

An Electrochemical Study of PCl_3 and POCl_3 in the Room Temperature Ionic Liquid $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$

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Voltammetric studies of PCl_3 and POCl_3 have not been reported in the literature to date, probably due to the instability of these molecules in conventional aprotic solvents giving unstable and irreproducible results. From a previous study [Amigues et al. *Chem. Commun.* **2005**, 1–4], it was found that ionic liquids have the ability to offer a uniquely stable solution phase environment for the study of these phosphorus compounds. Consequently, the electrochemistry of PCl_3 and POCl_3 has been studied by cyclic voltammetry on a gold microelectrode in the ionic liquid $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$ (1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonfyl)imide). For both compounds, reduction and oxidation waves were observed and a tentative assignment of the waves is given. For PCl_3 , the reduction was thought to proceed via the following mechanism: $\text{PCl}_3 + \text{e}^- \rightleftharpoons \text{PCl}_3^-$, $\text{PCl}_3^- \rightleftharpoons \text{Cl}^- + \text{P}^+\text{Cl}_2$, and $\text{Cl}^- + \text{PCl}_3 \rightleftharpoons \text{PCl}_4^-$. For POCl_3 , the suggested reduction mechanism was analogous to that of PCl_3 : $\text{POCl}_3 + \text{e}^- \rightleftharpoons \text{POCl}_3^-$, $\text{POCl}_3^- \rightleftharpoons \text{Cl}^- + \text{P}^+\text{OCl}_2$, and $\text{Cl}^- + \text{POCl}_3 \rightleftharpoons \text{POCl}_4^-$. In both cases P^+Cl_2 and P^+OCl_2 are likely to engage in further reactions. Potential step microdisk chronoamperometry was carried out on the reductive waves of PCl_3 and POCl_3 to measure diffusion coefficients and number of electrons transferred. It was found that the diffusion of PCl_3 was unusually slow ($3.1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$): approximately 1 order of magnitude less than that for POCl_3 ($2.2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$). For both PCl_3 and POCl_3 , a “split wave” was observed, with an overall electron count of 1. This observation is shown to be consistent with and to “fingerprint” the mechanisms proposed above.

1. Introduction

The interest in ionic liquids (ILs) is rapidly expanding. Since the discovery of molten salts in 1914,¹ there has been much interest in developing “tailor-made” ionic liquids for specific purposes. Simply by changing the nature of the cation and the anion, it has been possible to synthesize a wide number of variations which have different physical properties. The preparation of air and moisture stable ionic liquids based around hydrophobic anions such as bis(trifluoromethanesulfonyl)imide, $[\text{N}(\text{SO}_2\text{CF}_3)_2]^-/[\text{N}(\text{Tf})_2]^+$, has been a significant development in the field. These anions are classed as air and moisture stable, and are superior to their predecessors (based on haloaluminate ions) because they can be prepared and safely stored outside an inert atmosphere. The interested reader is directed to a recent review on nonhaloaluminate room temperature ionic liquids.²

Ionic liquids are fast becoming popular solvents for electrochemical experiments.^{2–6} They are intrinsically conductive, which is a great advantage for the electrochemist, as no supporting electrolyte needs to be employed. Ionic liquids have a much wider electrochemical window than regular solvents, often greater than 5 V,⁷ and this has allowed for applications such as electrodeposition of various metals and semiconductors⁸ which are deposited at potentials outside the range of conven-

tional solvents. Other electrochemical applications include the use of ILs as electrolytes in lithium batteries,⁹ electrochemical sensors,⁴ capacitors,¹⁰ and in solar cells.¹¹ Ionic liquids have a negligible vapor pressure, and their nonvolatility allows greener synthesis^{12,13} with reduced environmental impacts, in contrast to volatile organic compounds. They are also employed in catalysis such as hydrogenations, oxidations and hydroformylations with transition metals.¹⁴

In this work, we report the electrochemistry of PCl_3 (phosphorus trichloride) in a $[\text{N}(\text{Tf})_2]^+$ based ionic liquid. The world production of PCl_3 exceeds one-third of a million tons,¹⁵ making it a useful and important compound to study. PCl_3 is a reducing agent, being readily oxidized to phosphorus pentachloride or phosphorus oxychloride. It reacts rapidly and exothermically with water to form phosphorous acid, H_3PO_3 , and HCl . PCl_3 is used directly as a reagent in organic synthesis, for example to convert primary and secondary alcohols into alkyl chlorides, carboxylic acids into acyl chlorides, and primary nitro compounds into nitriles.¹⁶

PCl_3 is an important starting point for the manufacture of many industrial products containing phosphorus. It is used on an industrial scale to make phosphonates,¹⁷ the herbicide glyphosate,¹⁸ triphenylphosphine for the Wittig reaction,¹⁹ and phosphate esters which may be used as industrial intermediates, or used in the Horner–Wadsworth–Emmons reaction,²⁰ both important methods for making alkanes. It is also used as the starting material for the manufacture of insecticides such as diazinon,²¹ and of organic phosphates such as triphenyl phos-

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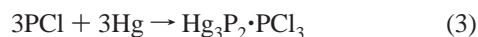
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phate and tricresyl phosphate, which have applications as flame retardants²² and plasticizers for PVC.²³

Literature data on electrochemical studies of phosphorus halogen compounds are scarce. The electroreduction of PCl_3 , PBr_3 , and PI_3 was reported by Kishil' et al.²⁴ in thoroughly dehydrated acetonitrile on a dropping mercury electrode, although no cyclic voltammetry was shown. They claimed that the reduction was "controlled by diffusion and was irreversible". They reported an $E_{1/2}$ value of -0.915 V vs mercury pool, an electron count of 1, a transfer coefficient, α , of 0.311, and a standard electrochemical rate constant, k_f^0 , of 1.3×10^{-7} cm s^{-1} using an LP-60 polarograph. From these findings, they proposed some simple equations for the reduction of PCl_3 , which are shown below:



and further chemical reactions, e.g.



