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Kinetics of Reduction of Aqueous Hexaammineruthenium(III) Ion at Pt and Au Microelectrodes: Electrolyte, Temperature, and Pressure Effects

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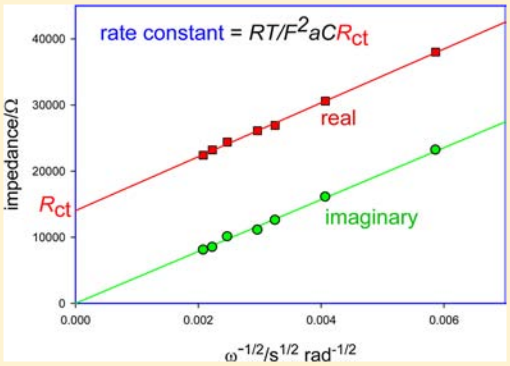
Supporting Information

ABSTRACT: Rate constants k_{el} obtained by impedance spectroscopy for the reduction of $Ru(NH_3)_6^{3+}$ at polycrystalline Pt and Au ultramicroelectrodes depend strongly on the identity and concentration of the anion present in the order $CF_3SO_3^- < Cl^- < ClO_4^-$, but not on the cation of the supporting electrolyte (Na^+, K^+, H^+). For Cl^- as the sole anion present, k_{el} is directly proportional to the total $[Cl^-]$, such that k_{el} would be zero if Cl^- were hypothetically absent, indicating that Cl^- is directly involved in mediation of the $Ru(NH_3)_6^{3+/2+}$ electron transfer. For $CF_3SO_3^-$ as the sole counterion, the dependence of k_{el} on the total $[CF_3SO_3^-]$ is not linear, possibly because blocking of the available electrode surface becomes dominant at high triflate concentrations. Volumes of activation $\Delta V_{el}^{\ddagger}$ for reduction of $Ru(NH_3)_6^{3+}$ at an electrode in presence of Cl^- or $CF_3SO_3^-$ are much more negative than predictions based on theory (Swaddle, T. W. *Chem. Rev.* **2005**, *105*, 2573) that has been successful with other electron transfer reactions but which does not take into account the involvement of the anions in the activation process. The strongly negative $\Delta V_{el}^{\ddagger}$ values probably reflect solvation increases peculiar to activation processes of $Ru^{III/II}$ am(m)ine complexes, possibly together with promotion of desorption of surface-blocking Cl^- or $CF_3SO_3^-$ from electrodes by applied pressure. Frumkin corrections for $Ru(NH_3)_6^{3+}$ within the diffuse double layer would make $\Delta V_{el}^{\ddagger}$ even more negative than is observed, although the corrections would be small. The strongly negative $\Delta V_{el}^{\ddagger}$ values are inconsistent with reduction of $Ru(NH_3)_6^{3+}$ in direct contact with the metallic electrode surface, which would entail substantial dehydration of both the electrode and $Ru(NH_3)_6^{3+}$. Reduction of $Ru(NH_3)_6^{3+}$ can be regarded as taking place in hard contact with adsorbed water at the outer Helmholtz plane.



INTRODUCTION

Research in our laboratory in recent years has focused on mechanistic insights provided by the effects of hydrostatic pressure on the rates of heterogeneous (electrode) and homogeneous electron transfer reactions of transition-metal complexes in solution.[1,2] Electrode reaction rates, however, are notoriously susceptible to the influence of the nature of the electrode surface. Although electron transfer at metal electrodes is traditionally viewed as adiabatic, we have suggested[1] that in many cases this sensitivity to the state of the surface probably reflects nonadiabatic electron transfer (i.e., coupling between the electronic wave functions in the reactant and the electrode is weak relative to thermal energies[3]), so that the electrode reaction rate becomes strongly distance dependent and consequently sensitive to adsorbed substances, oxides layers, and so forth on the electrode surface. The standard techniques of electrode kinetics at conventional electrodes used heretofore in variable-pressure studies, notably ac voltammetry (ACV), are limited to moderately slow reactions having standard rate constant k_{el} less than about 0.3 cm s^{-1}, the slowness of which may indicate substantial departure from adiabaticity. We have therefore sought information on the pressure dependence of k_{el} (conveniently expressed as the volume of activation $\Delta V_{el}^{\ddagger} = -RT(\partial \ln k_{el}/\partial P)_T$) for an electrode reaction that is likely to be close to fully adiabatic. Only aqueous systems are considered, since solvent dynamics can determine $\Delta V_{el}^{\ddagger}$ for electrode processes in nonaqueous media.[1]

The question of the extent of nonadiabaticity in electrode reactions is controversial. The reduction of quinones at graphite electrodes is the subject of a current debate[4,5] in which Compton et al.[4] favor a nonadiabatic interpretation. For reductions of other organic solutes at electrodes in nonaqueous solvents, Savéant[6] has derived a variant of the classical Marcus−Hush relationship which allows description of the passage from nonadiabatic to limiting adiabatic electron transfer. In a similar vein, Compton et al.[7,8] have estimated the degree of adiabaticity and the changeover between nonadiabatic and limiting adiabatic behavior for electroreduction of 3-nitrophenolate and 1-nitropentane at Hg microhemispheres in organic solvents, using an asymmetric version of Marcus−Hush theory to interpret the pre-exponential factor in the temperature dependence of k_{el}. For reductions of aqueous inorganic solutes at solid metal electrodes, it is typically assumed that the rate

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constant should be substantially independent of the nature of the metal—in the present study, Au vs Pt—if the reaction is fully adiabatic;[9] for a nonadiabatic process, k_{el} would depend on the density ρ_F of electronic states at the Fermi level of the electrode as well as on the electrode-reactant distance. Gosavi and Marcus,[10] however, point out that k_{el} can also be approximately the same at Pt and Au for a nonadiabatic reaction if a large ρ_F, as is typical for *d* bands as in Pt, is offset by the weaker coupling of *d* bands to the reactant relative to *s* bands as in Au. Thus, even if k_{el} for a particular reaction is approximately the same at Au and Pt electrodes, the reaction is not necessarily adiabatic. As far as the variable-pressure studies reported here are concerned, nonadiabaticity will affect k_{el} but probably not $\Delta V_{el}^{\ddagger}$.[11,12]

As remarked originally by Gennett and Weaver,[13] the low-spin/low-spin (t_{2g}^5/t_{2g}^6) $Ru(NH_3)_6^{3+/2+}$ electron transfer reaction, in which the Ru−N bond length difference between the effectively substitution-inert reactants (4.0 pm)[14] and consequently the internal reorganization energy are very small, is likely to be a fast, "well-behaved", adiabatic reaction. The $Ru(NH_3)_6^{3+/2+}$ couple has therefore come to be widely regarded as an electrochemical "reference reaction", whether the electrode material be metallic,[13,15−23] metallic with adsorbed monolayers,[20,24−36] pyrolytic graphite,[37−41] glassy carbon,[42] or boron-doped diamond.[43,44] For all these electrodes, it emerges that the $Ru(NH_3)_6^{3+/2+}$ couple is free of most of the aberrations associated with the $Fe(CN)_6^{3-/4-}$ couple,[1,24,39−44] traditionally used as a reference system in electrode kinetics. For metallic electrodes, the reported $Ru(NH_3)_6^{3+/2+}$ electron transfer rates are very fast, albeit somewhat scattered for reasons discussed below, and in most cases appear to be roughly independent of the metal of the electrode, consistent with substantially adiabatic election transfer.[9] Velmurugan et al.,[45] however, found somewhat higher rates of reduction of $Ru(NH_3)_6^{3+}$ at Pt than at Au disk nanoelectrodes in various electrolyte solutions, and suggested some degree of nonadiabaticity, so this remains an open question.

Successful measurements of the high k_{el} values for the $Ru(NH_3)_6^{3+/2+}$ electrode reaction were made by Gennett and Weaver[13] using ac voltammetry at a dropping Hg electrode, and were soon followed by those of Iwasita et al.[15,16] using various ring electrodes in turbulent pipe flow. In many of the early reports, however, it is unclear whether the uncompensated resistance of the solutions had been adequately allowed for in deriving k_{el} values.[46] For convenient adaptation to high pressure experiments, we chose to study the $Ru(NH_3)_6^{3+/2+}$ electrode kinetics by ac impedance measurements at Pt and Au ultramicroelectrodes, as used by Muzikář and Fawcett[22,23] in their studies of this system in dilute $HClO_4$ media at 25 °C. Oxidizing anions such as perchlorate and nitrate, however, are usually avoided in Ru ammine chemistry because of the risk of oxidation of $Ru(NH_3)_6^{3+}$ and especially $Ru(NH_3)_6^{2+}$;[47,48] this is unlikely to have been significant in the work of Muzikář and Fawcett because of the evidently short time-scales of their experiments, the moderate concentrations of ClO_4^-, and the merely transient presence of $Ru(NH_3)_6^{2+}$. In our study, the variable-pressure and -temperature experiments extended over several hours, and therefore only chloride and trifluoromethanesulfonate (triflate) media and $Ru(NH_3)_6^{3+}$ salts were used in them; no attempt was made to isolate solid $[Ru(NH_3)_6](ClO_4)_3$ as it is of limited solubility[24] and is potentially explosive.

