueous solutions containing 1 *F* Cl^-. [b] Reaction rate too fast for accurate measurement by means of dc thin-layer voltammetry.

with the measured standard potentials. Activation entropies were assumed to be small and constant. The reactions were taken to be adiabatic, with neglect of electron tunneling and nonclassical nuclear motion. The Gouy-Chapman-Stern theory of the diffuse layer, describing the reversible work of bringing the reactant from the bulk solution to the reactant plane, appears to suffice for these reactions. Best agreement with experiment was obtained when Pt(III), for which no experimental information is available, is assumed to have properties intermediate between those of the Pt(IV) and Pt(II) complexes of analogous geometry. Very modest computation times are required to treat the relatively complicated models considered here, suggesting that semiempirical quantum mechanical interpretation of electrode reactions is entirely feasible, not inconvenient, and likely to increase in usefulness as a result of the future general development of quantum theory.

List of Symbols

A	electrode area, cm^2
a_j	activity of species *j*, mol cm^{-3}
${}_2a_j$	magnitude of a_j at the reactant plane of closest approach, mol cm^{-3}
$\alpha_{j,k}$	charge-transfer coefficient for transition from valence *j* to *k*
C	differential capacitance of the electrode–solution interface, F
C_d	differential capacitance attributable to the diffuse layer, F
E	electrode potential, V
$E^{\circ}{}_{j,k}$	formal standard potential, V
E_Z	potential corresponding to zero net electrode electronic charge, V
F	Faraday constant, C equiv
G_j	Gibbs free energy of species *j*, eV
H_j	enthalpy of species *j*, eV
i	net current, A
i_a	anodic component of net current, A
i_c	cathodic component of net current, A
K_{eq}	equilibrium constant, defined by eq 8
${}_{j,k}k^{\circ}$	standard electrochemical rate constant for transition from valence *j* to *k*, cm sec^{-1}
L	ligand in the square-planar coordination sphere of Pt(II)
M_j	molecular weight of species *j*
n	net number of electrons transferred per reactant molecule
${}_2\phi_j$	potential at plane of closest approach of species *j*, V
R	gas constant, J mol^{-1} deg^{-1}
r_z	*z*-axis internuclear distance, cm or Å
T	temperature, °K
w_r	electrostatic work of moving reactant from bulk solution to reaction plane, J
X	bridging ligand
Z	ligand trans to the bridging ligand
Z_j	ionic charge of species *j*

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Registry No. $PtCl_6{}^{2-}$, 16871-54-8; $PtCl_6{}^{3-}$, 50790-36-8; $PtCl_6{}^{4-}$, 44464-81-5; *trans*-$Pt(CN)_4Cl_2{}^{2-}$, 20756-57-4; *trans*-$Pt(CN)_4Cl_2{}^{3-}$, 50883-27-7; *trans*-$Pt(CN)_4Cl_2{}^{4-}$, 50932-76-8; *trans*-$Pt(NH_3)_2Cl_4$, 16893-06-4; *trans*-$Pt(NH_3)_2Cl_4{}^-$, 50790-37-9; *trans*-$Pt(NH_3)_2Cl_4{}^{2-}$, 50790-40-4; *trans*-$Pt(NH_3)_4Cl_2$, 26745-71-1; *trans*-$Pt(NH_3)_4Cl_2{}^+$, 50790-38-0; *trans*-$Pt(NH_3)_4Cl_2{}^{2+}$, 16986-23-5; *trans*-$Pt(NH_3)_2(H_2O)Cl^+$, 44046-05-1; $Pt(CN)_4{}^{2-}$, 15004-88-3; $Pt(Cl_4)^{2-}$, 13965-91-8; $Pt(NH_3)_4{}^{2+}$, 16455-68-8; *trans*-$Pt(NH_3)_2Cl_2$, 14913-33-8; *trans*-$Pt(NH_3)_2Cl_3(H_2O)^+$, 34382-68-8; Pt, 7440-06-4.