

bonding between the ReO_4^- and $\text{Pn}(\text{AO})_2$ ligands causes the ReO_4^- group to lean in the direction of the hydrogen bonding in this case, and a strong Cu-CN bond results in a large displacement of the Cu(II) from the plane of the $\text{Pn}(\text{AO})_2$. $[\text{Rh}^{\text{III}}(\text{Pn}(\text{AO})_2\text{Cl}_2)]^{27}$ and $[\text{Co}^{\text{III}}(\text{Pn}(\text{AO})_2)(\text{NO}_2)_2]^{28}$ both form the expected octahedral complexes. However, steric interactions between one nitro group and the $\text{Pn}(\text{AO})_2$ ligand cause the Co(III) to lie significantly out of the plane of the $\text{Pn}(\text{AO})_2$ and result in unequal Co-NO₂ bond distances. In all of these examples, the tetradentate amine oxime ligand has lost an oxime proton, resulting in a strong intramolecular hydrogen bond. Several of these transition-metal complexes with $\text{Pn}(\text{AO})_2$ show considerable distortion from ideal geometries, yet in no case were the two amine protons of the tetradentate amine oxime ligand lost on coordination to the metal as has been found here for the technetium(V) complexes.

These two deprotonated nitrogen atoms exhibit sp^2 character. The Tc-N amide bond distances are considerably shorter than those observed for Tc-N amine bonds. The average Tc-N_{amide} bond distance for the complexes reported here is 1.913 (7) Å, while typical Tc-N_{amine} bond distances are in the range 2.088 (3)-2.259 (4) Å.^{15,20,21} The amide nitrogen, the technetium, and the two carbon atoms adjacent to this nitrogen are very close to coplanar (supplementary material), and the angles about the nitrogen are on the order of 120° rather than 109° as would be true if the nitrogen atoms were sp^3 hybridized.

Known technetium(V) complexes containing four-coordinated nitrogen atoms, such as the cyclam²¹ or bis(ethylenediamine)²⁰ complex, retain their amine protons. These complexes, however, form the *trans*-dioxo core to reduce the high charge of the Tc(V) center.

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The technetium(V) tetradentate amine oxime complexes contain the mono oxo core. Possibly, to avoid steric crowding of the bulky Tc=O group by the pendant methyl groups on the carbon atoms adjacent to the two amide nitrogens, the entire amine oxime ligand may be forced down and away from the oxo group on coordination. With the amine oxime ligand directed away from the oxo group, conditions would be sterically unfavorable for a second oxygen to be coordinated to the technetium in the position *trans* to the oxo group. This might then result in the deprotonation of the amine nitrogens to lower the charge on the Tc(V) center. Obviously the formation of two Tc-N multiple bonds through deprotonation and sp^2 hybridization adds more stabilization to the resultant Tc(V) complex than would be achieved by formation of the *trans* dioxo species, and additional stabilization is provided by the formation of the strong intramolecular O...O hydrogen bonds (2.403-2.448 (4) Å).

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Supplementary Material Available: Tables reporting the observed and calculated structure factors, molecular geometry, least-squares planes, anisotropic thermal parameters, and hydrogen positional parameters for the four structures (71 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
 State University of New York at Buffalo, Buffalo, New York 14214

Hydroquinone as a Proton Donor in Ambient-Temperature Chloroaluminate Ionic Liquids: Reaction with Chloride Ion

Marek Lipsztajn,*† Saeed Sahami, and Robert A. Osteryoung*

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The reaction of water and hydroquinone (H₂Q) as proton donors in either *N*-1-butylpyridinium chloride (BuPyCl)- or 1-methyl-3-ethylimidazolium chloride (ImCl)-aluminum chloride ambient-temperature ionic liquids has been investigated. Amperometric titrations of free chloride ion indicate that H₂Q reacts with 2 Cl⁻, suggesting that HCl is undissociated in the molten salt. Comparison of the $D\eta/T$ values, where D , η , and T are the diffusion coefficient, viscosity, and temperature, respectively, suggest that both water and H₂Q give rise to two HCl molecules. Other observations regarding the interaction of water with the ambient-temperature molten salt are reported.