■ EXPERIMENTAL SECTION

Fabrication of Ultramicroelectrodes (UMEs). Gold (⌀ 12.7 μm, 99.9%; ⌀ 25 μm, 99.95%) and Pt (⌀ 25 μm, 99.95%; ⌀ 10 μm, 99.95%) wires were obtained from Alfa Aesar. The wires were soldered to Cu connecting wire and then sealed in soft glass tubes by melting the latter cautiously in a Bunsen flame. The other end was closed with an insulating epoxy resin. Then the uniform microelectrode surface was exposed by grinding the tip with fine sandpaper (1500 grade) followed by polishing in a suspension of 0.05 μm alumina. For the high pressure work, the Au (⌀ 25 μm) and Pt (⌀ 25 μm) electrodes were constructed from polypropylene micropipet tips by melting the latter cautiously with an ethanol flame. The ends of the micropipet tips were then cut off squarely to expose a disk UME. The remainder of the tip was trimmed down and glued to the electrode holder with an insulating epoxy resin. The integrity of the UME disks and seals as checked with an optical microscope. The UME faces were polished with an aqueous suspension of 0.05 mm alumina, sonicated briefly in a $K_2S_2O_8/H_2SO_4$ bath to remove any traces of oxidizable matter, then sonicated for 2 min in deionized water. Final cleaning to eliminate any contaminants (e.g., a surface oxide layer) that might interfere with the electrochemical measurements was carried out at the start of each experiment by cycling the potential up to 16 times over the working range (typically −500 to +200 mV vs AgCl/Ag) at 20 mV s^{-1} until the cyclic voltammogram (CV) showed a constant limiting current I_{lim}. These measurements of I_{lim} gave values of the diffusion coefficient *D* of $Ru(NH_3)_6^{3+}$

$$D = I_{lim}/4FrC \tag{1}$$

(where *C* is the concentration of $Ru(NH_3)_6^{3+}$, *F* is the Faraday constant, and *r* is the radius of the UME disk) in reasonable agreement with those in the literature; as noted below, however, I_{lim} measured from a CV depends on the identity and concentration of the supporting electrolyte and comparisons can only be made where these are the same. For example, for UMEs made from Au or Pt wire of diameter $2r = 25.0$ μm (according to the wire manufacturer), I_{lim} for 5.0 mmol L^{-1} $[Ru(NH_3)_6]Cl_3$ in 0.1 mol L^{-1} KCl at 25 °C was 23−24 nA, corresponding to $D = 9.5 \times 10^{-6}$ cm^2 s^{-1}; literature values of *D* for $Ru(NH_3)_6^{3+}$ for these conditions range from 6.4×10^{-6} cm^2 s^{-1} to 9.4×10^{-6} cm^2 s^{-1}.[19,49−52] These observations, together with the consistency of the kinetic results between different experiments as described below, indicate that the potential cycling procedure did not have adverse effects on the electrochemical measurements.

Materials. Deionized water was further purified to ≥18.0 MΩ cm by passage through a Barnstead E-Pure train. $[Ru(NH_3)_6]Cl_3$ (Strem Chemicals, 99%), triflic acid (Sigma Aldrich, 98%), hydrochloric acid (Merck), perchloric acid (Baker), NaCl (Fisher Certified) and KCl (Fisher Certified) were used as received, and KCF_3SO_3 was either prepared as previously described[53] or purchased from Alfa Aesar and recrystallized from methanol. $[Ru(NH_3)_6](CF_3SO_3)_3$ was prepared from aqueous $[Ru(NH_3)_6]Cl_3$ by removal of Cl^- with $AgCF_3SO_3$, followed by precipitation and recrystallization of $[Ru(NH_3)_6](CF_3SO_3)_3$ from aqueous CF_3SO_3H, as described by Lavallee et al.;[54] the purity of the colorless needles was established by multiple CHN microanalyses (calc.: C, 5.54; H, 2.79; N, 12.92; found: C, 5.67; H, 2.84; N, 12.86%) and by the molar absorbance of aqueous solutions (460 ± 10 L mol^{-1} cm^{-1} at 275 nm[54]).

Electrochemical Measurements. CV and variable-frequency ac impedance measurements were made with either a thermostatted conventional three-electrode cell or the high-pressure three-electrode Teflon cell previously described,[53] using a Model CHI650C electrochemical workstation with a Model CHI200 picoamp booster and Faraday cage (CH Instruments, Austin, TX); backup measurements using a Model CHI650B workstation gave identical results. The reference electrode was Ag/AgCl/KCl (satd. aq. at 25 °C, or, for experiments at variable *P* or *T*, 4.0 mol L^{-1}, i.e., just below saturation[55]), freshly prepared before each day's series of measurements by anodic electrolysis of a silver wire in 4.0 mol L^{-1} KCl solution at 0.7 V vs Ag/AgCl/KCl(satd) for 20 min. The working electrode was a Pt or Au UME, and the counter electrode a Pt wire (typically ø 0.5 mm, ~1 cm long). Experiments at ambient pressure were conducted with the cell either in the CHI Faraday cage or completely enclosed in grounded Al foil, whereas for the high pressure experiments it was sufficient simply to ground the pressure vessel; in all cases, the external connectors were sheathed in grounded Al foil. The pressure vessel and pressure train have been described elsewhere;[53] the pressure transmitting fluid was mixed hexanes, separated from the hydraulic oil of the manual pump and intensifier by a vessel with a free piston. All variable-pressure experiments were run at 25.0 ± 0.1 °C, which was maintained with externally thermostatted water circulating through the pressure vessel jacket and measured inside the pressure vessel before and after the pressure cycle. For experiments at variable temperature and 0.1 MPa, a glass cell incorporating a jacket for circulating water from the external thermostat was used, and temperatures within the sample were measured (±0.1 °C) with a calibrated thermistor encased in an inert plastic.

All solutions contained 5.0 mmol L^{-1} $[Ru(NH_3)_6]Cl_3$ or $[Ru(NH_3)_6](CF_3SO_3)_3$ and were purged with Ar for 30 min before the experiments. For measurements at ambient pressure, an Ar atmosphere was maintained. Spectrophotometric measurements at 275 nm showed that $[Ru(NH_3)_6](CF_3SO_3)_3$ solutions underwent no significant decomposition at near-ambient temperatures over at least 24 h. Measurements of the cell impedance were made using the supplied CHI software by applying an ac signal of amplitude 10 mV and frequency f within the range 0.96−96 kHz (depending on reaction rate being measured) superimposed on a dc signal that was swept typically over 250−350 mV on each side of the formal potential of the $Ru(NH_3)_6^{3+/2+}$ couple (~ −130 mV vs Ag/AgCl/KCl(satd)). Scan rates were normally 10 mV s^{-1}.

■ RESULTS

In the following, the usual assumption[56] is made that the diffusion coefficients of $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{2+}$ are close enough to be taken as approximately the same, as literature data affirm.[16,21,57]

Electrode and Electrolyte Effects. Figure 1 shows a simplified equivalent (Randles) circuit relating the overall impedance of an electrochemical cell to the faradaic impedance Z_f, the Warburg (diffusional) impedance Z_W, the uncompensated solution resistance R_u, and the double-layer capacitance C_{dl}. The Warburg impedance can be neglected at the ac frequencies used in our experiments.[58] Before making an impedance measurement, the uncompensated resistance R_u was measured and automatic correction for it was implemented using the CHI software.

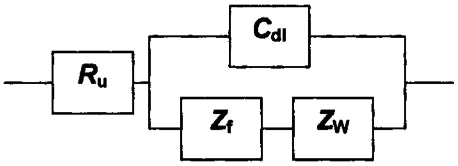

Figure 1. Simplified equivalent circuit for an electrochemical cell with UME working electrode.

The impedance Z_f can be resolved using the CHI software into real (Z_f') and imaginary (Z_f'') components, each of which should be a linear function of $\omega^{-1/2}$, where $\omega = 2\pi f$, with slope s for a simple electron transfer process:

$$Z_f' = R_{ct} + s\omega^{-1/2} \tag{2}$$

$$Z_f'' = s\omega^{-1/2} \tag{3}$$

where R_{ct} is the charge transfer resistance.[22,23,58] Extrapolation of Z_f' to infinite frequency gives R_{ct}, from which the standard rate constant k_{el} for the electrode reaction can be calculated from eq 3, in which n is the number of electrons transferred per mol (here, $n = 1$), a is the area of the UME disk, C is the bulk concentration of the electroactive species, and the other symbols have their usual meaning in the SI.

$$k_{el} = RT/n^2F^2aCR_{ct} \tag{4}$$

If a UME is performing correctly, the CV should be a tight sigmoidal trace rather than the "duck" shape familiar from measurements with conventional electrodes. This was checked as a prelude to each impedance measurement, as exemplified for a series of supporting-electrolyte concentrations by Figure 2 in which it may be seen that the ideal sigmoidal shape is more closely approached the higher the concentration of supporting electrolyte (i.e., the faster the electrode reaction, see below). Values of the transfer coefficient α were calculated from eq 5, in which E_{max} is the potential of maximum real admittance Y' (cf. Figure 3) and $E_{1/2}$ is the CV half-wave potential; in all cases, $|E_{max} - E_{1/2}| \leq 5$ mV, whence $\alpha = 0.50 \pm 0.05$ (cf. Muzikář and Fawcett[22]). For example, for $[Ru(NH_3)_6]Cl_3$ reduction on a 25 μm Au UME in 0.1 mol L^{-1} KCl at 25 °C, $E_{max} = -0.134$ V and $E_{1/2} = -0.135$ V, giving $\alpha = 0.51$.

$$E_{max} = E_{1/2} + (RT/F)\ln[\alpha/(1-\alpha)] \tag{5}$$

If the CV was satisfactory, impedance measurements were then made as a function of the dc potential at selected frequencies. The frequencies typed in differed slightly from the work-station's actual operating frequencies f, which were recorded and converted to angular frequencies $\omega = 2\pi f$. Whereas the uncompensated resistance can be corrected for by direct subtraction from the real impedance, correction for the double-layer capacitance C_{dl} requires conversion to admittances Y_f (reciprocals of Z_f). Typical real and imaginary admittances Y_f' and Y_f'' are plotted in Figure 3, which also illustrates the importance of correcting for R_u, at least in Y_f''. The absence of substantial distortions and baseline noise in admittance vs potential plots such as Figure 3 indicated that instrumental and other artifacts that may occur at high frequencies[59] were negligible.

