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Reaction of Chloride Ions in Low-Temperature Molten Salts and Application to the Study of Complex Ion Stoichiometry

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The oxidation of chloride ions added as a slight excess to a "neutral" ambient-temperature ionic liquid of either *N*-*n*-butylpyridinium chloride or 1-methyl-3-ethylimidazolium chloride mixed with an equivalent amount of aluminum chloride has been found to yield an oxidation wave indicating convective diffusion control at a rotating platinum electrode. The oxidation wave is linear in the square root of the rotation rate of the electrode and directly proportional to the amount of chloride in the molten salt up to ca. 0.1 mol dm^{-3}. Coulometry carried out under conditions similar to those prevailing at the rotating disk electrode indicates the oxidation of Cl^- is to Cl_3^-. This chloride oxidation wave in the neutral melt can be applied to study the stoichiometry of chloro-complex species formed, even if the chloro complex is itself not electroactive. Application to the determination of the number of chlorides bound to Fe(III) is presented.

Low-temperature molten-salt systems composed of aluminum chloride and alkylpyridinium salts, particularly *N*-*n*-butylpyridinium chloride (BuPyCl), have been found to be useful solvents for electrochemical and spectroscopic investigations of both organic and inorganic species.[1–3] Wilkes et al.[4] showed that 1-methyl-3-ethylimidazolium chloride (ImCl)–aluminum chloride melts have a more negative cathodic limit than the basic butylpyridinium chloroaluminates—e.g., one containing excess BuPyCl. Recently we have found[5] that a neutral melt with a mole ratio of components ($MC = n_{AlCl_3}/n_{RCl}$) equal to 1.00 extends the electrochemical "window" of the ImCl–$AlCl_3$ melts about 1.5 V. This enables us to investigate redox systems inaccessible in melts prepared by use of an excess of either RCl (basic melts), where R^+ is either the $BuPy^+$ or Im^+ cation, or $AlCl_3$ (acidic melts).

Although the potential of chloride oxidation constitutes the anodic limit of basic chloroaluminates and other melts containing excess chloride ions, the only data in the literature regarding chloride oxidation are Tafel *b* coefficients, usually determined at the foot of chloride voltammetric oxidation curves.[6–8]

The usually low *b* coefficients observed (~0.09 V on graphite electrodes in chloride-containing melts, e.g. molten LiCl at 656–767 °C) as well as other experimental data have been interpreted to indicate an anodic mechanism composed of a fast Cl^- discharge followed by a slow Cl(ads) combination, assuming either Langmuir or Temkin-type nonactivated adsorption.[7] At high current densities an increase in the *b* coefficients was found for graphite anodes,[8] and a mechanism implying a fast Cl^- discharge followed by a slow reaction

$$Cl^-(melt) + Cl(ads) \rightleftarrows Cl_2(g) + e^- \qquad (1)$$

under Temkin-type nonactivated adsorption conditions appears to fit the results best. The first mechanism has also recently been proposed[9] for interpretation of Tafel slopes observed in basic ImCl–$AlCl_3$ low-temperature melts.

With regard to chlorine reduction, it was concluded that the diffusion of dissolved chlorine to the graphite–melt interface was the rate-determining step at current densities higher than 1.2 A cm^{-2} in molten LiCl.[6,7] In the high-temperature CsCl–$AlCl_3$ and NaCl–$AlCl_3$ melts, chlorine has been studied and Henry's law coefficients for Cl_2 dissolution are given. For the CsCl–$AlCl_3$ system, Cl_3^- was indicated to form in the basic melt, but evidence for its formation in the NaCl–$AlCl_3$ melt is not as strong.[10] Using equilibrium measurements, Sato et al.[11] reported that the potential span of the melt changes dramatically with composition. This system has also been studied by Trêmillon and Letisse.[12]

We report here some experimental observations on chloride oxidation and chlorine reduction in the BuPyCl–$AlCl_3$ and ImCl–$AlCl_3$ ionic liquid systems.

Experimental Section

N-*n*-Butylpyridinium chloride and 1-methyl-3-ethylimidazolium chloride were prepared as previously described.[2,4] The neutral RCl–$AlCl_3$ melts, where R = Im^+ or $BuPy^+$, were prepared by slow mixing of appropriate amounts of these chlorides and carefully sublimed $AlCl_3$ (Fluka A. G. "iron free") and this "roughly" neutral melt was subsequently adjusted by addition of small amounts of either RCl or $AlCl_3$ to obtain the electrochemical window[5] indicative of a "true" neutral melt. For studies of Cl^- in ImCl–$AlCl_3$ melts, BuPyCl was usually added to provide the excess chloride. No difference in Cl^- behavior was noted if ImCl or BuPyCl was employed.