Berberova²⁵ reported the *oxidation* of PCl_3 on a platinum disk electrode, but again, no cyclic voltammetry was shown. The oxidation wave of PCl_3 in acetonitrile was extremely unstable and disappeared after applying several voltage pulses. PCl_3 was found to be most stable in methylene chloride with TBAP, or sodium perchlorate with a crown ether (dibenzo-16-crown-6). A single electron oxidation wave was reported on Pt at $+1.58$ V vs Ag/AgCl, which was partially reversible and diffusion limited. The radical cation of PCl_3 was also confirmed to be present in solution by electrochemical and ESR data in a different study.²⁶

In both these studies,^{24,25} no voltammetry was shown, and diffusion coefficients for PCl_3 were not calculated. It is a similar story for POCl_3 (phosphorus chloroxide); no voltammetry is reported in the literature. Berberova²⁵ states that reduction waves of phosphorus chloroxide were observed at -0.21 and -2.06 V vs Ag/AgCl, but mentions nothing about the size, shape, and/or reversibility of the waves. Various groups^{27–29} have attached electrons to gas-phase molecules of POCl_3 and have proposed equations which ultimately result in the formation of chloride ions, among other products.

Amigues et al.³⁰ recently discovered that both PCl_3 and POCl_3 were unusually stable in ionic liquid media. Their stability was dependent mainly upon the identity of the anion, but changing both the anion and cation had some effect. PCl_3 was found to be most hydrolytically stable ($>95\%$) in the RTIL 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ($[\text{C}_4\text{mpyr}][\text{N}(\text{Tf})_2]$) for weeks, even when stirred in air and without drying the ionic liquid. Conversely, POCl_3 hydrolyzed rapidly in wet ILs, even those based on $[\text{N}(\text{Tf})_2]^-$ anions, with the exception of $[\text{C}_5\text{mim}][\text{FAP}]$ (1-pentyl-3-methylimidazolium tris(perfluoroalkyl)trifluorophosphate). They reported the formation of various hydrolysis products, resulting either from reaction with the ionic liquids or from reaction with the water naturally present in the solvent (0.1 wt % water even in "dry" ILs). The products were identified by NMR and included species such as HPOClOH , $\text{PO}(\text{OH})_2\text{Cl}$, PF_3 (from $[\text{BF}_4]^-$ anions), $\text{HPO}(\text{OTf})_2$ (from $[\text{OTf}]^-$ anions), $\text{POCl}_2(\text{OMs})$ (from $[\text{OMs}]^-$ (methylsulfonate) anions), and $\text{PO}(\text{OH})_2\text{Cl}$, among others. It is surprising that, given the higher water content of "dry" ILs (0.1 wt %) compared to organic solvents (dry THF, 0.005 wt %), ionic

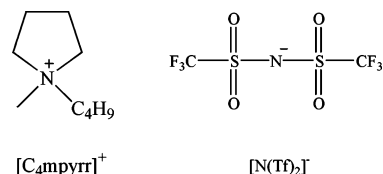


Figure 1. Molecular structures of the cation and anion employed in this study.

liquids have been shown to offer a more stable environment than organic solvents for storage of PCl_3 and POCl_3 .

This work reports the electrochemistry of PCl_3 and POCl_3 and chloride ($[\text{C}_4\text{mpyr}]\text{Cl}$) in $[\text{C}_4\text{mpyr}][\text{N}(\text{Tf})_2]$ (see Figure 1).

2. Experimental Section

2.1. Chemical Reagents. 1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide $[\text{C}_4\text{mpyr}][\text{N}(\text{Tf})_2]$ and 1-butyl-1-methylpyrrolidinium chloride $[\text{C}_4\text{mpyr}]\text{Cl}$ were prepared in house following standard procedures reported in the literature.³¹ PCl_3 (Aldrich, 99.999%), POCl_3 (Aldrich, 99%), ferrocene (Aldrich, 98%), tetra-*n*-butylammonium perchlorate (TBAP, Fluka, Puriss electrochemical grade, $>99\%$), and acetonitrile (Fischer Scientific, dried and distilled, $>99.99\%$) were used without further purification. PCl_3 and POCl_3 were kept under a constant stream of dried nitrogen (BOC gases) while handling.

2.2. Instrumentation. A computer controlled μ -Autolab potentiostat (Eco-Chemie, Netherlands) was used to perform electrochemical experiments. A three-electrode arrangement was employed, with a gold microelectrode (diameter 25 μm) as the working electrode, Ag/[Ag⁺] as the reference electrode, and a platinum coil wire as the counter electrode. The reference electrode consisted of a silver wire immersed in a glass tube containing 0.1 M AgNO_3 in $[\text{C}_4\text{mim}][\text{NO}_3]$ ionic liquid, separated from the bulk solution by a Vycor plug.

The microdisk working electrode was polished on soft lapping pads (Kemet Ltd., UK), using alumina (Buehler, Illinois) of size 1 μm and 0.3 μm , respectively. The steady-state voltammetry of a 2 mM solution of ferrocene in acetonitrile containing 0.1 M TBAP was used to calculate the electrode diameter, adopting a value for the diffusion coefficient of 2.3×10^{-5} cm² s⁻¹ at 298 K.³²

The electrodes were placed in a specially designed cell for volumes from 1 to 5 mL. This consisted of a glass vial topped with a 15 mm thick cylinder of PTFE with four holes of specific diameter (three for the electrodes and one for the nitrogen line), so as to keep a closed system throughout the measurements. The cell was housed in a Faraday cage to minimize background noise.