In accordance with eqs 2 and 3, Z_f' and Z_f'' for a given experiment were plotted together against $\omega^{-1/2}$ (a Randles plot),[58] as shown in Figure 4 for an experiment with 12 data points spanning a wide frequency range (0.962−46.3 kHz). A result was accepted only if, within the experimental uncertainty, the Z_f' and Z_f'' plots were linear, their slopes s were the same, and Z_f'' extrapolated to zero at infinite frequency ($\omega^{-1/2} = 0$), confirming the absence of instrumental distortions at high frequencies. The intercept of the Z_f' plot then gave R_{ct}, from which the rate constant k_{el} could be calculated from eq 4; in practice, however, errors in the impedances Z_f' and Z_f'' tended to be similar, and averaged values of ($Z_f' - Z_f''$) were therefore used in place of R_{ct}, giving a modest improvement in the standard error. For example, least-squares regression of the Z_f'' data of Figure 4 gave a slope s of 6.87 ± 0.09 MΩ $rad^{1/2}$ $s^{-1/2}$ and intercept −0.57 ± 0.54 kΩ ($r^2 = 0.9982$); thus, the intercept is negligible on the impedance scale, as eq 3 requires, and the lower straight line in Figure 4 is therefore plotted with the intercept set to zero. For Z_f', regression gave a slope s = 7.01 ± 0.13 MΩ $rad^{1/2}$ $s^{-1/2}$, which is not statistically distinguishable from that for Z_f'', as required by eqs 2 and 3,

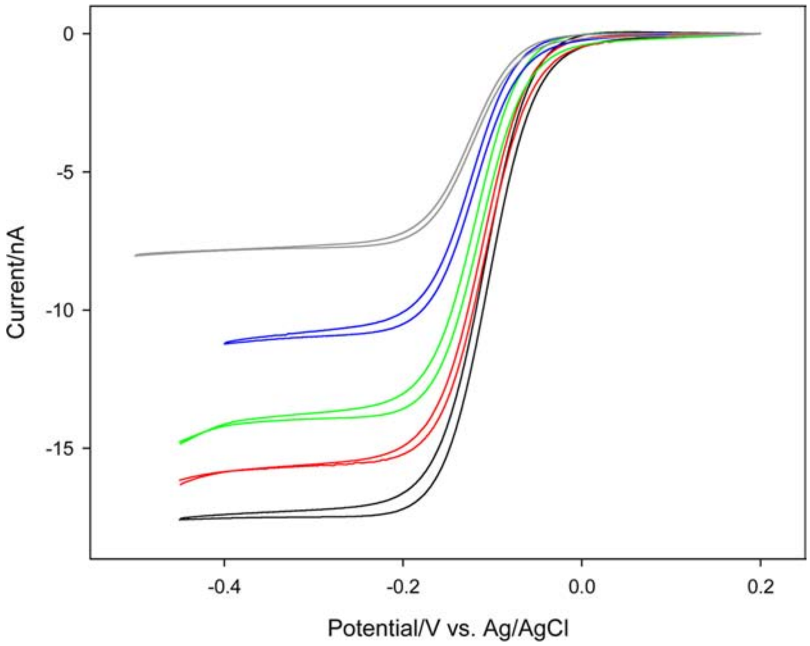

Figure 2. Cyclic voltammograms of the reduction of 5.0 mmol L^{-1} [Ru(NH$_3$)$_6$](CF$_3$SO$_3$)$_3$ at a Pt disk (⌀ 10 μm) at 25.0 °C; scan rate = 10 mV s^{-1}. Concentration of KCF$_3$SO$_3$ supporting electrolyte (mol L^{-1}) = 0 (black), 0.05 (red), 0.10 (green), 0.15 (blue), and 0.20 (gray).

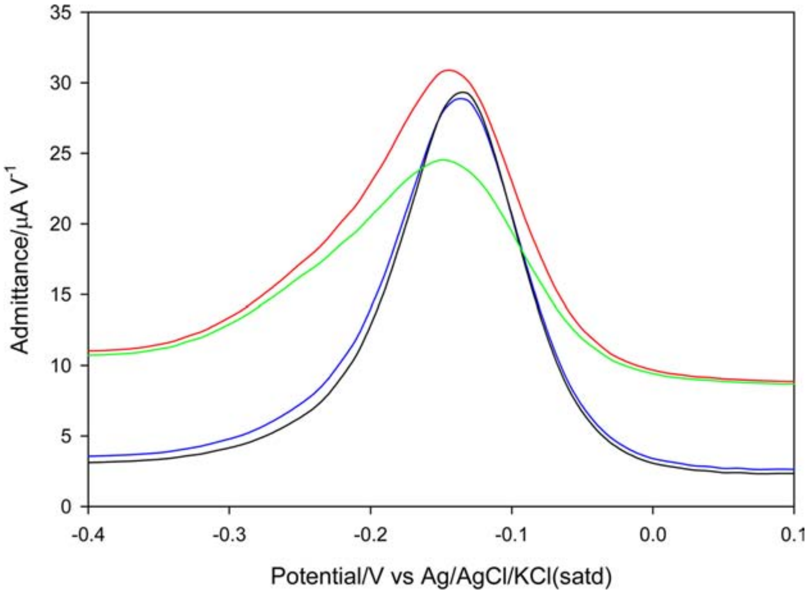

Figure 3. Real (Y') and imaginary (Y'') admittances as a function of potential vs Ag/AgCl for reduction of [Ru(NH$_3$)$_6$]Cl$_3$ (5.0 mmol L^{-1}) at a Pt disk (⌀ 25 μm) in 0.1 mol L^{-1} KCl at 30 °C and f = 3205 Hz. Blue, Y_f' uncorrected for uncompensated resistance R_u; black, corrected Y_f'; green, uncorrected Y_f''; red, corrected Y_f''. Scan rate 10 mV s^{-1}.

and an intercept R_{ct} = 17.9 ± 0.8 kΩ (r^2 = 0.9966), cf. an average ($Z_f' - Z_f''$) of 19.1 ± 0.4 kΩ which was used to calculate k_{el}. In practice, good Randles plots and acceptable values of k_{el} could usually be obtained with as few as 4−5 choices of f. Again, the consistency of the data at the highest frequencies with the rest of the plot affirmed correct instrumental function.[59]

Table 1 lists standard electrode reaction rate constants k_{el} derived from Randles plots in which the Z_f' and Z_f'' lines were parallel, the Z_f'' plot extrapolated to zero at $\omega^{-1/2} = 0$, and the data scatter was acceptable, all within the experimental uncertainty. The calculation of k_{el} from eq 4 required values of the effective areas a of the microelectrode disks; these could be determined either approximately from the manufacturer's wire diameters or more precisely from the limiting currents I_{lim} of CVs of either Ru(NH$_3$)$_6^{3+}$ or Fe(CN)$_6^{3-}$ solutions:

$$a = \pi(I_{lim}/4nFDC)^2 \qquad (6)$$

where D is the diffusion coefficient of Ru(NH$_3$)$_6^{3+}$[19,22,49−52] or Fe(CN)$_6^{3-}$ (7.63 × 10^{-6} cm^2 s^{-1}).[60] Values of a from eq 6 were slightly greater than calculated from the geometrical cross-section of the wire (e.g., in a typical experiment with Au and Pt UMEs made from wire of diameter 25.0 μm, the areas measured according to eq 6 corresponded to ⌀ 26.0 and 29.7 μm, respectively); these discrepancies are attributable to microscopic roughness of the UME surfaces.[61] For the

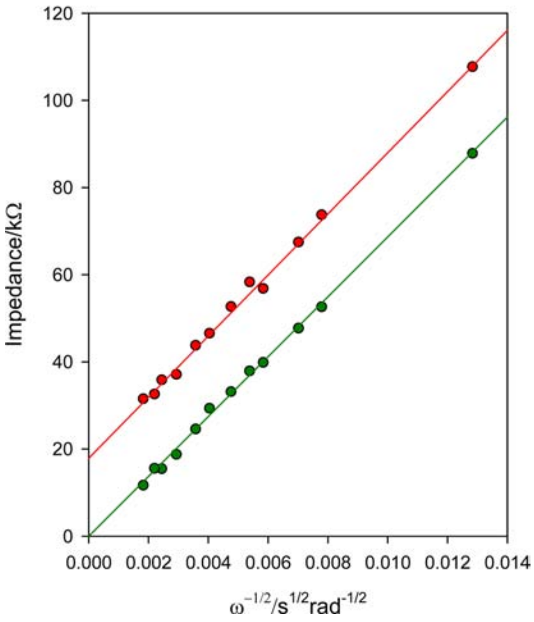

Figure 4. Randles plot for the reduction of $[Ru(NH_3)_6](CF_3SO_3)_3$ (5.0 mmol L^{-1}) in aqueous KCF_3SO_3 (0.20 mol L^{-1}) at a gold disk electrode (⌀ 25 μm) at 25.0 °C. Red data: real impedance Z_f'. Green data: imaginary impedance Z_f''. Average uncompensated resistance was 7.59 ± 0.08 kΩ.

purposes of this study, however, relative rather than absolute values of k_{el} are required in assessing electrolyte, pressure, and temperature effects, and geometrical values of a based on the wire diameters given by the manufacturers were used in calculating the k_{el} data of Table 1, which is common practice in UME studies; possible contamination of the UMEs in measuring I_{lim} prior to an experiment was thereby avoided. The uncertainties cited in Table 1 represent the goodness of fit to eqs 1 and 2 rather than absolute accuracy of k_{el}; nevertheless, reasonable agreement may be noted between k_{el} values obtained for given conditions but with different personnel and sources of chemicals and materials. Agreement with literature values of k_{el},[13,15−23] where conditions were comparable, was also satisfactory, given the difficulties in obtaining reproducible k_{el} for fast electrode reactions and the lack of clarity in some earlier publications (e.g., Iwasita et al.[15,16]) as to whether appropriate corrections (e.g., for uncompensated resistance, important for rapid electrochemical reactions such as $Ru(NH_3)_6^{3+/2+}$[50]) had been applied. Table 1 shows that the main influences on k_{el} are supporting electrolyte identity and concentration, and the UME diameter; the identity of the polycrystalline UME metal (Pt vs Au) has little effect.