The reference electrode was an Al wire (Alfa Inorganic) immersed in a 1.5:1 $AlCl_3$–RCl melt, and all potentials are given with respect to this electrode. The auxiliary electrode was also a coiled Al wire. The essential details of the experimental techniques, electrodes, and operation of the drybox (Vacuum Atmospheres Co.), in which all experiments were carried out, have been presented in an earlier publication.[13]

Working electrodes were glassy-carbon (GC) disk (area = 0.196 cm^2), tungsten (0.078 cm^2), and platinum (0.049 cm^2). The electrodes' surface preparation procedure has been described previously.[14]

Results

Rotating-Disk Voltammetry. The addition of RCl in the range of 25–100 mmol dm^{-3} to the "true" neutral melt causes the appearance of well-defined, rotating-disk voltammetric oxidation waves on all three electrodes used (GC, tungsten, and platinum). At lower (<25 mmol dm^{-3}) RCl concentrations two waves were observed (see Figure 1); howver, the results are not as reproducible, presumably because of the

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[1] Chum, H. L.; Koch, V. R.; Miller, L. L.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 3264.

[2] Robinson, J.; Osteryoung, R. A. *J. Am. Chem. Soc.* **1979**, *101*, 323.

[3] Gale, R. J.; Osteryoung, R. A. *Inorg. Chem.* **1979**, *18*, 1603.

[4] Wilkes, J. S.; Levisky, J. A.; Wilson, R. A.; Hussey, C. L. *Inorg. Chem.* **1982**, *21*, 1263.

[5] Lipsztajn, M.; Osteryoung, R. A. *J. Electrochem. Soc.* **1983**, *130*, 1968.

[6] Mussini, T.; Gaita, G. "Enclopedia of Electrochemistry of Elements"; Bard, A. J., Ed.; Marcel Dekker: New York, 1973; Vol. I, pp 4, 43.

[7] Triaca, W. E.; Solomons, C.; Bockris, J. O'M. *Electrochim. Acta* **1968**, *13*, 1949.

[8] Tunold, R.; Bø, H. M.; Paulsen, K. A.; Ittredal, J. D. *Electrochim. Acta* **1971**, *16*, 2101.

[9] Piersma, B. J.; Wilkes, J. S. Frank J. Seiler Research Laboratory Technical Report FJSRL-TR-82-0004; USAF Academy: Colorado Springs, CO, 1982.

[10] Carpio, R. A.; King, L. A.; Patvik, A. P.; Østvold, T.; Øye, H. A. *Light Met. (N.Y.)* **1981**, 325.

[11] Sato, T.; Ishikawa, T.; Midorikawa, R. *Denki Kagaku oyobi Kogyo Butsuri Kagaku* **1973**, *41*, 123.

[12] Trêmillon, B.; Letisse, G. *J. Electroanal. Chem. Interfacial Electrochem.* **1968**, *17*, 371.

[13] Robinson, J.; Osteryoung, R. A. *J. Electrochem. Soc.* **1978**, *125*, 1454.

[14] Robinson, J.; Osteryoung, R. A. *J. Electrochem. Soc.* **1980**, *127*, 122.

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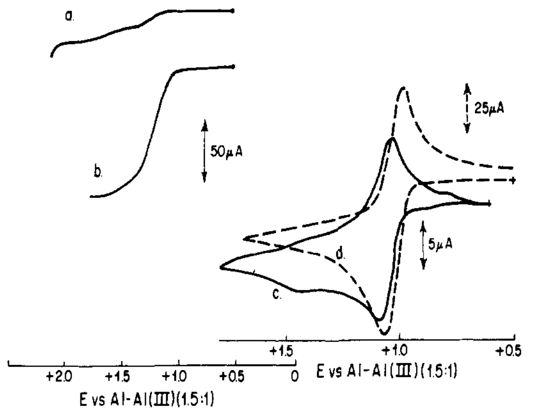

Figure 1. RDE voltammetric and cyclic voltammetric curves recorded for chloride oxidation in neutral melt: (a) 1:1 ImCl–AlCl$_3$ melt, C_{BuPyCl} = 10.5 mmol dm^{-3}, Pt electrode (0.0491 cm^2), ω = 400 rpm, t = 30 °C; (b) 1:1 ImCl–AlCl$_3$ melt, C_{BuPyCl} = 44 mmol dm^{-3}, Pt electrode (0.0491 cm^2), ω = 900 rpm, t = 30 °C; (c) 1:1 BuPyCl–AlCl$_3$, C_{BuPyCl} = 18 mmol dm^{-3}, tungsten electrode (0.0784 cm^2), sweep rate v = 0.02 V s^{-1}, t = 40 °C; (d) 1:1 BuPyCl–AlCl$_3$ melt, C_{BuPyCl} = 55 mmol dm^{-3}, tungsten electrode (0.0784 cm^2), v = 0.02 V s^{-1}, t = 40 °C.