Since the chemicals under study were not stable in conventional solvents such as acetonitrile, the "solvent evaporation" procedure used previously⁵ could not be employed. Instead, solutions of $[\text{C}_4\text{mpyr}]\text{Cl}$, PCl_3 , and POCl_3 were made up directly in 2 mL of ionic liquid to roughly 15 mM concentrations. The ionic liquid was dried at 70 °C under high vacuum (Edwards High Vacuum Pump, Model ES 50, 0.05 Torr) for at least 48 h prior to use, then stored under nitrogen. The solutions were further purged throughout the experiments by bubbling dried nitrogen into the solution. It should be noted that due to the instability of PCl_3 and POCl_3 in air, the stock solutions were only useful for one experiment, before redistilling was required. However, in the ionic liquid, the voltammetry was stable for weeks in the case of PCl_3 , but only hours for POCl_3 . The behavior of PCl_3 and POCl_3 in the ionic liquid changed after a

long period of time when exposed to air. This gave rise to extra peaks in the voltammetry, probably due to the reduction and/or oxidation of electroactive hydrolysis products. Interestingly, in a different batch of the same ionic liquid, solutions became opaque/cloudy soon after conducting electrochemical experiments, possibly due to the larger water content in this batch. We also note that the voltammetry of concentrations of PCl_3 above 30 mM was unstable, and accurate data could not be obtained. Concentrations below 15 mM PCl_3 were also not easily achieved, since this required a larger volume of the ionic liquid solvent (only small amounts were available), and the resulting solutions will contain a larger water to PCl_3 ratio, which will likely affect the stability of PCl_3 .

2.3. Chronoamperometric Experiments. Chronoamperometric transients were achieved by using a sample time of 0.1 s. The potential was stepped to the required value, and the current was measured for 10 s after pretreatment at 0 V for 20 s. The software package Origin 7.0 (Microcal Software Inc.) was used to fit the experimental data. The equations proposed by Shoup and Szabo³³ (below) were imported into the nonlinear curve fitting function, and the computer was instructed to perform 10 iterations on the data.

$$I = -4nFDcr_d f(\tau) \quad (4)$$

$$f(\tau) = 0.7854 + 0.8863\tau^{-1/2} + 0.2146e^{-0.7823\tau^{-1/2}} \quad (5)$$

$$\tau = \frac{4Dt}{r_d^2} \quad (6)$$

where n is the number of electrons transferred, F is the Faraday constant, D is the diffusion coefficient, c is the initial concentration of parent species, r_d is the radius of the disk electrode, and t is the time.

The value for the radius (previously calibrated) was fixed, and a value for the diffusion coefficient and the product of the number of electrons multiplied by concentration was obtained after optimization of the experimental data. The equations used in this approximation are sufficient to describe the current response to within an accuracy of 0.6%.

3. Theory

The reductions of both PCl_3 and POCl_3 (see section 4) gave rise to a “split wave” phenomenon, where two peaks arise close together, with the first resembling a shoulder on the second, larger wave. Chronoamperometry (see later) revealed that, in both cases, the overall electron count was 1. The discussion below describes how the “split waves” of PCl_3 and POCl_3 (reported in section 4) were simulated by using the one-dimensional digital simulation program DigiSim 3.03 (BAS Technicol),³⁴ applying a single one-electron-transfer step with subsequent follow-up chemistry.

3.1. Modeling the Reduction of PCl_3 and POCl_3 in DigiSim. It was found that a one-electron “split wave” could be successfully simulated by using the simple generic reaction scheme:



Figure 2a shows a simulated cyclic voltammogram following this generic reaction scheme over the voltage range studied experimentally. The cathodic wave was simulated to be electrochemically irreversible, in line with experimental volta-

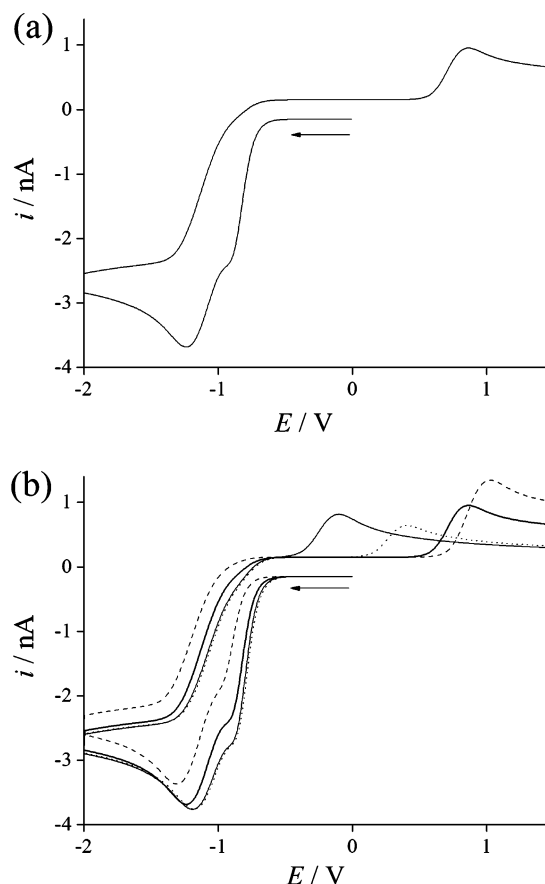


Figure 2. Simulated voltammograms of the reductive “split wave” of PCl_3 , at scan rates of 100 mV s^{-1} , obtained from the generic scheme given by eqs 7 and 8. (a) The best fit to the experimental data (see section 4.1), using standard electrochemical rate constant, k_s , of $1 \times 10^{-9} \text{ cm s}^{-1}$ and a K_{eq} value of 50. (b) The effect of employing various k_s values: (thin solid line) 10^{-5} , (dotted line) 10^{-7} , (thick solid line) 10^{-9} , and (dashed line) $10^{-10} \text{ cm s}^{-1}$, with a K_{eq} value of 50; other parameters adjusted accordingly.

mmograms. The simulation also revealed a significant anodic back peak. Figure 2b shows simulated voltammograms at scan rates of 100 mV s^{-1} , employing different values for the standard electrochemical rate constant, k_s , over 5 orders of magnitude (10^{-5} , 10^{-7} , 10^{-9} , and $10^{-10} \text{ cm s}^{-1}$), with an equilibrium constant, K_{eq} , for eq 8 of 50 in all cases. It can be seen that the separation between the cathodic and anodic peaks significantly increases when k_s is decreased. By employing a k_s value of $10^{-9} \text{ cm s}^{-1}$ (Figure 2a) and by careful selection of the kinetic parameters, it was possible to simulate the shape of the double wave, and position a back peak corresponding to that of peak II (see section 4.1.)

