

Figure 1. Viscosity of aqueous 5'-AMP solutions as a function of concentration (P_H : 7.0 ± 0.4).

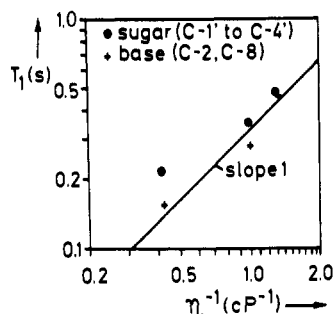


Figure 2. Double log plot of the average longitudinal ^{13}C relaxation rates of 5'-AMP^{1,2} vs. the reciprocal viscosity of the solutions: points, average of C-1' to C-4'; crosses, average of C-2, C-8.

nucleotide one calculates the rotational correlation time τ_c in the extreme narrowing case from³

$$1/T_1 = N\hbar^2\gamma_C^2\gamma_H^2r_{CH}^{-6}\tau_c \quad (1)$$

with N the number of protons bound to the carbon and γ_C and γ_H the magnetogyric ratios of the two nuclear spins involved. Taking the isotropic rotating sphere as a valid approximation for the motion of 5'-AMP in water, τ_c is described by

$$\tau_c = 4\pi\eta a^3/3kT \quad (2)$$

Inserting 0.105 ± 0.005 nm for r_{CH} one obtains at all concentrations a value of a , commonly taken as the diameter of the diffusing particle, of 0.45 ± 0.05 nm, which certainly is less than the actual dimensions of the single nucleotide. The relaxation times of the base carbons at the different concentrations are therefore determined by the macroscopic viscosity, and it is unnecessary to invoke any specific microscopic model to explain the experimental results. On the other hand, the relaxation rates of the sugar carbon, which possess several possibilities of internal motion, depend on two correlation times: the correlation time for overall molecular reorientation which increases with increasing viscosity and a correlation time for the internal motions which to a first approximation should not depend on the viscosity.^{4,5} It is then clear that the effect of the internal motions can only be observed in the more concentrated solutions, that is when the overall reorientation is slowed down.

Rhodes and Schimmel⁶ measured the energy of activa-

tion for the rotation around the glycosidic bond (syn \rightleftharpoons anti equilibrium) in some purine (β)ribosides to be 6.2 kcal mol⁻¹. Therefore the segmental motion may not come from rotation around the glycosidic bond. Röder et al.⁷ have determined the activation energy for the conformational mobility of the furanoside ring of the ribose moiety, as for example described by the N \rightleftharpoons S model of Altona and Sundaralingam⁸ by variable temperature ^{13}C relaxation measurements and comparison with the 2',3'-isopropylidene nucleosides to be 4.7 ± 0.5 kcal mol⁻¹. Assuming that these results are applicable to 5'-AMP one must conclude that the deviations observed in the more concentrated solutions for the relaxation rates of the sugar carbons from those of the base should not be explained by a greater diffusive mobility of the ribosephosphate moiety around the glycosidic bond but rather by transitions between the different possible conformations of the ribose ring.

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Simple Criteria for Distinguishing between Inner- and Outer-Sphere Electrode Reaction Mechanisms

Sir:

The well-known and widely applied distinction¹ between inner-sphere and outer-sphere mechanistic pathways in electron-transfer reactions involving homogeneous reactants has been extended to a few heterogeneous reactions proceeding at electrode surfaces.²⁻⁷ The clearest examples of inner-sphere electrode reactions involve certain transition metal isothiocyanate complexes^{5,7} which are strongly adsorbed on the surface of mercury electrodes by means of sulfur-mercury bonds. The kinetics of the electroreduction of these complexes in the adsorbed state have been investigated, and further testimony to their proceeding by inner-sphere pathways appeared in the form of unusual apparent reaction orders and potential dependences.^{6,7} Strong, although less direct evidence for inner-sphere electrochemical pathways has also been obtained for a second class of reactions involving the oxidation of $\text{Cr}(\text{OH}_2)_6^{2+}$ at mercury electrodes in the presence of anions which are adsorbed on the electrode and appear in the inner coordination sphere of the Cr(III) complexes resulting from the oxidation.²⁻⁵ This result is analogous to the classical and unequivocal demonstration of a ligand-bridging mechanism by means of ligand transfer between homogeneous reactants.⁸ However, anation of both $\text{Cr}(\text{OH}_2)_6^{2+}$ and mercury electrode surfaces proceeds rapidly and reversibly so that it is not always possible to distinguish between prior complexation and ligand bridging by adsorbed anions as the mechanism leading to anated chromium(III) complexes during the electrooxidation of $\text{Cr}(\text{OH}_2)_6^{2+}$.⁵