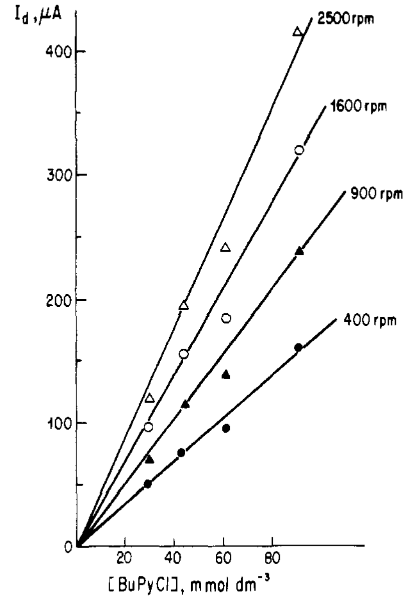

Figure 2. Dependence of limiting current of Cl$^-$ oxidation on concentration of BuPyCl in neutral ImCl–AlCl$_3$ melt, measured by RDE voltammetry on a platinum electrode (0.0491 cm^2) at various rotation rates; t = 30° C.

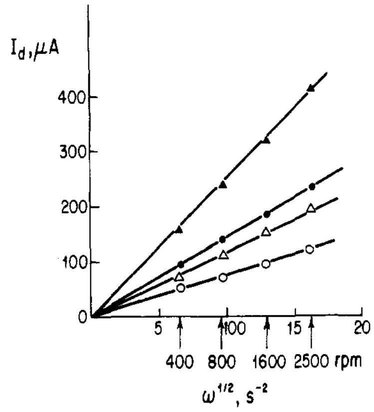

Figure 3. Dependence of limiting current of Cl$^-$ oxidation on $\omega^{1/2}$ in neutral ImCl–AlCl$_3$ melt, measured by RDE voltammetry on a platinum electrode (0.0491 cm^2) for various concentrations of RCl; t = 30 °C. Concentration of BuPyCl (mmol dmm^{-3}): ○, 30; △, 44; ●, 61; ▲, 91.

influence of impurities in the melt. Further studies of this second wave are in progress. The dependence of limiting current on RCl concentration and the square root of the electrode rotation rate are presented in Figures 2 and 3, respectively. Both plots are linear and pass through the origin, indicating that the oxidation is convective diffusion controlled.

The slopes of plots of E vs. log $[(I_d - I)/I]$ were dependent on the electrode material and also changed with RCl concentration and electrode rotation rate; these latter two variations may be related to the uncompensated resistance, since current measured at such high RCl concentrations was in the range of several tens to a hundred microamps and the conductivity of these melts is not very high. (For neutral ImCl–AlCl$_3$ melt at 30 °C the specific conductivity is ca. 2.5 × 10^{-2} Ω^{-1} cm^{-1}.[15]) The log-plot slopes in melts containing 40 mmol dm^{-3} RCl and for ω = 400 rpm were 0.07, 0.12, and 0.22 V/(log unit) on tungsten, platinum, and glassy-carbon electrodes, respectively.

Cyclic Voltammetry. The differences of anodic and cathodic peak potentials for the same RCl concentration and for sweep rate v = 0.02 V s^{-1} were 0.09, 0.24, and 0.65 V for tungsten, platinum, and GC electrodes, respectively, and were also influenced by changes of RCl concentration and sweep rate. The ratio of anodic and cathodic peak currents was close to 1 in neutral BuPyCl–AlCl$_3$ melt (the exact values of $i_{\mathrm{an}}/i_{\mathrm{cath}}$ changed slightly with sweep rate and for a 40 mmol dm^{-3} RCl solution were 1.2 at v = 0.02 V s^{-1} and 1.1 at v = 0.1 V s^{-1}, respectively). These values measured in neutral ImCl–AlCl$_3$ melt were higher (especially at lower Cl$^-$ concentrations); however, they became close to these measured in the neutral BuPyCl–AlCl$_3$ melt if the melt was additionally purified by preelectrolysis (see also ref 16)). These effects might be related to the higher purity of BuPyCl than of ImCl. The occurrence of a reaction of a chloride oxidation product with impurities in the melt was confirmed by double-step chronoamperometric and coulometric experiments—see below.

The dependence of anodic peak current on both the BuPyCl concentration and the square root of the sweep rate was linear, and the plot passed through the origin.

It is worth mentioning that in order to achieve reproducible electrochemical results, great care had to be taken in preparing the electrode surfaces. This is also the reason that no quantitative kinetic analysis of the chloride oxidation voltammetric curve will be presented in this paper. However, qualitatively this process is almost reversible on a tungsten electrode and fully irreversible on glassy carbon (see e.g. ref 17)).