However, this simple reaction scheme was not sufficient enough to simulate the reductive waves of PCl_3 and POCl_3 over a wide range of scan rates (0.01 – 2 V s^{-1}). It was found that dividing eq 8 into two separate equations allowed more manipulation of kinetic parameters which in turn made it easier to simulate the peak potentials and wave shapes for both PCl_3 and POCl_3 over this range of scan rates. The generic scheme used in the final simulation of the reductive waves of PCl_3 and POCl_3 is shown below:



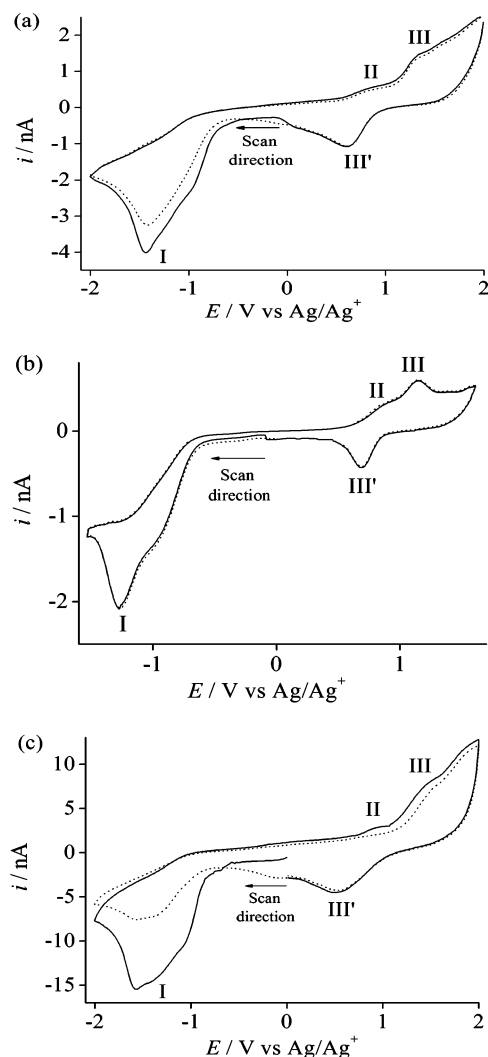


Figure 3. Cyclic voltammetry for the reduction of 14.8 mM PCl_3 in $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$ on a gold microelectrode (diameter $25\ \mu\text{m}$) at scan rates of (a) 100, (b) 10, and (c) $1\ \text{V s}^{-1}$. The first scan is shown as a solid line; the second scan is shown as dots.

The theoretical simulations fitted the experimental data approximately, even though the shapes of the reductive waves of PCl_3 and POCl_3 are quite unusual and complicated (because of irreversibility and slow diffusion). The mechanistic analysis shown above is thought to be the minimum sufficient to explain the appearance of a one-electron “split wave” feature for both species. The kinetic parameters used in the simulations are discussed in section 4.1 for PCl_3 and in section 4.2 for POCl_3 .

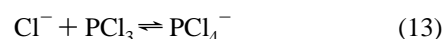
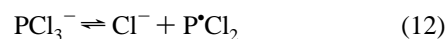
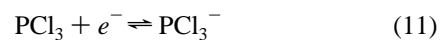
Given the second-order nature of some of the reactions in the scheme defined by eqs 7, 9, and 10, the simulations were performed for variable substrate concentrations and also for different concentrations of added chloride. In each case, the effect was quantified by monitoring the size of the shoulder on the larger wave relative to the size of the latter, as quantified by the fraction f ($0 \leq f \leq 1$), where $f = 0$ corresponds to no shoulder. The results are discussed below.

4. Results and Discussion

The ionic liquid $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$ was used as the solvent in all electrochemical experiments throughout this work, since this was shown³⁰ to be a highly suitable solvent in which to store PCl_3 for long periods of time, and POCl_3 for a few hours.

4.1. Voltammetry of PCl_3 in $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$. Figure 3a shows a typical cyclic voltammogram obtained for the reduction

of 14.8 mM PCl_3 on a gold microelectrode (diameter $25\ \mu\text{m}$) in $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$, at a scan rate of $100\ \text{mV s}^{-1}$. A second scan is overlaid (dots), which shows a decrease in the size of the reduction peak, I. It is thought that this is due to the slow diffusion of the electroactive species from the electrode surface. This is exemplified by Figure 3, panels b and c, recorded at scan rates of $10\ \text{mV s}^{-1}$ and $1\ \text{V s}^{-1}$, respectively, under the same conditions. A scan rate of $10\ \text{mV s}^{-1}$ (Figure 3b) is slow enough to allow diffusion of reduced material away from the surface, whereas at faster scan rates ($1\ \text{V s}^{-1}$, Figure 3c) the rate of diffusion is outrun. It is interesting that the reductive peak appears as a “split wave” at all scan rates, similar to that reported for the oxidation of bromide in $[\text{C}_2\text{mim}][\text{N}(\text{Tf})_2]$,³ and for the reduction of 4-nitrophenol in $[\text{C}_4\text{dmim}][\text{N}(\text{Tf})_2]$.⁵ In both of these cases, the split wave was attributed to the initial reduction of a parent molecule, followed by reaction of this reduced species with another parent molecule ($\text{A} + \text{e} \rightarrow \text{B}$, and $\text{B} + \text{A} \rightarrow \text{products}$). It is likely that an analogous process is happening here, according to eqs 11–13.



Section 3 describes how the reductive wave of PCl_3 can be explained (by digital simulation) to proceed by the proposed reaction scheme (eqs 11–13). There may also be further reactions which consume the radical P^*Cl_2 , although these were not included in the simulation.