In the past several years low-temperature molten salt systems composed of aluminum chloride and either *N*-1-butylpyridinium chloride (BuPyCl) or 1-methyl-3-ethylimidazolium chloride (ImCl) have been found to be useful solvents for electrochemical and spectroscopic studies of both organic and inorganic species.¹⁻⁴ The reactions of water with AlCl₃-RCl melts, where R⁺ = BuPy⁺ or Im⁺, are of particular importance since H₂O is one of the most common and obvious contaminants of the drybox atmosphere as well as of substrates used for preparation of these melts. The electrochemical behavior of water has been investigated in AlCl₃-BuPyCl melts,⁵ and it was found that, throughout the entire range of melt composition, water undergoes chemical reaction(s) to generate HCl, which can be electrochemically reduced at a

platinum electrode. However, the stoichiometry of these reactions remains unknown.

We described⁶⁻⁸ a method of studying the stoichiometry of certain complex ions based on monitoring chloride and heptachloroaluminate (Al₂Cl₇⁻) concentrations by observing changes in the diffusion-controlled chloride oxidation⁷ and heptachloro-

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* Present address: ERCO, Islington, Ontario, Canada.

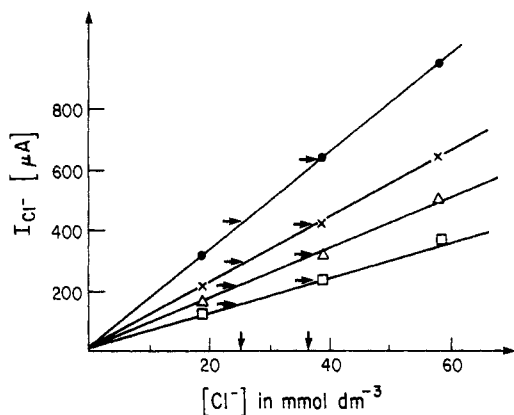


Figure 1. Dependence of chloride oxidation limiting (rde) current I_{mCl} and H_2Q concentrations in "neutral basic" $\text{AlCl}_3\text{-ImCl}$ melt (platinum electrode (0.12 cm^2), $T = 305 \text{ K}$). Rotation rates (rpm): (\square) 400; (Δ) 900; (\times) 1600; (\bullet) 3600. Arrows correspond to additions of 10.5 and 4.9 mmol dm^{-3} hydroquinone.

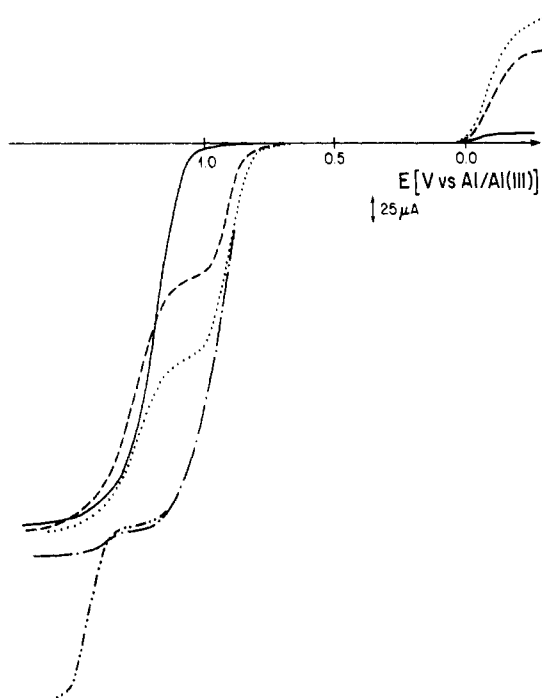


Figure 2. Rotating-disk voltammetric curves for "neutral basic" $\text{AlCl}_3\text{-ImCl}$ melt at various hydroquinone concentrations: (initial concentration of chlorides $58.1 \text{ mmol dm}^{-3}$, platinum electrode (0.12 cm^2), $\omega = 400 \text{ rpm}$; $T = 305 \text{ K}$): (-) no H_2Q ; (- - -) $10.5 \text{ mmol dm}^{-3}$ H_2Q ; (---) $15.4 \text{ mmol dm}^{-3}$ H_2Q ; (- · - ·) $29.0 \text{ mmol dm}^{-3}$ H_2Q ; (- · - ·) $35.5 \text{ mmol dm}^{-3}$ H_2Q .

alumininate reduction current in "neutral basic" and "neutral acidic" melts, respectively.⁸ This method, essentially an amperometric titration, was tested on electroactive Fe(III) -chloride complexes^{7,8} as well as nonelectroactive Nd(III) -chloride complexes.⁸

In this paper the application of this method to the study of the reaction of a proton donor, hydroquinone (H_2Q), with chloride is presented.