Temperature Dependence of k_{el}. The temperature dependence of k_{el} for $[Ru(NH_3)_6](CF_3SO_3)_3$ in 0.1 mol L^{-1} KCF_3SO_3 at a Pt UME is shown in Figure 5 as an Arrhenius plot ($\ln k_{el} = \ln A - E_a/RT$) for which the activation energy E_a = 18.8 ± 1.1 kJ mol^{-1} and $A = 4.3 \times 10^2$ cm s^{-1}. Thus, the temperature sensitivity of k_{el} is quite low. Use of Eyring enthalpies $\Delta H_{el}^{\ddagger}$ (= $E_a - RT$) and entropies $\Delta S_{el}^{\ddagger}$ of activation was avoided, as $\Delta S_{el}^{\ddagger}$ values as normally calculated depend on the units of the rate constants, and naïve comparison with other entropy parameters could be misleading. For the reduction of $[Ru(NH_3)_6]Cl_3$ in 0.1 mol L^{-1} KCl at a gold UME (⌀ 25 μm), 5.3−29.1 °C, E_a was found to be 24.8 ± 1.3 kJ mol^{-1} (Supporting Information, Figure S1).

Pressure Effects. The results reported in this section all refer to reductions of $Ru(NH_3)_6^{3+}$ at UMEs of diameter 25.0 μm, as UMEs of smaller diameters proved to be too fragile to give reproducible measurements at variable pressure. Figure 6 shows the pressure dependences of the half-wave potential ($E_{1/2}$, from the midpoints of CVs run before each set of impedance measurements at a given pressure P) and of the corresponding standard rate constant k_{el} for a typical $[Ru(NH_3)_6](CF_3SO_3)_3$ electrode reaction, in this case reduction at a gold UME in 0.10 mol L^{-1} KCF_3SO_3 at 25.0 °C. Both plots are linear within experimental uncertainties. It was important to show that the measurements taken with increasing pressure (filled symbols) were consistent with those subsequently taken with decreasing pressure (hollow symbols)—that is, that no time-dependent changes such as decomposition of the Ru complexes occurred over the several hours' duration of the experiment.[62] For the lower plot in Figure 6, $E_{1/2} = (-0.196 \pm 0.002) - (2.49 \pm 0.16) \times 10^{-4}P$, from which the volume of reaction $\Delta V_{el} = -F(\partial E_{1/2}/\partial P)_T$ cm^3 mol^{-1} for the $Ru(NH_3)_6^{3+}$ reduction half-cell relative to Ag/AgCl is 24.0 ± 1.6 cm^3. The UME-CV method, however, is not well suited to precise measurements of the small changes in $E_{1/2}$, and ΔV_{el} values obtained in this way ranged from 20.3 ± 1.6 cm^3 mol^{-1} for reduction of $[Ru(NH_3)_6](CF_3SO_3)_3$ in 0.10 mol L^{-1} KCF_3SO_3 at a Pt UME to about 25 cm^3 mol^{-1} for $[Ru(NH_3)_6]Cl_3$ in 0.1 mol L^{-1} KCl at Au and Pt UMEs. These results are nevertheless consistent with the definitive ΔV_{el} measurements of Tregloan and co-workers[63−65] for reduction of $Ru(NH_3)_6^{3+}$ made at conventional electrodes (20.2 ± 0.4 cm^3 mol^{-1} in 0.1 mol L^{-1} KNO_3 at Au, and 19.7 ± 0.6 cm^3 mol^{-1} in 0.1 mol L^{-1} $NaClO_4$ at Hg/Au, relative to Ag/AgCl).

The pressure dependence of ln k_{el} was linear, within the experimental uncertainty, in all cases studied; in other words, the volume of activation $\Delta V_{el}^{\ddagger}$ was effectively constant over the 200 MPa pressure range. For $[Ru(NH_3)_6](CF_3SO_3)_3$ in 0.10 mol L^{-1} KCF_3SO_3 at a gold UME (upper frame of Figure 6), $\ln k_{el} = (-1.999 \pm 0.030) + (6.15 \pm 0.30) \times 10^{-3}P$ for P in MPa, whence $\Delta V_{el}^{\ddagger} = -15.3 \pm 0.7$ cm^3 mol^{-1} for 0.10 mol L^{-1} KCF_3SO_3 at Au; for the same system at a Pt UME, $\Delta V_{el}^{\ddagger} = -15.9 \pm 1.1$ cm^3 mol^{-1}. For reduction of $[Ru(NH_3)_6]Cl_3$ (5.0 mmol L^{-1}) in 0.10 mol L^{-1} KCl, $\Delta V_{el}^{\ddagger} = -12.3 \pm 1.0$ and -12.3 ± 0.6 cm^3 mol^{-1} at 25 μm Au and Pt UMEs, respectively. Thus, $\Delta V_{el}^{\ddagger}$ is independent of the UME metal but shows some significant dependence on the nature of the anion of the supporting electrolyte.

Measurements of $\Delta V_{el}^{\ddagger}$ for perchlorate media at variable pressure were impractical, as the rate constants, already fast at ambient pressure, would become too fast for accurate measurement at increased pressures. The possibility of oxidation of the Ru complexes by ClO_4^- over the time-scale of a pressure cycle was also a concern.

■ DISCUSSION

Cyclic Voltammetry. The maxima $|I_{lim}|$ of the (negative) CV currents for reduction of $Ru(NH_3)_6^{3+}$ were markedly dependent on the concentrations of the supporting electrolyte, as shown for example in Figure 2. This reflects a substantial contribution from the migration current,[66] which is negative for the reduction of a cation at an electrode but tends to zero as the concentration of the supporting electrolyte (and hence the solution conductivity) is increased. Thus, as shown in Figure 2, the observed $|I_{lim}|$ for the reduction of $[Ru(NH_3)_6](CF_3SO_3)_3$ was largest when no supporting electrolyte was present, but

Table 1. Dependence of Standard Rate Constants k_{el} for the Reduction of Aqueous $Ru(NH_3)_6^{3+}$ at Polycrystalline Au and Pt UMEs on UME Disk Diameter and Supporting Electrolyte Concentration[a]

X in $[Ru(NH_3)_6]X_3$	electrolyte, mol L^{-1}	Au 25 μm	Pt 25 μm	Au 12.7 μm	Pt 10 μm
Cl	none	0.089 ± 0.001			
	KCl, 0.05	0.234 ± 0.005		0.66 ± 0.01	
				0.71 ± 0.01[b]	
	0.08			1.78 ± 0.03	
	0.10	0.54 ± 0.01	0.52 ± 0.01	2.20 ± 0.05	
		0.62 ± 0.03[c]	0.43 ± 0.01[c]		
			0.49 ± 0.03[b,c]		
	0.15	0.88 ± 0.03			
	0.20	1.05 ± 0.01	1.16 ± 0.17[b]		
	HCl, 0.02	0.063 ± 0.001		0.26 ± 0.01	
	0.05	0.29 ± 0.01		0.65 ± 0.01	
	0.10	0.62 ± 0.01		1.84 ± 0.13	
	NaCl, 0.10	0.66 ± 0.01		1.86 ± 0.06	
	KO_3SCF_3, 0.10	0.28 ± 0.01	0.38 ± 0.01	0.98 ± 0.02[b,c]	
			0.29 ± 0.02[b,c]		
	$HClO_4$, 0.02	0.21 ± 0.01		0.27 ± 0.01	
	0.05	0.84 ± 0.01			
CF_3SO_3	none	0.088 ± 0.001			0.21 ± 0.01
	KO_3SCF_3, 0.05	0.21 ± 0.01	0.18 ± 0.01	0.21 ± 0.01	0.68 ± 0.01
	0.10	0.39 ± 0.01	0.38 ± 0.01	0.46 ± 0.01	0.97 ± 0.01
	0.15				1.16 ± 0.01
	0.20	0.57 ± 0.01	0.53 ± 0.01	0.85 ± 0.02	
	$HClO_4$, 0.02			0.33 ± 0.01	
	0.05	0.95 ± 0.03			

[a] 25.0 °C, 0.1 MPa; $[Ru(NH_3)_6^{3+}]$ = 5.0 mmol L^{-1}. Uncertainties reflect standard errors in R_{ct} or average $(Z_f' - Z_f'')$. [b] Measurements by G.L.; all others by V.V. [c] Extrapolated to 0.1 MPa from high pressure kinetic measurements.