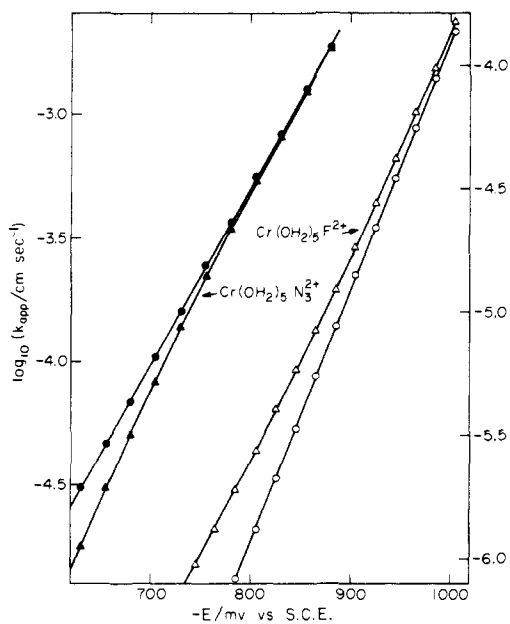


Figure 1. Rate-potential plots for the reduction of $\text{Cr}(\text{OH}_2)_5\text{F}^{2+}$ and $\text{Cr}(\text{OH}_2)_5\text{N}_3^{2+}$. The apparent rate constant, $k_{\text{app}} \equiv (i/FC^b)$ where i is the current density (corrected to eliminate any mass transfer effects), F is the Faraday, and C^b is the bulk concentration of the complex. Supporting electrolytes: (\bullet , \circ) 1 M NaClO_4 - 0.01 M HClO_4 ; (\blacktriangle , \triangle) 0.67 M NaClO_4 - 0.33 M NaI - 0.01 M HClO_4 . Ordinate axes: Left-hand, $\text{Cr}(\text{OH}_2)_5\text{N}_3^{2+}$; right-hand, $\text{Cr}(\text{OH}_2)_5\text{F}^{2+}$.

In recent experiments directed at understanding the effects of changes in double-layer structure on the kinetics of the electrode reactions of several transition metal complexes, we have developed a procedure for distinguishing between complexes which follow inner-sphere or outer-sphere pathways. The method is extremely simple and appears to have considerable generality so that we wish to draw attention to it by reporting its essential features at this time.

The method consists of measuring the rate of the reduction (or oxidation) of a complex at the electrode, first in the absence and then in the presence of an anion which is known to be strongly adsorbed on the electrode surface and which can be shown not to act as a bridging ligand under the experimental conditions (e.g., electrode potentials) employed. If the complex of interest reacts by an inner-sphere pathway, the transition state will be formed at the inner Helmholtz plane⁹ and the presence of another species which is strongly adsorbed on the surface will lead to a competition for adsorption sites which should raise the energy of the transition state and produce a lower reaction rate.

By contrast, if an outer-sphere reaction pathway is involved, the addition of a strongly adsorbing substance should produce changes in rate only by means of the alterations its adsorption produces in the potential at the outer Helmholtz plane⁹ and the magnitude of the resulting rate changes can be calculated by means of well-established procedures.¹⁰

At the relatively negative potentials where most complexes of Cr(III) are reduced to Cr(II), iodide anions meet the necessary criteria for a competitively adsorbed and kinetically inert species. Figure 1 shows rate-potential data for the reduction of $\text{Cr}(\text{OH}_2)_5\text{F}^{2+}$ in the presence and absence of added iodide. Note that the addition of iodide results in a significant rate enhancement which becomes gradually less pronounced at more negative potentials as adsorption of iodide diminishes. This behavior is in qualitative (but not quantitative¹¹) agreement with that expected for an outer-sphere electrode reaction mechanism with a

cationic complex whose concentration at the electrode surface is increased by the greater electrostatic attraction it experiences when negative iodide anions are adsorbed on the electrode surface.¹⁰