Coulometry and Spectroscopy. To determine the number of electrons participating in the chloride oxidation process, constant-potential electrolysis on a large glassy-carbon electrode at a potential of +1.6 V was carried out. Platinum or tungsten electrodes are sensitive to corrosive attack by the Cl$_2$/Cl$^-$ couple—see, e.g. ref 6. Coulometry was performed by passing a charge (ca. 18 C) sufficient to oxidize about 25% of the chloride through a solution containing 121 mmol dm^{-3} of BuPuCl in excess of the neutral melt. The decrease in the limiting current of chloride oxidation was monitored at the rotating disk electrode. Three experiments gave n values of 0.68, 0.68, and 0.72, indicating formation of Cl$_3^-$ (theoretical n = 0.67). In addition, following the electrolysis, appropriate amounts of BuPyCl were added to the melt to return the

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(15) Fannin, A. A.; Floreani, D. A.; King, L. A.; Landers, J. S.; Piersma, B. J.; Stech, D. J.; Vaughn, R. L.; Wilkes, J. S.; Williams, J. L. Frank J. Seiler Research Research Laboratory Technical Report FJSRL-TR-82-0006; USAF Academy: Colorado Springs, CO, 1982.

(16) Gale, R. J.; Osteryoung, R. A. "Molten Salt Techniques"; Lovering, D. G., Gale, R. J., Eds.; Plenum: New York, 1983; Vol. I, p 60.

(17) Shuman, M. S. *Anal. Chem.* **1969**, *41*, 142.

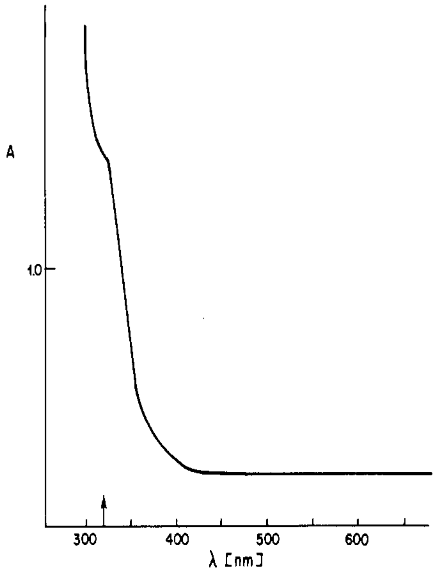

Figure 4. UV-visible spectrum recorded for a solution containing the product of chloride oxidation in neutral ImCl-$AlCl_3$ melt. The arrow indicates the position of maximum of absorption obtained for Cl_3^- in molten KCl-LiCl.[18]

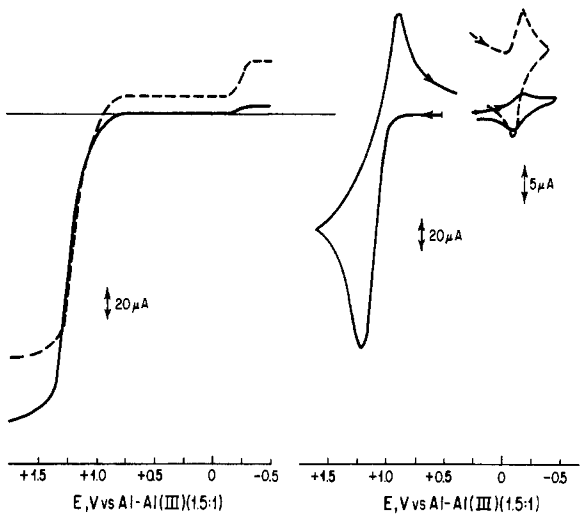

Figure 5. RDE voltammetric curve recorded on a platinum electrode (0.0491 cm^2) before (solid line) and after (dotted line) passing 18.1 C through the 121 mmol dm^{-3} solution of BuPyCl in neutral ImCl-$AlCl_3$ melt; ω = 400 rpm; t = 30 °C. The right-hand figure shows the cyclic voltammogram recorded before electrolysis; the current sensitivity has been changed at +0.3 V. For details, see text.

chloride oxidation wave to its original value. The amounts required were in agreement with the coulometric results. The product solution was not very stable, and after about 3 h the chlorine reduction wave disappeared; however, no significant and expected increase of the chloride oxidation wave was observed (see below).

The UV-visible spectrum recorded after electrolysis is presented in Figure 4. This spectrum exhibited an absorption shoulder at about 320 nm (near the UV cutoff of the melt), which is in very good agreement with the value measured for the Cl_3^- ion in KCl-LiCl melt at 400 °C.[18-20]

In Figure 5 the voltammograms recorded before and after electrolysis are compared. The wave at -0.4 V (observed on a platinum electrode), which increased significantly after electrolysis, has been found[21] to correspond to the HCl/H_2 couple in a basic melt. From this experiment it follows that Cl_3^- seems to be a sufficiently strong oxidant to oxidize hydroxide-containing species in the melt, presumably according to the reaction

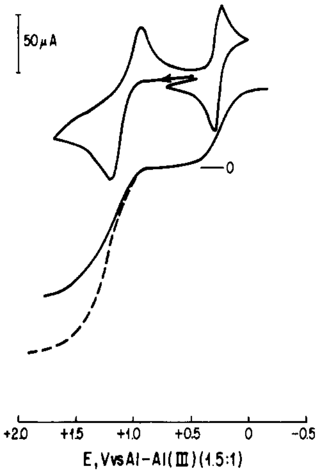

Figure 6. Effect of addition of $FeCl_3$ (29 mmol dm^{-3}) to a 91 mmol dm^{-3} solution of BuPyCl in neutral ImCl-$AlCl_3$ melt: RDE voltammetric curve recorded on a Pt electrode before (---) and after (—) addition of $FeCl_3$, ω = 400 rpm; cyclic voltammetric curve at sweep rate v = 0.05 V s^{-1} after addition of $FeCl_3$, t = 30 °C.