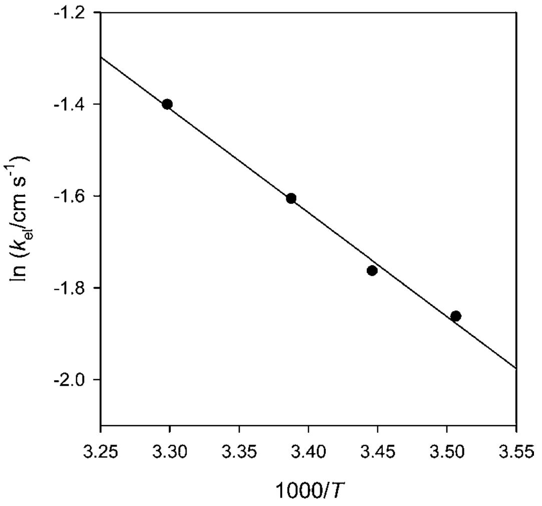

Figure 5. Temperature dependence of k_{el} for reduction of $[Ru(NH_3)_6](CF_3SO_3)_3$ in aqueous 0.1 mol L^{-1} KCF_3SO_3 at a Pt UME (ø 25 μm).

decreased with increasing concentrations of added KCF_3SO_3 (cf. the reduction of $Tl(aq)^+$ at a mercury-on-silver UME in aq. $LiClO_4$[67]). Moreover, the shape of the CVs approached the ideal tight sigmoid more closely in presence of ≥0.1 mol L^{-1} supporting electrolyte, which also gave higher rate constants (Table 1) and generally better fits to eqs 2 and 3. Measurements of k_{el} at variable temperature and pressure were therefore conducted using 0.1 mol L^{-1} KCl or KCF_3SO_3 as supporting electrolyte.

Factors Affecting the Rate Constants. The following observations emerge from Table 1.

(1) Although one special advantage of UMEs is that they can yield kinetic data in absence of a supporting electrolyte, values of k_{el} for $[Ru(NH_3)_6]X_3$ without an added electrolyte are presented only for X = Cl and CF_3SO_3 at a 25 μm gold UME; for measurements on other systems without a supporting electrolyte, the data quality criteria given above were not met.

(2) For a given anion X, k_{el} is about the same at polycrystalline Au and Pt UMEs *of the same diameter*—compare, for example, data for 0.10 mol L^{-1} added KCl, or for 0.10 mol L^{-1} KCF_3SO_3, at 25 μm UMEs. Muzikář and Fawcett[23] found that, for reduction of $Ru(NH_3)_6^{3+}$ at single-crystal Au UMEs, k_{el} at Au(111) was significantly larger than at Au(100), which may account in part for the difficulty in obtaining reproducible k_{el} values between polycrystalline UMEs but also diminishes the effectiveness of an apparent lack of dependence of k_{el} on the identity of the metal of the electrode

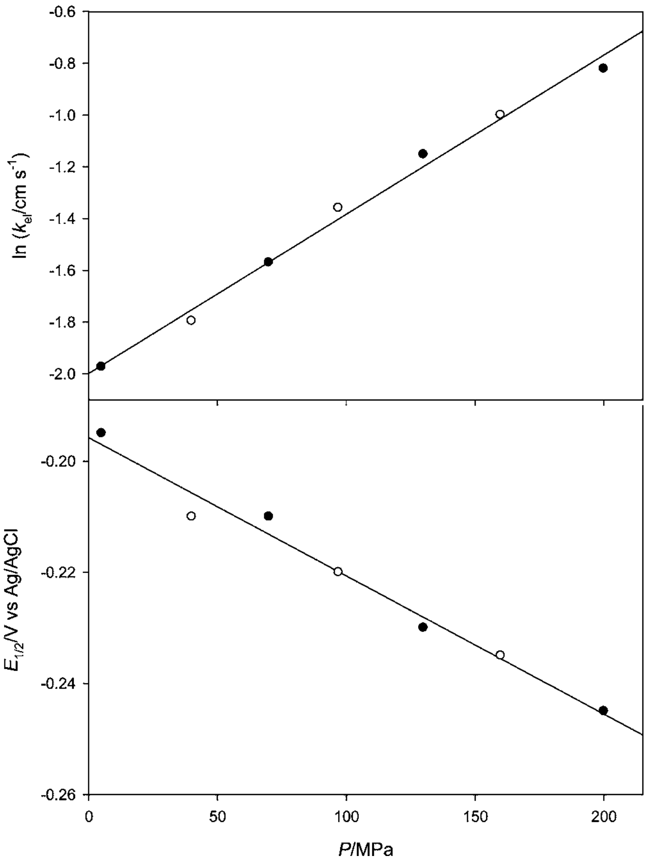

Figure 6. Pressure dependences of the half-wave potential $E_{1/2}$ relative to Ag/AgCl (lower frame), and the standard rate constant k_{el} (upper frame), for reduction of $[Ru(NH_3)_6](CF_3SO_3)_3$ (5.0 mmol L^{-1}) in 0.10 mol L^{-1} KCF_3SO_3 at a gold UME (⌀ 25 μm) at 25.0 °C; pH ≈ 5. Filled symbols: increasing pressure. Open symbols: decreasing pressure.

as a criterion of adiabaticity. With this reservation, and noting the argument of Gosavi and Marcus[10] discussed in the Introduction, the reduction of $Ru(NH_3)_6^{3+}$ at Au and Pt UMEs can be taken to be either essentially adiabatic or at least not strongly nonadiabatic—our data do not distinguish definitively between these two possibilities. In any event, the practical issue is that the metal of the electrode (Au vs Pt) has no bearing on the interpretation of the measurements reported here.

(3) The apparent values of k_{el} increase substantially on going from an electrode diameter of 25 μm to 12.7 and then to 10 μm. Although the upper limit of disk diameter for true UME behavior, with convergent radial diffusion of the electroactive species to the disk, is usually taken to be ~50 μm (i.e., radius 25 μm),[61] it is possible that a contribution from planar diffusion of $Ru(NH_3)_6^{3+}$ may have persisted in the disks of larger diameter, resulting in the observation of reaction rates slower than the "true" value. The slightly broadened shapes of some of the CVs in Figure 2 are consistent with this interpretation.[68] Indeed, Sun and Mirkin[69] found that the reduction of $[Ru(NH_3)_6]Cl_3$ in 0.5 mol L^{-1} KCl at Pt nanoelectrodes of radii 282−14.7 nm gave k_{el} values that increased from ~14 to ~19 cm s^{-1} over that range of radii (mean k_{el} = 17.0 ± 0.9 cm s^{-1}), so that it would appear that the electrode disk radius effect continues below the UME size range (extrapolation of our data for a Pt UME of diameter 25 μm to the KCl concentration used by Sun and Mirkin gives k_{el} = 2.6 cm s^{-1}). For our purposes of determining electrolyte, pressure, and temperature effects, however, comparison of apparent values of k_{el} at disk UMEs of a common diameter was sufficient.

(4) The strong accelerating effect of supporting electrolytes on k_{el} is a function of the electrolyte concentration but is due specifically to the anion. Thus, for supporting electrolytes MX at 0.1 mol L^{-1}, k_{el} was essentially the same for M = K, Na, and H when X was Cl. For different X, however, k_{el} increased in the sequence $CF_3SO_3 < Cl \ll ClO_4$. For reduction of $[Ru(NH_3)_6]Cl_3$ at a gold electrode (⌀ 25 μm) at 25.0 °C (the most extensive data set), k_{el} was a linear function of $[Cl^-]$ (Supporting Information, Figure S2), and a least-squares regression of the data of Table 1 gave k_{el}/cm s^{-1} = (−0.02 ± 0.05) + (5.11 ± 0.34)$[Cl^-]_{total}$, where $[Cl^-]_{total}$ includes Cl^- from both KCl (if present) and $[Ru(NH_3)_6]Cl_3$; the fact that the intercept is zero within the error limit implies that the reduction reaction rate would be negligibly small in the hypothetical case in which no chloride was present. Thus, for the system with chloride as the only anion present, the electrode reaction mechanism intimately involves the anion, even in absence of the supporting electrolyte. The limited data for the triflate-only system at 25 and 10 μm disks are better represented by curves passing through the origin; for the 10 μm Pt disk, an empirical quadratic fit with R^2 = 0.9994 extrapolated to hypothetical zero triflate with k_{el}^0 = 0.050 ± 0.020 cm s^{-1} (Supporting Information, Figure S3), from which case it can again be inferred that the $Ru(NH_3)_6^{3+/2+}$ electrode reaction rate would be very small in the hypothetical absence of the anion.

(5) Instrumental limitations set the upper limit of k_{el} obtainable at about 2 cm s^{-1}, and accordingly no data for [MX] > 0.20 mol L^{-1} are listed in Table 1. For the same reason, k_{el} values for reduction of $[Ru(NH_3)_6]X_3$ (X = Cl or CF_3SO_3) in $HClO_4$ are listed only for $[ClO_4^-]$ up to 0.05 mol L^{-1}, beyond which the reaction rates were too high to measure with the desired accuracy. The standard rate constants at a gold UME of diameter 12.7 μm in 0.02 mol L^{-1} $HClO_4$ are somewhat lower than that reported by Muzikář and Fawcett[22] (0.54 cm s^{-1}) for the same system (X presumably was Cl) at a polycrystalline gold UME of diameter 12.5 μm (6.25 μm radius—apparently misprinted as diameter in Table 2 of ref 22).