The reductive wave, I, is electrochemically irreversible at all scan rates studied (0.01 – $2\ \text{V s}^{-1}$), and the equilibrium position of reaction 14 is shifted toward the product PCl_4^- , in accordance with DigiSim fits. The reduction does not appear to be fully *chemically* irreversible, if the back peak II relates to the reoxidation of PCl_4^- . The peak potential of wave I occurs at $-1.45\ \text{V vs Ag/Ag}^+$ (at a scan rate of $100\ \text{mV s}^{-1}$), which is 535 mV more negative than that observed by Kishil’ et al.²⁴ vs mercury pool in anhydrous acetonitrile. A distinct one-electron wave was reported for the reduction in acetonitrile,²⁴ indicating that the “split wave” seen here is a feature of the slower diffusion in the ionic liquid, probably via promotion of second-order follow-up kinetics.

The best theoretical fit to the experimental “split wave” was achieved (assuming a transfer coefficient, α , of 0.5) when the following conditions applied: (a) the standard rate constant for the electrochemical step, k_s , was very slow ($\sim 1 \times 10^{-9}\ \text{cm s}^{-1}$, 2 orders of magnitude smaller than in MeCN)²⁴ subject to the assignment of peak II discussed below, (b) the forward rate constant, k_f , for both the homogeneous reactions (eqs 12 and 13) was made to be fast ($> 1 \times 10^7\ \text{s}^{-1}$), and (c) when the equilibrium constant, K_{eq} , of eq 13 was shifted toward the product PCl_4^- (in the range 50 to $100\ \text{mol}^{-1}\ \text{dm}^3$). It is therefore thought that peak II is either (a) a “back peak” resulting from the reduction scheme (Figure 2, following eqs 11–13) or (b) the oxidation of chloride on a filmed electrode (see section 4.4), or a combination of both. If (a) is not the case, then it is possible that the standard rate constant for the electrochemical step, k_s , is smaller than $1 \times 10^{-9}\ \text{cm s}^{-1}$, which would shift the back peak to an even more positive position than the peak potential of wave II (and would appear somewhere under wave III). The electrochemical rate constant is clearly unusually small, raising the possibility that cleavage of the P–Cl bond may be concerted

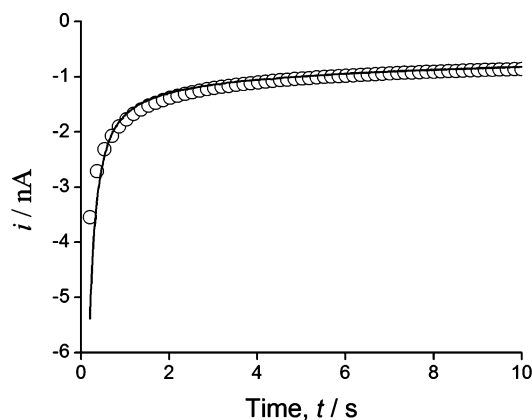


Figure 4. Experimental (solid line) and fitted theoretical (circles) chronoamperometric transient obtained for the reduction of 14.8 mM PCl_3 in $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$ on a gold microelectrode (diameter $25\ \mu\text{m}$). The potential was stepped from 0.0 to $-2.0\ \text{V}$.

TABLE 1: Diffusion Coefficients and Electron Counts Obtained from Analysis of Potential Steps Performed on the Reductive Waves of 14.8 mM PCl_3 and 15.3 mM POCl_3 in the Ionic Liquid $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$ at 298 K

	diffusion coefficient ^a / $\text{m}^2\ \text{s}^{-1}$	no. of electrons transferred ^a
reduction wave of PCl_3	$(3.1 \pm 0.2) \times 10^{-12}$	1.05 ± 0.04
reduction wave of POCl_3	$(2.2 \pm 0.1) \times 10^{-11}$	1.08 ± 0.04

^a Obtained from chronoamperometric fitting of experimental data to the Shoup and Szabo³³ equation.

(electron transfer and bond cleavage take place together) in the ionic liquid medium studied. In this case, peak II could be related to the oxidation of PCl_4^- . The identity of peaks III and III' is thought to be due to the oxidation of POCl_3 , formed from PCl_3 , and will be discussed later in section 4.4, based on comparisons in peak potential with that of POCl_3 .

Steady state behavior for the reduction wave of PCl_3 could not be achieved on a $25\ \mu\text{m}$ diameter electrode, even at scan rates as slow as $1\ \text{mV}\ \text{s}^{-1}$, suggesting that diffusion of PCl_3 from the electrode surface is very slow. Chronoamperometry data further support this observation. Figure 4 shows a chronoamperometric transient obtained for the reduction wave of 14.8 mM PCl_3 on a $25\ \mu\text{m}$ gold microelectrode. The potential was stepped from 0.0 V (corresponding to no Faradaic current) to $-2.0\ \text{V}$ (a potential cathodic of the reductive peak) and the current was measured for 10 s. The fitting of experimental data to the Shoup and Szabo³³ equation gave an approximate diffusion coefficient and electron count as given in Table 1. The diffusion coefficient for PCl_3 is very small, even when compared to other species in ionic liquid media (cf. $1.95 \times 10^{-11}\ \text{m}^2\ \text{s}^{-1}$ for nitrobenzene in $[\text{C}_4\text{dmim}][\text{N}(\text{Tf})_2]$).⁵ Given that the viscosity values for the two ionic liquids are similar (80.1 cP for $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$ at 298 K, compared to 106.6 cP for $[\text{C}_4\text{dmim}][\text{N}(\text{Tf})_2]$),³⁵ the diffusion coefficient of PCl_3 is unusually small. The electron count achieved is similar to that reported by Kishil' et al.²⁴ in dehydrated acetonitrile on a dropping mercury electrode, further supporting the reaction mechanism given by eqs 11–13.