$$Cl_3^- + Al(OH)Cl_2 \rightarrow AlCl_4^- + HCl + {}^1/_2O_2 \qquad (2)$$

and $E°_{Cl_3^-/Cl^-} > E°_{O_2/O^{2-}}$ (see also cyclic voltammetric curves recorded on a Pt electrode for the HCl/H_2 couple, when, during an anodic scan, the potential was reversed before and at the potential of chloride oxidation, shown on the right side of Figure 5).

Diffusion Coefficient of Cl^-. By the use of the n value obtained in coulometric experiments, the diffusion coefficient of Cl^- was determined from RDE (rotating disk electrode) voltammetric measurements. D_{Cl^-} was equal to (6.25 ± 0.30) × 10^{-7} cm^2 s^{-1} in 1:1 BuPyCl-$AlCl_3$ melt (t = 40 °C, η = 0.22 P) and (9.55 ± 0.15) × 10^{-7} cm^2 s^{-1} in 1:1 ImCl-$AlCl_3$ melt (t = 30 °C, η = 0.156 P). The corresponding $D\eta/T$ values are 4.4 × 10^{-10} and 4.9 × 10^{-10} g cm s^{-2} K^{-1}, respectively. This small difference might result from an R^+-Cl^- ion pair being oxidized. This is supported by a small difference between the potentials measured as $(E^p_{an} + E^p_{cath})/2$ in both BuPyCl-$AlCl_3$ and ImCl-$AlCl_3$ melts under the same conditions (these values measured at RCl concentration equal to 40 mmol dm^{-3} are +1.04 and +1.08 V in these melts, respectively).

More detailed data on potentiometric measurements will be presented elsewhere.[22]

Application of the Convective Diffusion-Controlled Cl^- Oxidation Wave. The convective diffusion-controlled chloride oxidation wave has been used to determine the stoichiometry of complexation in the Fe(III)-Cl^- system. Since this system is well described in the literature,[23-25] we have used it as a model to test the application of Cl^- oxidation waves to studies of stoichiomery of complexation reactions in the melt. Figure 6 shows the voltammograms recorded before and after addition of a known amount of $FeCl_3$ (29 mmol dm^{-3}) to the neutral ImCl-$AlCl_3$ melt containing an excess of 91 mmol dm^{-3} of ImCl. The decrease of the chloride oxidation wave corresponds quantitatively to the reaction

$$Cl^- + FeCl_3 \rightarrow FeCl_4^- \qquad (3)$$

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(18) Greenberg, J.; Sundheim, B. R. *J. Chem. Phys.* **1958**, *29*, 1029.

(19) Katzin, L. I. *J. Chem. Phys.* **1952**, *20*, 1165.

(20) Zimmerman, G.; Strong, F. C. *J. Am. Chem. Soc.* **1957**, *79*, 2063.

(21) Sahami, S.; Osteryoung, R. A. *Anal. Chem.* **1983**, *55*, 1970.

(22) Karpinski, Z.; Osteryoung, R. A., in preparation.

(23) Hussey, C. L.; King, L. A.; Wilkes, J. S. *J. Electroanal. Chem. Interfacial Electrochem.* **1979**, *102*, 321.

(24) Laher, T. M.; Hussey, C.L. *Inorg. Chem.* **1982**, *21*, 4079.

(25) Nandjundiah, C.; Shimizu, D.; Osteryoung, R. A. *J. Electrochem. Soc.* **1982**, *129*, 2474.

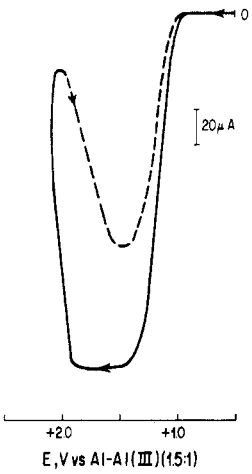

Figure 7. RDE voltammogram obtained on a Pt electrode in a 121 mmol dm^{-3} solution of BuPyCl in neutral InCl-AlCl$_3$ melt; ω = 400 rpm; t = 30 °C.

which is in agreement with potentiometric studies of this system.[24,25] The $FeCl_4^-$ diffusion coefficient calculated from the Fe(III) reduction wave ($D\eta/T = 3.74 \times 10^{-10}$ gm cm s^{-2} K^{-1}) is in good agreement with previously published values (3.71×10^{-10} gm cm s^{-2} K^{-1} from ref 25) for the BuPyCl-AlCl$_3$ melt.