The direct proportionality of k_{el} for the $Ru(NH_3)_6^{3+/2+}$ cation−cation electron transfer reaction at Au or Pt UMEs in all-chloride systems to the total anion (chloride) concentration, independently of the accompanying alkali-metal or H cations, recalls (reversed charge-type notwithstanding) that of both k_{el} and the corresponding homogeneous self-exchange rate constant k_{ex} for the $AlW_{12}O_{40}^{5-/6-}$ anion−anion electron transfer reaction on the cation (various alkali metal ions) concentration, independently of the accompanying anions.[53] For $AlW_{12}O_{40}^{5-/6-}$, it was shown[53] that the variable relevant to the cation-specific catalysis was simply the concentration of the cation, and not Debye−Hückel, Gouy−Chapman, ion-pairing, or other medium effects. Specific alkali-metal ion catalysis of other anion−anion electrode and self-exchange reactions such as $PW_{12}O_{40}^{3-/4-}$, $CoW_{12}O_{40}^{5-/6-}$, $Mo(CN)_8^{3-/4-}$, $W(CN)_8^{3-/4-}$, and $Os(CN)_6^{3-/4-}$ has also been described,[70−72] while for the $Fe(CN)_6^{3-/4-}$ homogeneous self-exchange reaction alkali-metal cation catalyzed pathways are completely dominant unless the alkali-metal cations are sequestered with crypt-2.2.2 or 18-crown-6 to expose the very slow direct exchange of $Fe(CN)_6^{3-}$ with $Fe(CN)_6^{4-}$.[62] Measurement of k_{ex}

for the $Ru(NH_3)_6^{3+/2+}$ self-exchange[73−75] is technically challenging (k_{ex} = 3.2 × 10^3 L mol^{-1} s^{-1} at 25 °C in 0.1 mol L^{-1} CF_3SO_3H[74]), but a linear dependence of k_{ex} for that reaction on chloride concentration has been reported, although a definitive separation of a specific Cl^- catalysis from ionic strength effects could not be made.[75] In this connection, we note that, for the homogeneous $Ru(en)_3^{3+/2+}$ self-exchange reaction (en = 1,2-diaminoethane), k_{ex} is some 20-fold higher in chloride than in comparable triflate media,[76] so that the Cl^- catalysis effect found in this study may reflect a specific affinity of Cl^- for Ru am(m)ine complexes. To summarize, the dominant counterion (Cl^- and $CF_3SO_3^-$) catalysis of the $Ru(NH_3)_6^{3+/2+}$ electrode reaction reported here, and possibly also Cl^- catalysis of the homogeneous $Ru(NH_3)_6^{3+/2+}$ self-exchange,[75] have precedents in the counterion catalysis of the electrode and homogeneous self-exchange electron transfer kinetics of several anion−anion couples.

In interpreting the role of $CF_3SO_3^-$, Cl^-, and ClO_4^- in promoting the $Ru(NH_3)_6^{3+/2+}$ electrode reaction, the tendency of these anions to adsorb on the Au and Pt electrode surfaces should be considered. For the Cl^--catalyzed electrode reaction, the direct proportionality of k_{el} to $[Cl^-]$ suggests that any such adsorption is far from saturation over the concentration ranges used in our experiments, whatever the kinetic role of Cl^- might be. The specific adsorption of Cl^- on Pt[77−82] and Au[81,83−85] is known to be well advanced at potentials on the order of +0.8 V vs NHE, but only incipient at the formal potential of the $Ru(NH_3)_6^{3+/2+}$ electrode reaction (∼ −0.13 V vs Ag/AgCl-(satd. KCl), ∼ +0.07 V vs NHE; the potential sweeps in our impedance measurements, however, extended 250−350 mV on either side of this). The adsorption of ClO_4^- on Pt or Au in this potential range is generally considered negligible (most of the Cl^- adsorption studies cited here involved background perchlorate), although specific adsorption of perchlorate does occur at high potentials (>1 V).[86,87] For our study, $CF_3SO_3^-$ was chosen as an alternative to perchlorate for reasons given in the Introduction, on the assumption that triflate would behave similarly to perchlorate with respect to adsorption on Au and Pt electrode surfaces. Indeed, Lipkowski, Burgess, and co-workers have reported[88] that $CF_3SO_3^-$ adsorbs only very weakly at a positively charged Au electrode surface, and experimental data supplied privately by Lipkowski and Burgess confirm this (although coadsorption of $CF_3SO_3^-$ with a cationic surfactant on Au was noted[89]). Bockris et al.,[90] however, found that adsorption of aqueous $CF_3SO_3^-$ was extensive on a Pt electrode at 0.8 V vs NHE ($\Delta H_{ads}{}^0$ = −44 kJ mol^{-1} and $\Delta S_{ads}{}^0$ = −97 J K^{-1} mol^{-1}; cf. −30 kJ mol^{-1} and −80 J K^{-1} mol^{-1}, respectively, for Cl^- on Pt[82]), and was substantial even at −0.05 V, with the consequence that an adsorption-free reference potential could not be reached before H_2 evolution set in. It is possible that adsorption of triflate is important on Pt but not on Au. However, since the data of Table 1 show that k_{el} for the $Ru(NH_3)_6^{3+/2+}$ electrode reaction at both Au and Pt increased in the sequence $CF_3SO_3^- < Cl^- < ClO_4^-$, it may be conjectured that partial blockage of the electrode surface by specific adsorption of these ions occurred and decreased in this order—if the results of Bockris et al.[90] are applicable at the formal potential of the $Ru(NH_3)_6^{3+/2+}$ couple on Au and Pt UMEs, then the bulky triflate ion could be particularly effective in blocking a substantial fraction of the electrode surface. The anion-free surface would then carry the anion-modulated electron transfer reaction. Only a small fraction of the electrode surface would be blocked by chemisorbed Cl^-, giving the linear k_{el} vs $[Cl^-]$ plot of Supporting Information, Figure S2, while still less surface would be blocked by the very weakly adsorbed ClO_4^- (in our experiments with perchlorate media, however, either Cl^- or $CF_3SO_3^-$ was also present to the extent of 15.0 mmol L^{-1}). For $CF_3SO_3^-$, an approach to saturated blocking at high [triflate] even at the $Ru(NH_3)_6^{3+/2+}$ formal potential of +0.07 V vs NHE could give the curve of Supporting Information, Figure S3. Thus, anions could affect the $Ru(NH_3)_6^{3+/2+}$ exchange rate in two opposing ways—retardation through partial electrode surface blockage (more so with triflate), and acceleration through an essential involvement in the $Ru(NH_3)_6^{3+/2+}$ electron transfer process (particularly with chloride, which may interact in a specific way with the Ru complexes).

Temperature Effects on the Electrode Reaction Rate. The primary purpose in estimating the temperature dependences of k_{el} in various environments was the empirical one of assessing the relevance of measurements at 25 °C to the broader near-ambient range. The observed Arrhenius activation energies E_a are small, as expected in view of the very small change in Ru−N bond lengths on going from $Ru(NH_3)_6^{3+}$ to $Ru(NH_3)_6^{2+}$ (+4.0 ± 0.4 pm[91]) with a correspondingly small Marcus internal reorganization energy (4 ± 2 kJ mol^{-1}[92] for the homogeneous electron transfer reaction and hence 2 ± 1 kJ mol^{-1} for the electrode reaction[1]). Values of E_a ranged from 19 kJ mol^{-1} for the triflate salt in 0.1 mol L^{-1} KCF_3SO_3 at a Pt UME to 25 kJ mol^{-1} for $[Ru(NH_3)_6]Cl_3$ in 0.1 mol L^{-1} KCl at a gold UME. These activation energies cannot, however, be simply interpreted in terms of electron transfer dynamics unless it can be shown that the double layer does not change with temperature. This will not be the case if the analysis of the preceding paragraph is applicable, since, as noted above, literature values of $\Delta H_{ads}{}^0$ are substantially negative for both $CF_3SO_3^-$ and Cl^-, meaning that the degree of anion adsorption would be reduced as the temperature is increased. As only a minor fraction of the electrode surface would be blocked by either $CF_3SO_3^-$ or Cl^- at the formal potential of the $Ru(NH_3)_6^{3+/2+}$ couple, the correction of E_a for this effect, if real, would not be large.

Pressure Effects on the Electrode Reaction Rate. It is possible to predict a value of $\Delta V_{el}^{\ddagger}$ for a simple electrode reaction from the analogous parameter $\Delta V_{ex}^{\ddagger}$ for the corresponding homogeneous self-exchange reaction using the relation

$$\Delta V_{el}^{\ddagger} \approx \frac{1}{2}\Delta V_{ex}^{\ddagger} \tag{7}$$

derived from Marcus theory,[1] but the numerous reported experimental difficulties[73−75] effectively precluded a direct determination of $\Delta V_{ex}^{\ddagger}$ for the $Ru(NH_3)_6^{3+/2+}$ self-exchange reaction in homogeneous solution. A procedure described elsewhere[1] that works well for simple electron transfers in aqueous solutions allows the calculation of a theoretical $\Delta V_{ex}^{\ddagger}$ for a homogeneous self-exchange reaction

$$\Delta V_{ex}^{\ddagger}(\text{theor}) = \Delta V_{IS}^{\ddagger} + \Delta V_{OS}^{\ddagger} + \Delta V_{COUL}^{\ddagger} + \Delta V_{DH}^{\ddagger} \tag{8}$$

where IS, OS, COUL, and DH refer respectively to the contributions of the pressure-dependences of the inner-sphere reorganization, outer-sphere (solvational) reorganization, Coulombic work terms, and activity coefficient (Debye−Hückel) corrections. For $Ru(NH_3)_6^{3+/2+}$, $\Delta V_{IS}^{\ddagger}$ will be negligible (the corresponding reorganization energy is only 4 ± 2 kJ mol^{-1}[92]).