Figure 1 also contains a pair of rate-potential curves for the reduction of the analogous complex, $\text{Cr}(\text{OH}_2)_5\text{N}_3^{2+}$. In this case the reaction rates in the absence of iodide are higher than those for $\text{Cr}(\text{OH}_2)_5\text{F}^{2+}$ and addition of iodide results in a slight decrease in rate instead of the marked increase observed with the fluoro complex. The most reasonable explanation for this behavior is that an inner-sphere pathway is followed by this complex with the coordinated azide anion attached to the electrode surface in the transition state. This anion bridging is responsible for the larger reduction rates; it is impeded by the presence of adsorbed iodide and this is reflected in a decreased reduction rate. Strong mutual repulsion is a prominent feature of the adsorption isotherms of simple anions on mercury¹² and it seems reasonable to expect repulsion between adsorbed iodide anions and the coordinated azide anions which hold the complex on the surface in the transition state even though these anions are also coordinated to a cationic center which is probably located on the solution side of the inner Helmholtz plane. The difference in the behavior of the two complexes shown in the figure is particularly striking because the average concentrations of both complexes at the outer Helmholtz plane are *increased* by the adsorption of iodide. The fact that a net decrease in the reaction rate of $\text{Cr}(\text{OH}_2)_5\text{N}_3^{2+}$ is observed nevertheless is very strong evidence for an inner-sphere mechanism. This interpretation is supported by the observation that the reduction rates of both complexes are enhanced when the ionic strength of the nonadsorbing perchlorate supporting electrolyte is decreased and the resulting increase in the electrostatic attraction between the negatively charged electrode surface and the cationic complexes produces an increase in their concentrations at the outer Helmholtz planes.

The preference of $\text{Cr}(\text{OH}_2)_5\text{N}_3^{2+}$ for inner sphere and of $\text{Cr}(\text{OH}_2)_5\text{F}^{2+}$ for outer-sphere mechanisms is in accord with the relative tendencies of these two anions to adsorb at the mercury-aqueous interface. Azide exhibits moderate specific adsorption¹³ while the adsorption of fluoride is the weakest of all anions.

The method described here has been used to diagnose inner-sphere mechanisms for the reductions of a number of cationic complexes of Cr(III) of the class $\text{Cr}(\text{OH}_2)_5\text{X}^{2+}$ ($\text{X}^- = \text{Br}^-, \text{Cl}^-, \text{NCS}^-, \text{N}_3^-, \text{NO}_3^-$) as well as for the reduction of the substitutionally labile Eu^{3+} cation in solutions containing thiocyanate anions. In addition to $\text{Cr}(\text{OH}_2)_5\text{F}^{2+}$, outer-sphere mechanisms were indicated for $\text{Cr}(\text{OH}_2)_6^{3+}$, Eu^{3+} (in perchlorate electrolytes), and $\text{Cr}(\text{OH}_2)_5\text{SO}_4^+$. The method should be applicable to most complexes that contain anionic potential bridging ligands so long as the net charge on the complex remains positive. With neutral or anionic complexes ambiguities may result because the effect of anion adsorption would be to depress the rates for both inner-sphere and outer-sphere mechanisms (although there should be quantitative differences). A related diagnostic criterion based on the slopes of rate-potential plots such as those in the figure has also been recently developed¹¹ and offers the possibility for an independent check of the conclusions based on the results of iodide-addition experiments. Experiments designed to explore these diagnostic criteria for additional classes of reactants are currently in progress in this laboratory.

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Concerning the Superoxide Electrodes in Nitrate Melts

Sir:

This note is written in the hope of preventing confusion that may be caused by an error in a recent communication¹ by Schlegel, concerning oxygen electrode in molten nitrates.

Work in this laboratory has shown² that the potential of the superoxide/oxygen electrode in molten (sodium, potassium) nitrate at 503 K can be described by the half-reaction



and that its standard potential, E_1^0 in the equation

$$E = E_1^0 - (RT/F) \ln [\text{O}_2^-]/[\text{O}_2] \quad (2)$$

can be deduced both from potentiometric² data and from the reversible²⁻⁵ voltammetric half-wave potential of the redox couple O_2/O_2^- : $E_1^0 = E^0_{\text{O}_2/\text{O}_2^-} = -0.645$ V vs. a Ag/Ag⁺ (0.07 *m*) reference electrode.