Discussion

No second oxidation wave of Cl$^-$ to Cl$_2$(g) at $C_{RCl} > 25$ mmol dm^{-3} was observed. This result is supported by the "strange" behavior of a platinum electrode at potentials more positive than +1.8 V during RDE experiments. Figure 7 shows a very significant decrease of oxidation current at these potentials. This effect is very reproducible and is not observed if the rotating electrode is polarized at a potential that is on the plateau of the Cl$^-$ oxidation wave but is less positive than 1.8 V. Similar effects were observed with the tungsten electrode but were not as reproducible. Marchon and Badoz-Lambling[26] have found similar behavior at platinum rotating disk electrodes in nitromethane on the plateau of the Cl$^-$ oxidation wave. This phenomenon can be explained by assuming that at sufficiently positive potentials Cl$_2$(g) evolution occurs, and this gas covers the electrode surface. No observation of a similar effect on GC electrodes indicates that the Cl$_2$(g) evolution overpotential in this case is much greater.

This explanation is also consistent with results obtained in electrochemical studies of Cl$^-$ oxidation in several aprotic solvents.[27-29] In acetonitrile two oxidation waves have been observed[27] on rotating platinum electrodes with limiting current ratio $I_{d,1}/I_{d,2} = 2$ and an $E_{1/2}$ separation close to 0.6 V. However, in nitromethane and acetone a single voltammetric wave, attributed to the oxidation of Cl$^-$ to Cl$_3^-$, was observed.[28] According to the authors, the second wave for the oxidation of chloride ions in these two solvents must occur at a potential more positive than that at which the background wave appears.[29] It is also worth mentioning that in the case of other halogen/halide couples two waves were observed in aprotic solvents,[28] and $E_{1/2}$ separations were much less than in the case of Cl$^-$ oxidation in acetonitrile. These facts are also in accord with our assumption of a rather high value of gas evolution overpotential.

On the other hand, this couple has also been studied in nitromethane,[26] dimethylformamide,[30] and acetonitrile.[31] Only one anodic oxidation wave was found, and this has been attributed to the formation of Cl$_2$(g) as the major product of Cl$^-$ oxidation. However, the evidence presented for the formation of Cl$_2$(g) in these papers is open to question. For example, the values of the diffusion coefficient determined in ref 31, under the assumption that n = 1 for Cl$^-$ oxidation, were 0.81×10^{-5} cm^2 s^{-1} for Cl$^-$ and 2.76×10^{-5} cm^2 s^{-1} for Cl$_2$, both at 0 °C. Recently, however, another determination of the diffusion coefficient of Cl$^-$ was carried out in acetonitrile[32] using the anodic oxidation wave of mercury in the presence of chloride ion. These latter authors obtained a value of $2.4 \pm 0.3 \times 10^{-5}$ cm^2 s^{-1} at 25 °C. A recalculation of this value to 0 °C gives a value of ca. 1.7×10^{-5} cm^2 s^{-1}. This suggests that the value of the diffusion coefficient of Cl$^-$ previously measured in acetonitrile[31] is much too small, not only in comparison to the data indicated above[32] but also in comparison to their own value of D_{Cl_2}. However, if one assumes that the n value for Cl$^-$ oxidation under the RDE conditions of ref 31 is 0.67, the D_{Cl^-} value would be increased to 1.5×10^{-5} cm^2 s^{-1}, in our view a much more reasonable value.

If one also compares diffusion coefficient values for chloride determined in aqueous solutions on platinum electrodes under the assumption that n = 1 and compares the value of D_{Cl^-} given as 0.82×10^{-5} cm^2 s^{-1}, in 1 M H$_2$SO$_4$ with that obtained from the equivalent conductance of Cl$^-$ at infinite dilution, $D = 2.03 \times 10^{-5}$ cm^2 s^{-1},[33] it is reasonable to assume that the former value in fact is indicative of an "n" value of 0.67, rather than the value of 1 assumed.

The D_{Cl^-} value has also been measured in molten nitrates by pulse voltammetry on a mercury electrode.[34] A value in equimolar NaNO$_3$-KNO$_3$ at 245 °C was 6.91×10^{-6} cm^2 s^{-1}, which corresponds to a $D\eta/T$ value of 6.3×10^{-10} gm cm s^{-2} K^{-1}, which is even larger than that determined in this present work.

The n value of 1 obtained in ref 26 also may be questioned; it is based on exhaustive electrolysis of Cl$^-$ solutions in nitromethane, but the authors mention that chlorine can react with the solvent with regeneration of substrate.

While the discussion above is indicative of the formation of Cl$_3^-$, we must mention experiments in our own laboratory,[22] although under experimental conditions significantly different from those reported above, which indicate the stability of Cl$_3^-$ is rather low. At this time, we are not certain if there is a real discrepancy or whether the different experimental conditions are determinate.