If r_1 and r_2 are the radii of $Ru(NH_3)_6^{3+}$ and $Ru(NH_3)_6^{2+}$, respectively, z_1 and z_2 are the charge numbers, σ is the separation between these ions at the moment of electron transfer (presumed = $r_1 + r_2$), ε and n are the relative permittivity (dielectric constant) and refractive index of the solvent, A and B are the Debye–Hückel parameters at atmospheric pressure, $\mathring{a}$ is the DH contact distance (effectively r_1 plus the anion radius), I is the ionic strength, and β is the isothermal compressibility of the solvent, then

$$\Delta V_{OS}^{\ddagger} = (N_A e^2/16\pi\varepsilon_0)[(2r_1)^{-1} + (2r_2)^{-1} - \sigma^{-1}] [\partial(n^{-2} - \varepsilon^{-1})/\partial P]_T \quad (9)$$

$$\Delta V_{COUL}^{\ddagger} = [N_A z_1 z_2 e^2/4\pi\varepsilon_0\sigma](\partial\varepsilon^{-1}/\partial P)_T \quad (10)$$

$$\Delta V_{DH}^{\ddagger} = [RTz_1z_2AI^{1/2}/(1 + B\mathring{a}I^{1/2})^2][(\partial \ln \varepsilon/\partial P)_T (3 + 2B\mathring{a}I^{1/2}) - \beta] \quad (11)$$

If the effective radii of $Ru(NH_3)_6^{3+}$, $Ru(NH_3)_6^{2+}$, Cl^-, and $CF_3SO_3^-$ are taken to be 340, 344, 181, and 340 pm, respectively, then, for 25 °C and I = 0.12 mol L^{-1} as in our variable-pressure experiments and the midrange pressure of 100 MPa, $\Delta V_{OS}^{\ddagger}$ (−8.9 cm^3 mol^{-1}) is seen to be dominant because $\Delta V_{DH}^{\ddagger}$ (+2.7 cm^3 mol^{-1} for triflate, +2.8 cm^3 mol^{-1} for Cl^-) and $\Delta V_{COUL}^{\ddagger}$ (−4.2 cm^3 mol^{-1}) effectively cancel, giving $\Delta V_{ex}^{\ddagger}$(theor) = −10.3 cm^3 mol^{-1} for Cl^- as counteranion and −10.4 cm^3 mol^{-1} for $CF_3SO_3^-$. If, as suggested by Muzikář and Fawcett,[23] the effective charge on $Ru(NH_3)_6^{3+}$ is only about +1, $\Delta V_{DH}^{\ddagger}$ and $\Delta V_{COUL}^{\ddagger}$ will be +0.9 and −1.4 cm^3 mol^{-1}, respectively, and their net contribution will be within the experimental uncertainty, with $\Delta V_{ex}^{\ddagger}$(theor) = −9.4 cm^3 mol^{-1} and $\Delta V_{el}^{\ddagger}$(theor) = −4.7 cm^3 mol^{-1}.

For a simple $Ru(NH_3)_6^{3+/2+}$ electrode reaction, then, the expectation is that $\Delta V_{el}^{\ddagger}$(theor) (averaged over the 200 MPa pressure range) should be $0.5\Delta V_{ex}^{\ddagger}$(theor) or about −5 cm^3 mol^{-1}, which is well within the range of observed $\Delta V_{el}^{\ddagger}$ values for electrode reactions of metal ion complexes that do not involve large spin-state changes.[1] The observed values of $\Delta V_{el}^{\ddagger}$ for $Ru(NH_3)_6^{3+/2+}$, however, were −12 ± 1 cm^3 mol^{-1} for 0.1 mol L^{-1} KCl and −16 ± 1 cm^3 mol^{-1} for 0.1 mol L^{-1} KCF_3SO_3, which are the most negative $\Delta V_{el}^{\ddagger}$ recorded to date for electrode reactions of transition-metal complexes in water. The only couples for which $\Delta V_{el}^{\ddagger}$ has been found to approach these values are $Co(en)_3^{3+/2+}$, $Co(bpy)_3^{3+/2+}$, and $Co(phen)_3^{3+/2+}$ (bpy = 2,2′-bipyridyl, phen = 1,10-phenanthroline),[1] for which large distortions due to electronic spin state changes accompany the electron transfer process; such distortions are not expected to occur in the $Ru(NH_3)_6^{3+/2+}$ couple, in which both members are in low-spin $4d^5/4d^6$ electronic configurations.

In fact, we have shown above that the $Ru(NH_3)_6^{3+/2+}$ electrode reaction is not simple, being specifically catalyzed by anions, and that $\Delta V_{el}^{\ddagger}$ is distinctly more negative for $CF_3SO_3^-$ than for Cl^-. Ion pairing of $Ru(NH_3)_6^{3+}$ with the anion present might be invoked to explain the catalysis, and indeed Waysbort et al.[93] gave evidence for about 30% pairing of $Ru(NH_3)_6^{3+}$ with Cl^- in 0.1 mol L^{-1} aqueous chloride at 25 °C. The strongly negative $\Delta V_{el}^{\ddagger}$, however, is not attributable to ion pairing because increasing pressure works against ion pairing by increasing the relative permittivity ε and also favoring hydration of the separated ions—for example, the ion pair formation constant for $\{Ru(NH_3)_6^{3+},Cl^-\}$, calculated as per Fuoss,[94] declines by 27% from 0 to 200 MPa at 25 °C. This decline would reduce any catalysis due to ion pairing, leading to less negative values of $\Delta V_{ex}^{\ddagger}$ and $\Delta V_{el}^{\ddagger}$ than otherwise expected.

The same factors that favor breakup of ion pairs by increasing pressure will also promote desorption of anions from electrode surfaces. For example, molecular dynamics calculations[95] show that chloride ion is "contact adsorbed" on a Pt electrode and solvated locally by adsorbed water, which implies that Cl^-(aq) is partially desolvated on adsorption and also displaces some existing adsorbed water—both of which processes will be disfavored by increasing pressure. Consequently, if, as suggested above, the catalytic efficacy sequence $CF_3SO_3^- < Cl^- \ll ClO_4^-$ reflects in part decreasing electrode surface blockage, increasing pressure will be particularly effective in accelerating the $Ru(NH_3)_6^{3+/2+}$ electrode reaction for $CF_3SO_3^-$ as the anion (most negative $\Delta V_{el}^{\ddagger}$, −16 cm^3 mol^{-1}), less so for Cl^- ($\Delta V_{el}^{\ddagger}$ = −12 cm^3 mol^{-1}), and least for ClO_4^- which is presumably not specifically adsorbed ($\Delta V_{el}^{\ddagger}$ was not measurable for ClO_4^-). Against this interpretation are the uncertainty in the article by Bockris et al.[90] regarding the extent of adsorption of $CF_3SO_3^-$ on Pt at potentials near 0.0 V vs NHE, and the report by Lipkowski et al.[88] that adsorption on Au is negligible at such potentials; this topic deserves to be revisited. In any event, since the anions are evidently intimately involved in the electron transfer process itself, the predictions of the simple Marcus-based theory (eqs 6–11) are not applicable to $\Delta V_{el}^{\ddagger}$.

An alternative interpretation of the unexpectedly strongly negative $\Delta V_{el}^{\ddagger}$ for $Ru(NH_3)_6^{3+/2+}$ electrode reaction notes that, for the comparable RuN_6 couple $Ru(en)_3^{3+/2+}$, the measured $\Delta V_{el}^{\ddagger}$ and $\Delta V_{ex}^{\ddagger}$ are also more negative than expected from theory, being respectively −7.5 ± 0.3 (at glassy C in 0.4 mol L^{-1} KCl or CF_3COONa) and −15.1 ± 1.7 cm^3 mol^{-1} (from the Marcus cross-relation—encouragingly, $\Delta V_{el}^{\ddagger} = 0.5\Delta V_{ex}^{\ddagger}$ as predicted),[76] suggesting that the departure from theoretical expectations has origins peculiar to Ru am(m)ine chemistry; the fact that $\Delta V_{el}^{\ddagger}$ is more negative for the $Ru(NH_3)_6^{3+/2+}$ couple than for $Ru(en)_3^{3+/2+}$ may reflect the cation size difference (eqs 6–11).[1] Since the free energy barrier for $Ru^{III/II}$ electron transfer is almost entirely due to solvent reorganization, it may be inferred that a strong increase in specific solvation, over and above the Born-continuum solvent effects invoked in basic Marcus theory, occurs in electron transfer in $Ru^{III/II}$ am(m)ine couples and makes strongly negative contributions to $\Delta V_{el}^{\ddagger}$ and $\Delta V_{ex}^{\ddagger}$. Indeed, specific interactions between $Ru(NH_3)_6^{3+}$ and the surrounding water molecules in aqueous solution are evident in ^1H_2O and $H_2{}^{17}O$ NMR spectra,[96] and theoretical calculations indicate that electron transfer to polar solvents such as water affects the metal-to-ligand charge transfer bands of ruthenium(II) ammines.[97] Strong solvent dependences of the optical spectra of complexes containing the $Ru(NH_3)_5^{3+}$ group confirm that H-bonding of the ammine protons to polar solvent molecules is extensive, probably resulting in mixing of solvent character into the d_π orbitals of Ru.[98−100] The intervalence electron transfer band due to weakly coupled Ru^{II} and Ru^{III} in $(NH_3)_5Ru^{II}(\mu\text{-}L)Ru^{III}(NH_3)_5^{5+}$ (L = 2,6-dithiaspiro[3.3]heptane) in D_2O exhibits a large red shift with rising pressure, rather than the expected blue shift, and this is attributable to pressure-enhanced hydrogen bonding of the ammine ligands to the solvent.[101] In electron transfer between Ru ammines and cytochrome c, either in Ru-modified cyt c or between $Ru(NH_3)_5(\text{ligand})^{3+/2+}$ and cyt $c^{II/III}$, the volume changes are dominated by large solvational effects at the Ru ammine centers.[102] In retrospect, even the puzzling strongly negative volumes of activation found for the aquation of $Ru(NH_3)_5Cl^{2+}$ and its reverse could be understood in terms of solvation increases specific to activation processes in Ru^{III} ammines.[103,104] In short, there is ample precedent for specific hydrational interactions involving Ru^{III} and Ru^{II} ammine complexes.