Experimental Section

N-1-Butylpyridinium chloride and 1-methyl-3-ethylimidazolium chloride were prepared as previously described.^{2,4} The neutral $\text{AlCl}_3\text{-RCl}$ melts were prepared by slow mixing of equimolar amounts of these chlorides and carefully sublimed AlCl_3 (Fluka A.G., "Ironfree"), and this "roughly" neutral melt was subsequently adjusted by addition of small amounts of either RCl or AlCl_3 to obtain the electrochemical window⁶ indicative of a "true" neutral melt.

Hydroquinone (Aldrich) was dried under reduced pressure; 1,4-benzoquinone (Aldrich) was twice sublimed and stored in the drybox.

The reference electrode was an Al wire (5N Alfa Inorganic) immersed in a 1.5:1 $\text{AlCl}_3\text{-RCl}$ melt, and all potentials are given with respect to

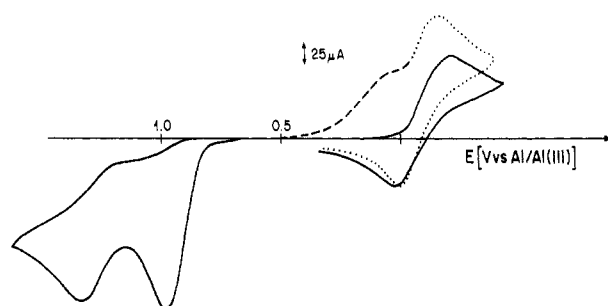


Figure 3. Cyclic voltammogram for "neutral basic" $\text{AlCl}_3\text{-ImCl}$ melt containing $15.4 \text{ mmol dm}^{-3}$ H_2Q (initial concentration of chlorides $58.1 \text{ mmol dm}^{-3}$, platinum electrode (0.12 cm^2), sweep rate $v = 0.05 \text{ V s}^{-1}$, $T = 305 \text{ K}$). The dashed line denotes the second scan.

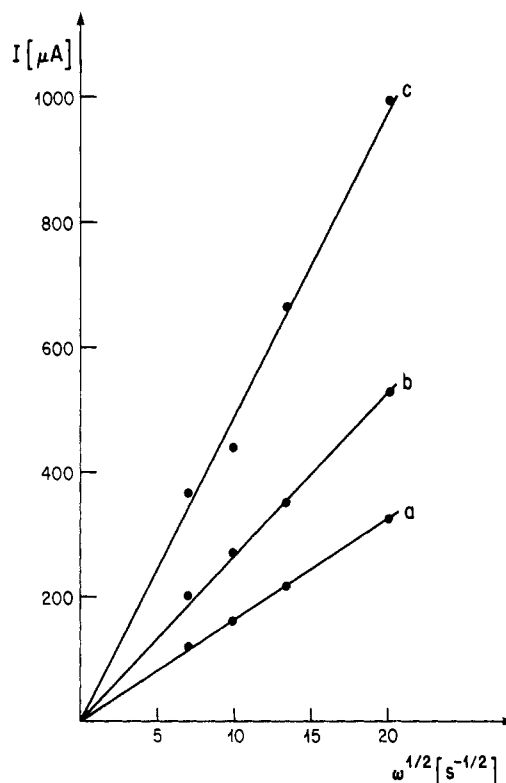


Figure 4. Levich plot for oxidation of H_2Q in "neutral basic" $\text{AlCl}_3\text{-ImCl}$ melt at a rotating-platinum-disk electrode (0.12 cm^2) (initial concentration of chlorides $58.1 \text{ mmol dm}^{-3}$, $T = 305 \text{ K}$, electrode potential +1.0 V). H_2Q concentration (mmol dm^{-3}): (a) 10.5; (b) 15.4; (c) 29.0.

this electrode. The auxiliary electrode was a coiled Al wire. The essential details of the experimental techniques, electrodes, and operations in the drybox (Vacuum Atmospheres Co.), in which all experiments were carried out, have been presented in an earlier publication.⁹

Working electrodes were platinum disks (0.049 and 0.12 cm^2). The electrode surface preparation procedure has been described previously.¹⁰