Interestingly, the diffusion coefficient is similar to that of the self-diffusion coefficient of the anion and cation in $[\text{C}_4\text{mim}][\text{PF}_6]$ measured by using pulse field gradient NMR.³⁶ Therein, the anion and cation values were found to be similar between 3 and $6 \times 10^{-12}\ \text{m}^2\ \text{s}^{-1}$. Furthermore, preliminary structural data on the dissolution of PCl_3 in 1,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide showed that there

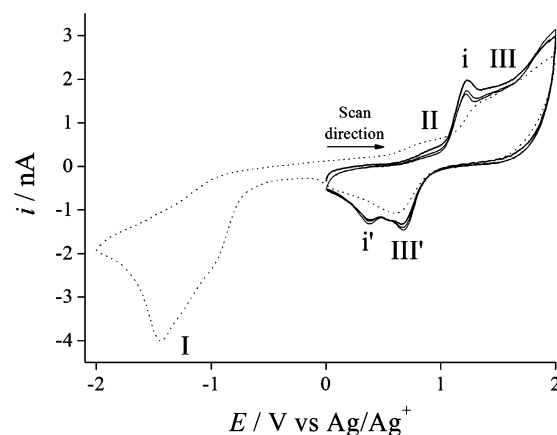


Figure 5. Cyclic voltammetry for the oxidation of 14.8 mM PCl_3 in $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$ on a gold microelectrode (diameter $25\ \mu\text{m}$) at a scan rate of $100\ \text{mV}\ \text{s}^{-1}$. Three repeat scans are shown, overlaid on the reductive cycle from Figure 4.

was little structural rearrangement of the ionic liquid in the presence of the solute.³⁷ The combination of the diffusion coefficient and the structural information indicates that the solute dissolves in the interstices of the ionic liquid and that there is a strong interaction with the ionic liquid. For the PCl_3 to move, the interstices must move, which requires a motion involving both the anion and cation hence the low diffusion coefficient. This may also contribute to the high stability of the PCl_3 in the $[\text{N}(\text{Tf})_2]^-$ based ionic liquids.

Figure 5 shows three consecutive scans for the oxidation of 14.8 mM PCl_3 on a gold microelectrode (diameter $25\ \mu\text{m}$) in $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$ at a scan rate of $100\ \text{mV}\ \text{s}^{-1}$, overlaid on that of the first reductive scan (from Figure 3a). When the cycle was scanned positively from 0.0 V an additional peak, i, was observed, with a corresponding reductive peak i'. This redox couple was not observed when first scanning reductively, probably due to the consumption of parent molecules in solution (eq 13). A potential step could not be performed on the oxidative wave i, since it overlaps with another anodic peak; fitting of chronoamperometric transients would be a combination of wave i and wave II, and data would not be reliable. Peak i can therefore be tentatively assigned to the direct one-electron oxidation of PCl_3 , which is partially reversible (peak i'). This is analogous to that observed by Berberova²⁵ in acetonitrile, and is further supported by an ESR study²⁶ in acetonitrile that reported the formation of a radical cation of PCl_3 .

Next, we considered the possible voltammetric information to be obtained by means of variable concentration studies as revealed by simulation. First, varying the concentration of PCl_3 over the range 1.5 to 150 mM was predicted to change the fraction, f , of current caused by the shoulder (vide supra) from 0.55 to 0.51, suggesting that within the likely experimental error (vide supra) no insights were likely. That said, voltammetric experiments performed with 75 mM, while being rather more un-reproducible from scan to scan than those reported above, showed no substantial deviation in the value of f from that obtained with 15 mM, consistent with the predictions of the simulation. Second, simulations were carried out for 15 mM PCl_3 in the presence of 0 to 0.1 M added chloride ions; the value of f varied from 0.55 to 0.49, again suggesting that experiments of this nature would shed little conclusive insight.

4.2. Voltammetry of POCl_3 in $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$. Partly in order to try to identify whether any of the peaks obtained from the reduction of PCl_3 were due to POCl_3 , the voltammetry of POCl_3 was next studied. Figure 6 shows the reduction of

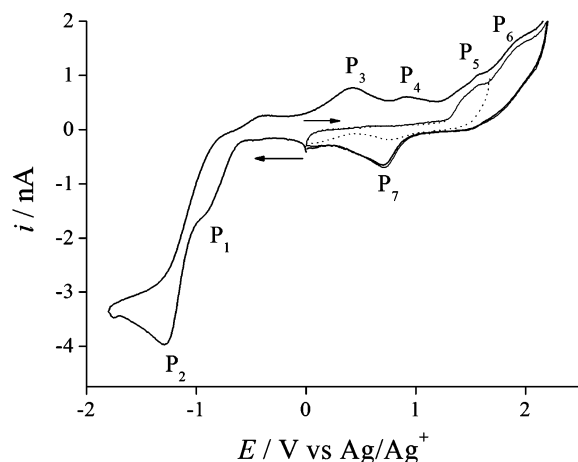
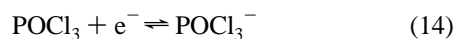


Figure 6. Cyclic voltammetry for the reduction of 15.3 mM POCl_3 in $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$ on a gold microelectrode (diameter $25\ \mu\text{m}$) at a scan rate of $100\ \text{mV s}^{-1}$. Two oxidative sweeps are shown with anodic limits of $+1.7$ and $+2.2\ \text{V}$, respectively.

15.3 mM POCl_3 on a gold microdisk electrode (diameter $25\ \mu\text{m}$) in $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$ at a scan rate of $100\ \text{mV s}^{-1}$. The reductive behavior observed was similar to that of PCl_3 (section 4.1) in that a “split wave” was seen (waves P_1 and P_2), with a combined electron count of approximately 1 (see Table 1). A potential step was performed on the reductive wave from 0.0 (corresponding to no Faradaic current) to $-1.8\ \text{V}$ (a potential past that of the reductive peak), and fitting to experimental data revealed an electron count of 1 and a diffusion coefficient of $2.2 \times 10^{-11}\ \text{m}^2\ \text{s}^{-1}$ for POCl_3 , which is more comparable in magnitude to other species in ionic liquids (cf. $1.95 \times 10^{-11}\ \text{m}^2\ \text{s}^{-1}$ for nitrobenzene in $[\text{C}_4\text{dmim}][\text{N}(\text{Tf})_2]$),⁵ indicating that diffusion of POCl_3 from the electrode surface is not as slow as that of PCl_3 .