There remains the possibility that the strongly negative $\Delta V_{el}^{\ddagger}$ for the $Ru(NH_3)_6^{3+}$ reduction at an electrode reflects pressure effects on the electrical double layer. Experience with supporting electrolyte (KCl) concentration effects on the kinetics of the $Fe(CN)_6^{3-/4-}$ electrode reaction (Table 2), however, has been that $\Delta V_{el}^{\ddagger}$ is independent of the concentration of a particular supporting electrolyte within the experimental error (average $\Delta V_{el}^{\ddagger} = 11.4 \pm 0.9$ cm^3 mol^{-1}) even though k_{el} is strongly dependent on it (actually on $[K^+]$). The implication is that, for $Fe(CN)_6^{3-/4-}$ at least, the reactants are in hard (i.e., effectively incompressible) contact with either the electrode surface or an inert adsorbed layer at the outer Helmholtz plane (OHP) and hence $\Delta V_{el}^{\ddagger}$ is insensitive to double-layer effects. It is reasonable to expect the same to hold for the $Ru(NH_3)_6^{3+/2+}$ couple which, although of the opposite charge-type, shows a similar dependence of k_{el} on the total counterion concentration.

Table 2. Dependence of k_{el} and $\Delta V_{el}^{\ddagger}$ for the $Fe(CN)_6^{3-/4-}$ Electrode Reaction at a Pt Electrode[a]

[KCl]/mol L^{-1}	k_{el}/cm s^{-1} at 25 °C, $P = 0.1$ MPa	$\Delta V_{el}^{\ddagger}$/cm^3 mol^{-1}
0.06	0.017	12.0 ± 1.8
0.20	0.047	10.4 ± 1.4
0.50	0.072	11.9 ± 1.3

[a] Data from Table 5 of ref 1.

Finally, we may consider briefly how $\Delta V_{el}^{\ddagger}$ might be affected if $Ru(NH_3)_6^{3+}$ were not in hard contact with the electrode or at the OHP but were moving freely within the diffuse double layer when reduction occurs. A Frumkin correction[105] to be applied to the observed volume of activation $\Delta V_{el(obsd)}^{\ddagger}$ may be estimated as outlined in the Supporting Information; the concept of the Frumkin correction has recently been discredited,[106] but it serves to give an indication of the sign and order of magnitude of the effect. The key results are that the Frumkin correction to $\Delta V_{el(obsd)}^{\ddagger}$ is zero at distance $x = 0$ (i.e., at hard contact of $Ru(NH_3)_6^{3+}$ with an adsorbed layer at the OHP) and at distances greater than about 8 nm, but at intermediate distances the correction is always *negative*—that is, it cannot explain the already strongly negative values of $\Delta V_{el}^{\ddagger}$. For a reasonable φ value of ~100 mV, and with the effective z set at +1,[23] the greatest correction would be only about −1 cm^3 mol^{-1} near $x = 1.0$ nm which is quite far out in terms of electron transfer probability. It may therefore be safely inferred that $\Delta V_{el}^{\ddagger}$, unlike k_{el}, is insensitive to double-layer effects (cf. Table 2), and that electron transfer may be treated as occurring with $Ru(NH_3)_6^{3+}$ either in contact at the OHP or close to it. Direct contact with the electrode, however, would result in expulsion of adsorbed water molecules and partial dehydration of $Ru(NH_3)_6^{3+}$, both of which would tend to make $\Delta V_{el(obsd)}^{\ddagger}$ less negative than predicted.

CONCLUSIONS

Neither the rate constant k_{el} nor the volume of activation $\Delta V_{el(obsd)}^{\ddagger}$ for the reduction of $Ru(NH_3)_6^{3+}$ at a polycrystalline metallic UME depend significantly upon the identity of the metal, be it Au or Pt. According to traditional views,[3,45] this is consistent with substantially full adiabaticity for the electron transfer process, but, as originally pointed out by Gosavi and Marcus,[10] it does not preclude a modest level of nonadiabaticity. The question of the extent of nonadiabatic character is better pursued through adaptations of Marcus theory as proposed by Savéant[6] and Compton;[7,8] for the purposes of this study, the essential observation is that the kinetic parameters for reduction of $Ru(NH_3)_6^{3+}$ are independent of the choice of electrode material, Au vs Pt, within the experimental uncertainty. The apparent k_{el} does, however, increase as the area of the UME decreases.

Values of k_{el} for the reduction of $Ru(NH_3)_6^{3+}$ depend strongly on the identity and concentration of the anion present in the order $CF_3SO_3^- < Cl^- < ClO_4^-$, but not upon the cation of the supporting electrolyte (Na^+, K^+, H^+). For Cl^- as the counterion of both $Ru(NH_3)_6^{3+}$ and the supporting electrolyte, k_{el} is directly proportional to the total Cl^- concentration, such that k_{el} would be zero, within the experimental uncertainty, if Cl^- were hypothetically absent. This result echoes (with charge reversal) the dependences of both k_{el} and k_{ex} for many anion–anion electron transfer reactions on total cation concentrations, and suggests that Cl^- is directly involved in mediation of the $Ru(NH_3)_6^{3+/2+}$ electron transfer. For triflate as the sole counterion, the dependence of k_{el} on the total $[CF_3SO_3^-]$ is not linear, possibly because the blocking of the available electrode surface becomes dominant at high triflate concentrations. In experiments with a perchlorate as the supporting electrolyte, 15 mmol L^{-1} chloride or triflate was also present as the counterion of $Ru(NH_3)_6^{3+}$ because of risks in preparing its perchlorate salt, so that interpretation of the results was less clear-cut except that ClO_4^- was nevertheless associated with the fastest $Ru(NH_3)_6^{3+/2+}$ electrode reaction rates. No variable-pressure experiments were conducted with ClO_4^- because the already fast reaction became too fast for accurate measurement at elevated pressures, and besides the likelihood that ClO_4^- would oxidize the Ru complexes over the longer time-scale of a pressure cycle is well recognized.[47,48] A more orthodox explanation of the accelerating effect of added electrolytes might be the collapsing of the diffuse double layer by the supporting electrolyte, but it is evident that the relevant factor is the total concentration of the specific anion rather than of the supporting electrolyte.

The observed $\Delta V_{el}^{\ddagger}$ values for reduction of $Ru(NH_3)_6^{3+}$ at an electrode in presence of 0.115 mol L^{-1} Cl^- or $CF_3SO_3^-$ are much more negative than predicted by a theory that has been successfully applied to other electrode reactions[1] but which is not directly applicable in this case because of the specific involvement of the anions in promoting the electron transfer process. The strongly negative values of $\Delta V_{el}^{\ddagger}$ probably reflect solvation increases peculiar to activation processes in reactions of $Ru^{III/II}$ am(m)ine complexes. These solvation effects may be amplified by involvement of the anion in the activation process. A further anion-specific contribution to $\Delta V_{el}^{\ddagger}$ may be the promotion of desorption of surface-blocking Cl^- or especially $CF_3SO_3^-$ from electrodes by applied pressure. Increase of the available electrode surface area through pressure-induced desorption of specifically adsorbed anions could also explain the fact that $\Delta V_{el}^{\ddagger}$ is about 4 cm^3 mol^{-1} more negative for the triflate system than for the chloride, if indeed the bulky $CF_3SO_3^-$ ion is more strongly adsorbed than Cl^- on Au and Pt at the $Ru(NH_3)_6^{3+/2+}$ formal potential as reported by Bockris et al.[90]—a point that merits reinvestigation. Frumkin corrections for reduction of free $Ru(NH_3)_6^{3+}$ within the diffuse double layer would make $\Delta V_{el}^{\ddagger}$ even more negative than is observed, although the corrections would be small. Conversely, the strongly negative $\Delta V_{el}^{\ddagger}$ values are inconsistent with reduction of $Ru(NH_3)_6^{3+}$ in direct contact with the metallic electrode surface, which would entail substantial dehydration of both the electrode surface and $Ru(NH_3)_6^{3+}$ with consequent positive contributions to $\Delta V_{el}^{\ddagger}$. Reduction of $Ru(NH_3)_6^{3+}$ can be regarded as taking place either in hard contact with adsorbed water at the OHP or close to it.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Plots of temperature dependence of k_{el} in 0.1 mol L^{-1} KCl and dependences of k_{el} on $[Cl^-]$ and $[CF_3SO_3^-]$; pressure dependence of the Frumkin correction. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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