Studies of the solubility of chlorine in molten chlorides also support the hypothesis of Cl$_3^-$ formation; this has been mentioned previously in comments on previous measurements in CsCl-AlCl$_3$ and NaCl-AlCl$_3$.[10] Øye et al.[35] investigated the enthalpy and entropy of solutions of Cl$_2$ in molten NaCl, KCl, RbCl, CsCl, and MgCl$_2$, using a manometric technique, and found that the solubility increases in the order MgCl$_2$ < NaCl < KCl < RbCl < CsCl. This fact, the positive ΔS, and the high and positive interaction energy for dissolution of Cl$_2$ in alkali chlorides suggest that the dissolved species is not simply Cl$_2$. The increase of solubility of Cl$_2$ with increasing radius of the alkali-metal cation was interpreted in terms of ion pairing between M$^+$ and Cl$^-$ as a reaction competitive with Cl$_3^-$ formation.[36,37] Since the larger organic cations are in-

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(26) Marchon, J. C.; Badoz-Lambling, J. *Bull. Soc. Chim. Fr.* **1967**, 4660.

(27) Kolthoff, I. M.; Coetzee, J. F. *J. Am. Chem. Soc.* **1957**, *79*, 1852.

(28) Nelson, I. V.; Iwamoto, R. T. *J. Electroanal. Chem.* **1964**, *7*, 218.

(29) Benoit, R. L.; Guay, M.; Desbarres, J. *Can. J. Chem.* **1968**, *46*, 1261.

(30) Sinicki, C.; Desportes, P.; Breant, M.; Rosset, R. *Bull. Soc. Chim. Fr.* **1968**, 829.

(31) Sereno, L.; Macagno, V. A.; Giordano, M. C. *Electrochim. Acta* **1972**, *17*, 561.

(32) Wojciechowski, M.; Osteryoung, J. *J. Phys. Chem.* **1983**, *87*, 4725.

(33) Mayer, J. S.; Langer, S. H. *Electrochim. Acta* **1964**, *9*, 1411.

(34) O'Deen, W.; Osteryoung, R. A. *Anal. Chem.* **1971**, *43*, 1879.

(35) Andresen, R. E.; Østvold, T.; Øye, H. A. "Proceedings of the International Symposium on Molten Salts"; Pemsler, J. P., Braunstein, J., Nobe, K., Morris, D. R., Richards, N. E., Eds.; Electrochemical Society: Princeton, NJ, 1976; p 111.

volved in ion-pair interactions in the low-temperature molten salts under consideration, the formation of Cl_3^- should be even easier.

The convective diffusion-controlled wave of chloride oxidation can be applied successfully to studies of stoichiometry of many complexation reactions occurring in these molten salts. This is of particular importance in the case of nonelectroactive chloride-containing complexes, such as the rare earths. Since the Cl^- oxidation current is proportional to RCl concentration over a wide range of concentrations—up to at least 0.1 mol dm^{-3}—the complexation reactions can be studied under conditions of a large excess of the ligand (Cl^-) over the metal ion. In addition, the ability to obtain a discrete reduction wave for the heptachlorodialuminate ion[14] suggests that the interaction of a metal ion with the $Al_2Cl_7^-$ ion may be studied in a similar manner. For instance, if a metal chloride, MCl_2, is dissolved in a "neutral" melt containing a small excess of $Al_2Cl_7^-$, the tendency of the metal ion to yield a chloride to the $Al_2Cl_7^-$ species will result in a decrease of the $Al_2Cl_7^-$ wave; if the metal chloride accepts a chloride from the "neutral" melt, the wave due to $Al_2Cl_7^-$ will increase. Preliminary experiments indicate that this approach is both feasible and useful.[38]

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Note Added in Proof. We have recently learned from Dr. John Wilkes, Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado Springs, CO, that he has observed, via NMR studies, a fairly slow reaction between chlorine and the 1-methyl-3-ethylimidazolium chloride melt to form 4,5-dichloro-1-methyl-3-ethylimidazolium chloride as a substitution product. This could explain the disappearance of chlorine referred to in this paper in the discussion under Coulometry and Spectroscopy.

Registry No. Cl^-, 16887-00-6; Cl_3^-, 18434-33-8; $AlCl_3$, 7446-70-0; BuPyCl, 1124-64-7; ImCl, 65039-09-0; carbon, 7440-44-0; tungsten, 7440-33-7; platinum, 7440-06-4.

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(36) Wilkes, J. S.; Pflug, J. L.; Levisky, J. A.; Hussey, C. L.; Fanin, A. A.; King, L. A. Frank J. Seiler Research Laboratory Technical Report FJSRL-TR-82-0005, USAF Academy: Colorado Springs, CO, 1982.

(37) Osteryoung, R. A., paper presented at the 4th International Symposium on Molten Salts, The Electrochemical Society, San Francisco, CA, May 1983. Tait, S.; Osteryoung, R. A., in preparation.

(38) Lipsztajn, M.; Osteryoung, R. R., paper presented at the Spring meeting of the Electrochemical Society, Cincinnati, OH, May 1984.