The suggested mechanism for the reduction of POCl_3 is thought to follow eqs 14–16, as indicated by digital simulation (see section 3).



This is analogous to the reduction scheme proposed for PCl_3 (see section 4.1), with the best fit achieved when (a) the standard rate constant for the electrochemical step, k_s , was very slow ($\sim 1 \times 10^{-9}\ \text{cm s}^{-1}$ or less) assuming peak P_3 in Figure 6 relates to the reoxidation of POCl_4^- and (b) the forward rate constant, k_f , for both the homogeneous reactions (eqs 15 and 16) was made to be fast ($> 1 \times 10^7\ \text{s}^{-1}$), and also assuming a value for the transfer coefficient, α , of 0.5. As with PCl_3 , it is possible that k_s for POCl_3 is equal to, or smaller than $\sim 1 \times 10^{-9}\ \text{cm s}^{-1}$, which would shift the simulated back peak to potentials close to that of peaks P_3 and P_4 (Figure 5). A k_s value of $\sim 1 \times 10^{-9}\ \text{cm s}^{-1}$ may account for the observation that peak P_3 is larger than peak P_4 (cf. chloride oxidation, section 4.3), since the back peak from the reduction may add to the current of P_3 . The only difference in the parameters used in the simulation was that the equilibrium constant for eq 16 was smaller ($1\text{--}10\ \text{mol}^{-1}\ \text{dm}^3$) than that for PCl_3 ($50\text{--}100\ \text{mol}^{-1}\ \text{dm}^3$), suggesting that POCl_4^- is a less stable species than PCl_4^- . Additionally, the higher diffusion coefficient of POCl_3 compared to PCl_3 (see Table 1) gives a wave shape closer to steady state behavior,

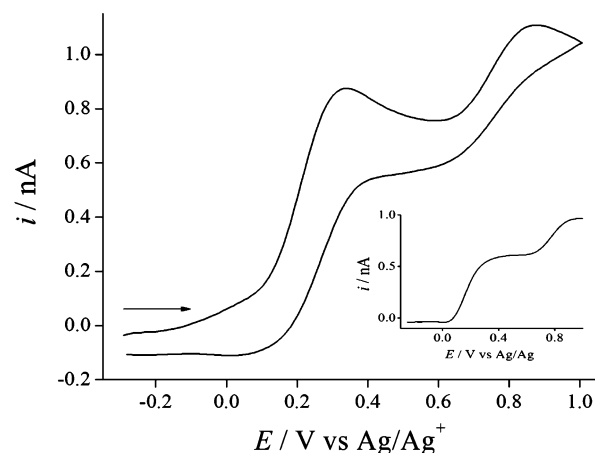
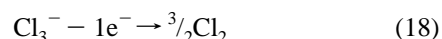
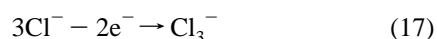


Figure 7. Cyclic voltammetry for the oxidation of 15.9 mM chloride (from $[\text{C}_4\text{mpyrr}]\text{Cl}$) in $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$ on a gold microelectrode (diameter $25\ \mu\text{m}$) at a scan rate of $100\ \text{mV s}^{-1}$. The inset shows a steady-state linear sweep voltammogram under the same conditions, at a scan rate of $5\ \text{mV s}^{-1}$.

but one which is still electrochemically irreversible at all scan rates studied ($0.01\text{--}2\ \text{V s}^{-1}$). Peaks P_3 and P_4 are attributed to the oxidation of chloride ions (see sections 4.3 and 4.4) which are formed as a result of the initial reduction of POCl_3 from eq 15. Peaks P_5 , P_6 , and P_7 are a result of the oxidation of POCl_3 . The appearance of these oxidative features was not diminished when first scanning reductively, which further supports the suggestion that the equilibrium of eq 16 is not sufficiently shifted toward products (since there will still be a large enough concentration of POCl_3 molecules present after reduction to give rise to these oxidative features), or that the diffusion from the electrode surface is much faster than that for PCl_3 .

4.3. Oxidation of Chloride ($[\text{C}_4\text{mpyrr}]\text{Cl}$) in $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$. Figure 7 shows the oxidation of 15.9 mM chloride (from $[\text{C}_4\text{mpyrr}]\text{Cl}$) on a gold microdisk electrode (diameter $25\ \mu\text{m}$) in $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$ at a scan rate of $100\ \text{mV s}^{-1}$. Two oxidative processes were resolved, as previously observed in $[\text{C}_4\text{mim}][\text{BF}_4]$ ³⁸ and $[\text{C}_4\text{mim}][\text{N}(\text{Tf})_2]$ ³⁹ at gold macroelectrodes, which have been ascribed³⁹ to



The inset of Figure 7 shows a linear-sweep steady-state voltammogram for the oxidation of 15.9 mM $[\text{C}_4\text{mpyrr}]\text{Cl}$ in $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$ on a gold microdisk electrode (diameter $25\ \mu\text{m}$) at a scan rate of $5\ \text{mV s}^{-1}$. Steady state behavior was easily achieved at this scan rate, and gave a relative peak current ratio of 2:3 between the two waves. Electron counts obtained from fitting to chronoamperometric transients gave values of two-thirds of an electron, and a further one-third of an electron for the respective processes. These values coincide with the processes presented in eqs 17 and 18. The diffusion coefficient of chloride was found to be $(1.02 \pm 0.05) \times 10^{-11}\ \text{m}^2\ \text{s}^{-1}$, comparable to that previously obtained for chloride ($1.1 \times 10^{-11}\ \text{m}^2\ \text{s}^{-1}$) in $[\text{C}_4\text{mim}][\text{BF}_4]$ ³⁸ and for bromide ($1.4 \times 10^{-11}\ \text{m}^2\ \text{s}^{-1}$) in $[\text{C}_4\text{mim}][\text{N}(\text{Tf})_2]$.³ This voltammetry will be compared to that of PCl_3 and POCl_3 in order to assign the necessary waves to the oxidation of chloride.