Results

Hydroquinone was used as a source of protons. Gilbert¹¹ has shown that this compound is a proton donor in ambient-temperature molten salts. Upon addition of H_2O to the "neutral basic" $\text{AlCl}_3\text{-ImCl}$ melt, a decrease of chloride oxidation current was observed; the stoichiometry of this reaction was 1:2 $\text{H}_2\text{Q}:\text{Cl}^-$ (see Figure 1). At the same time an oxidation current at less positive potentials, proportional to the concentration of added hydroquinone, and a reduction current of HCl (at a platinum electrode only) were observed (Figures 2 and 3). When the concentration of hydroquinone reached half the initial chloride concentration, no chloride oxidation current was observed; all the chloride ions

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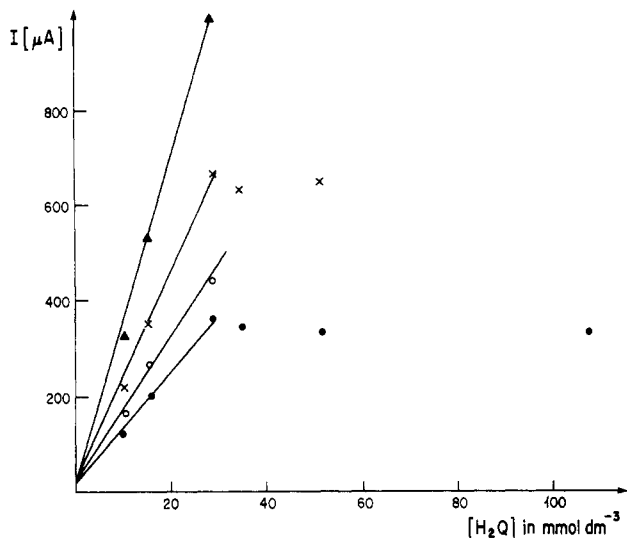


Figure 5. Concentration dependence of the first oxidation wave of hydroquinone in "neutral basic" $\text{AlCl}_3\text{-ImCl}$ melt at a rotating-platinum-disk electrode (0.12 cm^2) ($T = 305 \text{ K}$). Rotation rate (rpm): (●) 400; (○) 900; (×) 1600; (Δ) 3600.

Table I. Comparison of Diffusion Coefficients of HCl Formed in Reactions of H_2O and H_2Q with $\text{AlCl}_3\text{-RCl}$ Melts^a

melt, conditions	$10^7 D$, $\text{cm}^2 \text{ s}^{-1}$	$10^{10} D\eta/T$, $\text{g cm s}^{-2} \text{ K}^{-1}$
$\text{AlCl}_3\text{-BuPyCl}$; ^b MC = 0.8, $T = 313 \text{ K}$, $\eta = 0.404 \text{ P}$	1.38	1.78
$\text{AlCl}_3\text{-ImCl}$; MC = 0.98, $T = 305 \text{ K}$, $\eta = 0.15 \text{ P}$	3.5	1.72

^a It is assumed that in both cases the same number of protons per molecule of proton donors ($n = 2$) is released. ^b Data taken from ref 5.

were titrated. The oxidation current at potentials more negative than the chloride oxidation ($E_{1/2} = 1.3 \text{ V}$) most probably corresponds to the oxidation of deprotonated hydroquinone, i.e., the dianion of benzoquinone, Q^{2-} . The linear Levich plot (Figure 4) indicates that the limiting current of Q^{2-} is convective-diffusion-controlled. In the reverse scan on a cyclic voltammogram (Figure 3) a new cathodic peak was observed prior to HCl reduction, which corresponds to the reduction of the product of the oxidation of deprotonated hydroquinone. This product was electrochemically identified as 1,4-benzoquinone by comparison to the behavior of added 1,4-benzoquinone. The addition of H_2Q in excess of that required to react with the free chloride did not change the limiting current of the Q^{2-} oxidation (see Figure 5), but a new anodic wave at potentials more positive than the chloride oxidation peak was observed (Figure 2). This current, most probably corresponding to the oxidation of undissociated H_2Q , increased proportionally to the concentration of hydroquinone.