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Decamethylvanadocene Chemistry: Synthesis, Structure, and Reactions of Vanadium(II) and Vanadium(III) Derivatives with Carbon Monoxide and Isocyanides

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The synthesis and structure of decamethylvanadocene $(cp^*)_2V$ ($cp^* = \eta^5\text{-}C_5Me_5$) are reported. Decamethylvanadocene contains planar C_5Me_5 rings [$cp^*\text{-}V_{av}$ = 1.91 (5) Å] in a sandwich structure. The magnetic moment for $(cp^*)_2V$ is in agreement with the presence of three unpaired electrons (3.71 μ_B at 291.5 K). It reacts with carbon monoxide leading to a 17-electron monocarbonyl compound, $(cp^*)_2V(CO)$ (1.75 μ_B at 293 K), which has a very low C–O stretching frequency [ν(C–O)(Nujol) = 1845 cm^{-1}] and whose structure was determined by an X-ray analysis. A structural change from a sandwich to a bent arrangement occurs when carbon monoxide is bonded [V–C = 1.879 (8), C–O = 1.17 (1) Å]. Decamethylvanadocene reacts with isocyanides, RNC (R = C_6H_{11}, *t*-Bu), promoting the homolytic cleavage of the R–N bond to form $(cp^*)_2V(CN)(RNC)$ complexes [ν(C–N)(Nujol): R = C_6H_{11}, 2050 and 2070 cm^{-1}; R = *t*-Bu, 2020 and 2060 cm^{-1}]. The structure of $(cp^*)_2V(CN)(C_6H_{11}NC)$ shows a bent $(cp^*)_2V$ unit bonding in the equatorial plane of the CN^- and RNC ligands. The V–C and C–N bond distances are very close for both ligands [$V\text{–}C_{av}$ = 2.04 (2), $C\text{–}N_{av}$ = 1.18 (2) Å]. Dealkylation of *t*-BuNC is promoted by $(cp^*)_2V(CO)$, which is a free-radical-like reagent. The reaction allowed the isolation of the two interrelated complexes $(cp^*)_2V(CO)(CN)$ [ν(C–O) = 1910, ν(C–N) = 2070 cm^{-1}] and $(cp^*)_2V(CN)$ [ν(C–N) = 2080 cm^{-1}], which is isostructural with $(cp^*)_2V(CO)$. One-electron oxidation of decamethylvanadocene with various reagents leads to the corresponding vanadium(III) complexes, $(cp^*)_2V(X)$ (X = Cl, I, $SC_6H_4Me\text{-}p$), which are paramagnetic *per* two electrons. They absorb carbon monoxide (X = I, $SC_6H_4Me\text{-}p$) in nonpolar solvent to form the corresponding diamagnetic monocarbonyl $(cp^*)_2V(X)(CO)$ [ν(C–O): X = I, 1890 cm^{-1}; X = $SC_6H_4Me\text{-}p$, 1890 cm^{-1}]. If the reaction is carried out in a polar solvent or in the presence of an ionizing agent, the formation of $[(cp^*)_2V(CO)_2]^+$ is observed. *tert*-Butyl isocyanide promotes the ionization of the V–X bond in $(cp^*)_2V(X)$ complexes, forming the corresponding diisocyanide compounds $[(cp^*)_2V(t\text{-}BuNC)_2]X$ (X = Cl, I, $SC_6H_4Me\text{-}p$). Crystallographic details for $(cp^*)_2V$: space group *Cmcm* (orthorhombic), *a* = 15.049 (6) Å, *b* = 8.660 (4) Å, *c* = 29.663 (10) Å, *Z* = 8. The final *R* factor is 0.12 for 464 observed reflections. Crystallographic details for $(cp^*)_2V(CO)$: space group $P2_1/n$ (monoclinic), *a* = 15.699 (7) Å, *b* = 13.353 (6) Å, *c* = 9.452 (5) Å, β = 99.26 (5)° for *Z* = 4. The final *R* value is 0.055 for 1563 observed reflections. Crystallographic details for $(cp^*)_2V(CN)(CNC_6H_{11})$: space group $P2_1/c$ (monoclinic), *a* = 10.342 (5) Å, *b* = 13.146 (7) Å, *c* = 18.956 (10) Å, β = 92.60 (6)° for *Z* = 4. The final *R* value is 0.067 for 1163 observed reflections. Crystallographic details for $(cp^*)_2V(CN)$: space group $P2_1/n$ (monoclinic), *a* = 15.895 (4) Å, *b* = 13.441 (3) Å, *c* = 9.209 (2) Å, β = 97.92 (2)° for *Z* = 4. The final *R* value is 0.051 for 1508 observed reflections.

Introduction

Bis(cyclopentadienyl)metal derivatives have been considered among the most promising model compounds for studying the activation of small molecules and organic functional groups, including some general aspects of a few classes of organometallic reactions.[1]

Such a utilization may be ascribed to some peculiarities of these complexes, namely (i) the $(cp)_2M$ unit has a limited number or orbitals available for the intraction with a molecule

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(1) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–42 and references therein.

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