Schlegel¹ used our data² to obtain a different value of the standard potential, $E_2^0 = -1.185$ V, by the unstated assumption that

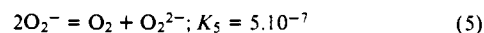
$$E = E_2^0 - (RT/F) \ln [\text{O}_2^-]/p_{\text{O}_2} \quad (3)$$

where p_{O_2} is the partial pressure (atm) of oxygen in equilibrium with the melt. Neither E_1^0 nor E_2^0 is incorrect per se, and both pertain to the redox couple O_2/O_2^- , but they do differ in the choice of the standard state for oxygen, which is a 1 *m* solution (as for superoxide) for E_1^0 and a partial pressure of 1 atm for E_2^0 . Because of this difference it is impossible to compare E_2^0 directly with the voltammetric half-wave potential, as Schlegel attempted to do. At the half-wave potential of any couple, $\text{ox} + ne = \text{red}$, the activities of ox and red are equal if both are contained in the same phase, but only if they are expressed in the same units. For the O_2/O_2^- couple the potential at which $p_{\text{O}_2} = m_{\text{O}_2^-}$ is very different from the half-wave potential.

Schlegel was apparently misled by the fact that the difference between E_1^0 and E_2^0 , which involves the Henry's law coefficient⁵ for oxygen ($K_H = 4.10^{-6}$ mol kg⁻¹ atm⁻¹)

$$E_1^0 - E_2^0 = -(RT/F) \ln K_H \quad (4)$$

is fortuitously almost equal to the difference between the standard² (and half-wave⁴) potentials of the O_2/O_2^- and $\text{O}_2^-/\text{O}_2^{2-}$ couples, which involves the disproportionation constant² of superoxide ion



so that

$$E^0_{\text{O}_2/\text{O}_2^-} - E^0_{\text{O}_2^-/\text{O}_2^{2-}} = -(RT/F) \ln K_5 \quad (6)$$

Schlegel¹ concluded that the potential of an oxygen electrode under these conditions is governed by the $\text{O}_2^-/\text{O}_2^{2-}$ couple rather than by the O_2/O_2^- couple. This is not proven by his argument, could not be proven by any purely thermodynamic argument, and has no real meaning at the present time. A potential determining process can be identified only with the aid of kinetic data. At present it is known only that the rate constants for electron transfer at the standard potentials are high enough so that both couples are voltammetrically reversible,^{3,6} and they are interrelated through reaction 5, for which both the forward and backward rate constants are also high.⁷ Hence it is as yet possible only to identify the half-reaction responsible for the two voltammetric waves and to evaluate their standard potentials, and this was correctly done in our previous studies. The standard potentials (vs. Ag/Ag⁺, 0.07 *m*) for the oxygen/superoxide and superoxide/peroxide couples in a (Na, K)NO₃ equimolar melt at 503 K are the following: $E^0_{\text{O}_2/\text{O}_2^-} = -0.645 \pm 0.005$ V (from both potentiometric² and RDE voltammetric⁸ data); $E^0_{\text{O}_2^-/\text{O}_2^{2-}} = -1.26 \pm 0.01$ V (from RDE voltammetric⁸ data).

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$$E^0 = E_{1/2} - (RT/nF) \ln (D_{\text{red}}/D_{\text{ox}})^{2/3}$$

The diffusion coefficients data for oxygen, superoxide, and peroxide are given in ref 2 and 4.

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One-Step Preparation of Metacyclophanes and (2,6)Pyridinophanes by Nickel-Catalyzed Grignard Cyclocoupling

Sir:

There is much current interest in the chemistry of cyclophanes and heterophanes;¹ however, the overall product yields in the wide variety of synthetic methods so far developed generally suffer from the multistep sequences involved.^{1a,2} We report here a one-step preparation of [*n*]metacyclophanes and [*n*](2,6)pyridinophanes by the cyclocoupling of di-Grignard reagents with aromatic dihalides in the presence of catalytic quantities of a nickel-phosphine complex