The changes of the HCl reduction current (observed only at platinum electrodes) during these experiments are shown in Figure 6. As seen, this current increases proportionally to the concentration of H_2Q up to the point where the H_2Q concentration reaches half the initial concentration of chloride. The $D\eta/T$ value (where D , η , and T denote diffusion coefficient, viscosity, and temperature, respectively) calculated from these experiments is in good agreement with the value previously reported for the $\text{AlCl}_3\text{-BuPyCl}$ melt⁵ (see Table I). At H_2Q concentrations exceeding half the initial concentration of chloride, the HCl reduction current continues to increase with increasing H_2Q concentration, but *much* more slowly than previously (see change of slope in Figure 6). This may be due to a direct reduction of the proton from the H_2Q itself.

The calculations of the diffusion coefficients for "HCl" in this study, with H_2Q as proton donor, and the previous study, with

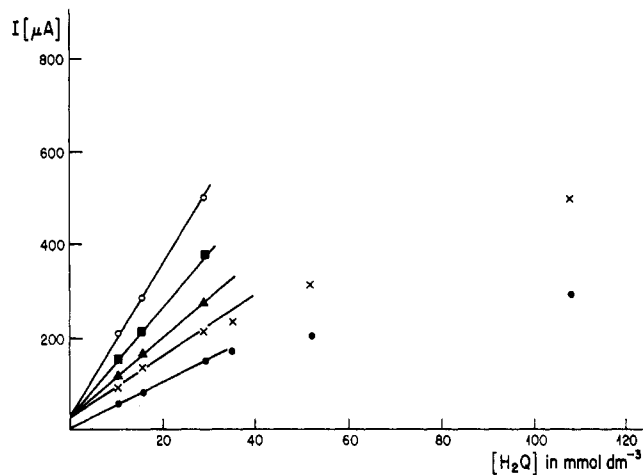


Figure 6. Dependence of HCl reduction current on the concentration of H_2Q added to a "neutral basic" $\text{AlCl}_3\text{-ImCl}$ melt (initial concentration of chloride $58.1 \text{ mmol dm}^{-3}$ platinum electrode (0.12 cm^2), $T = 305 \text{ K}$): (●) peak current at $v = 0.05 \text{ V s}^{-1}$; (×) rde limiting current at $\omega = 400 \text{ rpm}$; (▲) rde limiting current at $\omega = 900 \text{ rpm}$; (■) rde limiting current at $\omega = 1600 \text{ rpm}$; (○) rde limiting current at $\omega = 3600 \text{ rpm}$.

H_2O ,⁵ were made by assuming the same "n" value. In the case of H_2Q each molecule of proton donor acts to remove two chlorides and, by implication, as a source of two protons to form two HCl molecules. This means that in both cases considered each mole of H_2O or H_2Q forms the same quantity of HCl and hence both proton donors supply the same number of protons, which are subsequently neutralized by chloride ions. Hence, each water molecule also appears to supply two protons to form the same quantity of HCl, which implies that what remains from the addition of the H_2O is an oxide incorporated into aluminoxy species.

Discussion

The quantitative decrease of the Cl^- oxidation current in a "neutral basic" melt on addition of H_2Q suggests that HCl is undissociated in the melt.

As discussed above, water may also be a source of two protons per molecule and hence the formation of aluminoxy species rather than aluminohydroxy should be expected. It must be realized that this conclusion is based on the equality of the $D\eta/T$ values as discussed above. It is important in these considerations to estimate possible errors. The reproducibility of the HCl reduction current is poor. As shown previously,⁵ the slopes of the calibration curves (which permit an estimation of the diffusion coefficient of the reducible species) vary by 20% from one set of experiments to another. A similar error is involved in a comparison of $D\eta/T$ values collected in Table I, which used an average from the data of ref 5. Moreover, Tait and Osteryoung,¹² on the basis of FTIR studies, postulated the formation of aluminohydroxy species such as AlOHCl_2 rather than AlOCl_2^- in acidic $\text{AlCl}_3\text{-ImCl}$ melts. On the other hand, simple aluminoxy species like AlOCl_2^- were not accessible in the infrared region covered. Additions of $\text{H}_2\text{O}/\text{D}_2\text{O}$ to a basic melt gave a very complex IR spectrum, showing similarities to spectra obtained by Riesgraf and May,¹³ who added freshly prepared aluminum hydroxide gels to aluminum chloride solutions.

Additional work on the details of the interaction of proton and water in these systems is in progress.

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Registry No. BuPyCl, 1124-64-7; ImCl, 65039-09-0; H_2Q , 123-31-9; AlCl_3 , 7446-70-0; H_2O , 7732-18-5.

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