4.4. Comparison of Peak Positions of PCl_3 , POCl_3 , and Cl^- in $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$. It was essential that this study was carried out with a stable reference electrode, since the positions of peaks shifted significantly over the course of an experiment

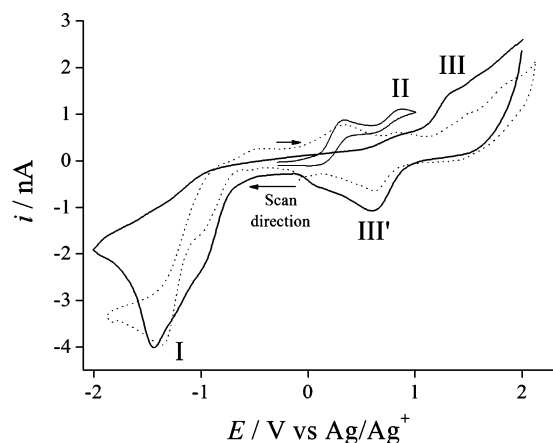


Figure 8. A comparison of cyclic voltammetry of 14.8 mM PCl_3 (solid line), 15.3 mM POCl_3 (dots), and 15.9 mM chloride (from $[\text{C}_4\text{mpyrr}]\text{Cl}$) (thin solid line) in $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$ on a gold microelectrode (diameter 25 μm) at scan rates of 100 mV s^{-1} .

when a silver-wire reference was used. To accurately compare anodic peak positions, a silver/silver⁺ reference electrode was employed, and this was shown to give stable peak positions over a number of days and in various different solutions of PCl_3 in the IL. Figure 8 shows a comparison of the voltammetry of 14.8 mM PCl_3 , 15.3 mM POCl_3 , and 15.9 mM chloride (from $[\text{C}_4\text{mpyrr}]\text{Cl}$) in $[\text{C}_4\text{mpyrr}][\text{N}(\text{Tf})_2]$ on a gold microelectrode (diameter 25 μm) at scan rates of 100 mV s^{-1} . Although the peaks above +1.0 V are not very well defined for PCl_3 , it can be seen that peak III' occurs at the same potential as peak P₇ of POCl_3 (Figure 6). From the position of the peaks, it is possible to tentatively assign waves III and III' from PCl_3 (solid line) to the oxidation of POCl_3 . This oxidation has been shown to occur in molecular solvents in the presence of Cl_2 , shown by eq 19.⁴⁰ This process is possible due to the oxidation of chloride to chlorine via eqs 17 and 18. PCl_3 has also been shown to react directly with water⁴¹ (in the absence of chlorine) to form mainly H_3PO_3 , but with a number of other byproducts including POCl_3 . It is more likely that the reaction requires the presence of chlorine as no evidence for POCl_3 was found when the PCl_3 was stirred in air in any $[\text{N}(\text{Tf})_2]^+$ -based ionic liquids, even those where hydrolysis was eventually observed.³⁰



The chloride oxidation peaks overlay well with peaks P₃ and P₄ (which are seen following the reduction of POCl_3), and hence P₃ and P₄ are identified according to eqs 16 and 17. P₃ may also have some contribution to the current from a back peak of the initial reduction (see Section 3). Surprisingly, PCl_3 does not show the characteristic chloride peaks even though it is likely that chloride ions are released after the reduction. It is possible that either a film of some sort was forming on the surface, such that the electrode no longer displays the characteristic two-step oxidation of Cl^- at Au, or the equilibrium of eq 12 is sufficiently shifted to the left so that there is very little free chloride present in the solution.

5. Conclusions

For the first time, cyclic voltammetry for the reduction and oxidation of both PCl_3 and POCl_3 has been shown. A split wave was observed for the reduction of PCl_3 , and this was shown (by chronoamperometry and digital simulation) to be due to an electrochemical step (involving a one-electron transfer) followed by a chemical step. Similar reductive behavior was observed

for POCl_3 , and an identical reaction scheme was proposed. Two oxidative features were observed for PCl_3 after initially reducing the parent: One wave was thought to be either a back peak from the reduction, or chloride oxidation on a filmed electrode surface. The second peak is most likely the oxidation of POCl_3 (formed by reaction of PCl_3 with trace water in the presence or absence of chlorine). An extra redox couple was observed when the scan was swept positively from 0 V, and this is thought to be the partially reversible one-electron oxidation to the radical cation of PCl_3 . Several oxidative features were observed on the anodic sweep after reduction of POCl_3 . Two were due to the oxidation of chloride, confirmed by matching the peak potentials with those of authentic chloride samples, and a further two peaks were due to the oxidation of parent molecules, shown by oxidative sweeps of the same solution. The most interesting finding from this study was the observation that the diffusion coefficient of PCl_3 was very small ($3 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$) in comparison to POCl_3 ($2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$) and with other species from previous studies in RTILs (4-nitrophenol, $2 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$)⁵ but is comparable with the self-diffusion coefficient of the anion and cation in $[\text{C}_4\text{mim}][\text{PF}_6]$.³⁶ This suggests that PCl_3 binds with the anion or cation of the ionic liquid, and moves with it. This may be why PCl_3 is so stable in this medium. The slowness ($\leq 1 \times 10^{-9} \text{ cm s}^{-1}$) of the standard electrochemical rate constant, k_s , was also unusual, possibly indicating a concerted cleavage of the phosphorus–chlorine bond during electron transfer. It is clear that this particular ionic liquid shows promise for use as a solvent in which to store unstable compounds which would otherwise hydrolyze in traditional media.

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