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Catalytic carbon–chlorine bond cleavage *via* electrochemical reduction of $[ReCl_6]^{2-}$ *

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Electrochemical reduction of hexachlororhenate(IV) in chlorinated solvents gave rise to a catalytic cycle producing free chloride and radical dimerisation products. Chlorine-36 tracer experiments showed this free chloride to be derived not from the solvent, as would be expected for a classical redox catalysis, but from the metal complex. A co-ordinatively unsaturated rhenium(III) intermediate capable of abstracting chlorine atoms to regenerate the starting material is proposed as the reactive species.

When $[MCl_6]^{2-}$ (where M is rhenium, osmium or iridium) is reduced electrochemically in solvents such as acetonitrile and pyridine, which can function as σ-donor ligands, a chloride ligand is replaced by a solvent molecule, L, to give $[MCl_5L]^{2-}$, thus stabilising the lower oxidation state of the metal through the replacement of a π-donating ligand.[1,2] In less co-ordinating solvent systems, such as 0.4 mol dm^{-3} $[NBu^n_4][BF_4]$–dichloromethane, cyclic voltammetry of $[IrCl_6]^{2-}$ and $[OsCl_6]^{2-}$ at a platinum microelectrode reveals reversible one electron reductions to $[OsCl_6]^{3-}$ and $[IrCl_6]^{3-}$, which are stable at 223 and 243 K respectively when generated by bulk electrolysis. The situation for the reduction of $[ReCl_6]^{2-}$ in dichloromethane however, is quite different, as will be shown below.

Results and Discussion

Fig. 1 shows cyclic voltammograms of $[NBu^n_4]_2[ReCl_6]$ (hereafter referred to as **1**) in 0.4 mol dm^{-3} $[NBu^n_4][BF_4]$–dichloromethane at 253 (trace A) and 293 K (trace B), the current being scaled such that the height of the oxidative wave, corresponding to the $[ReCl_6]^{2-/-}$ couple, is the same in both scans. The $E_{\frac{1}{2}}$ values for the reductive and oxidative processes are −1.27 and +1.19 V respectively. It is immediately evident that at room temperature the height of the reductive wave has increased out of all proportion to that of the oxidation. Closer inspection shows that the wave has become sigmoidal, with no peaks on either forward or reverse scans. From this it can be concluded that the rate of transport of the analyte has been greatly increased by a mechanism that is inoperative at low temperature.

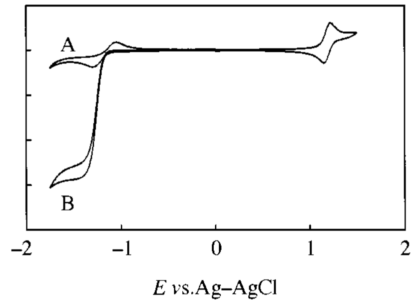

Fig. 1 Cyclic voltammograms recorded for a 2 mmol dm^{-3} solution of complex **1** in 0.4 mol dm^{-3} $[NBu^n_4][BF_4]$–dichloromethane at 253 (trace A) and 293 K (trace B). The current scales are arbitrarily chosen such that the height of the oxidative wave is the same for both scans

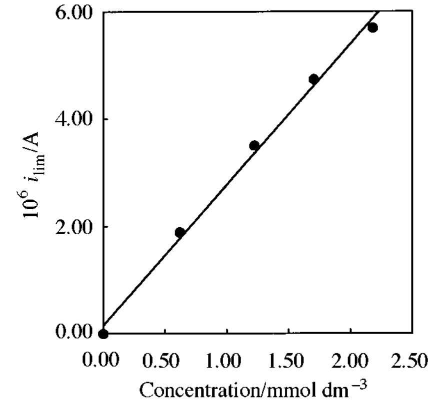

Fig. 2 Variation of limiting current with concentration of complex **1**

The height of the reductive wave is proportional to the concentration of the rhenate salt as shown in Fig. 2. Fig. 3 shows cyclic voltammograms recorded before (trace A) and after (trace B) bulk electrolysis of the solution at −1.6 V. The reductive wave due to **1** and the UV/VIS absorption spectrum of the solution are unaffected by the passage of 10 molar equivalents of charge, whilst the oxidative wave has been obscured by a new wave, with a forward peak potential of 1.2 V. This peak is due to free chloride, as evidenced by comparison with a voltammogram recorded under identical conditions for $[NBu^n_4]Cl$. The latter voltammogram was also used to calibrate the chloride response in the electrogeneration experiment, and thus obtain the concentration of free chloride in solution. Fig. 4 shows the relationship between the concentration of chloride present and the total charge passed, both quantities being expressed as molar equivalents, based on a one-electron reduction of the quantity of **1** present. The slope of 1.2 found almost certainly corresponds to a real value of 1, the error resulting from the practical difficulties involved in obtaining genuinely anhydrous $[NBu^n_4]Cl$.

At first sight it might appear that a classical redox catalysis is taking place, the reduced hexachlororhenate(III) species being oxidised by the chlorinated solvent to give chloride, an organic radical and the original rhenium(IV) starting material, which would again be reduced at the electrode to reinitiate the cycle. Such mechanisms have been widely reported.[3] To show that the overall products were consistent with such a mechanism, a second electrolysis similar to that described above was carried out, samples of the solution in the working electrode compartment being withdrawn at regular intervals for gas chromatographic analysis. The relationship between the concentration of 1,2-dichloroethane, the expected radical dimerisation product, found and the total charge passed is also shown in Fig. 4. The

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* *Non-SI units employed*: Bq = s^{-1}, eV ≈ 1.60 × 10^{-19} J.

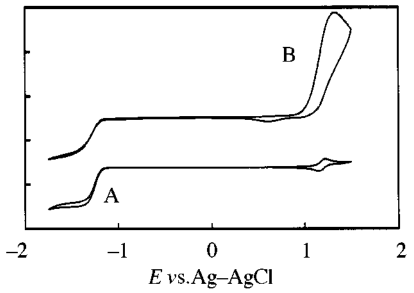


Fig. 3 Cyclic voltammograms recorded in 0.4 mol dm^{-3} [NBu$^n_4$][BF$_4$]–dichloromethane at 293 K before (trace A) and after (trace B) the passage of 10 molar equivalents of charge at −1.6 V in the presence of a 2 mmol dm^{-3} solution of complex **1**. Each division on the vertical axis represents 5 μA

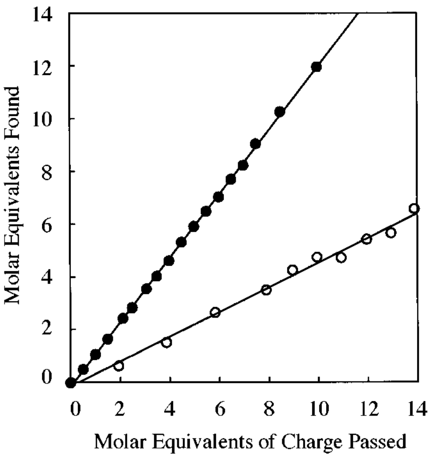


Fig. 4 Variation of the quantities of chloride (closed circles) and 1,2-dichloromethane (open circles) found with charge passed in the bulk electrolysis of complex **1** in 0.4 mol dm^{-3} [NBu$^n_4$][BF$_4$]–dichloromethane at −1.6 V

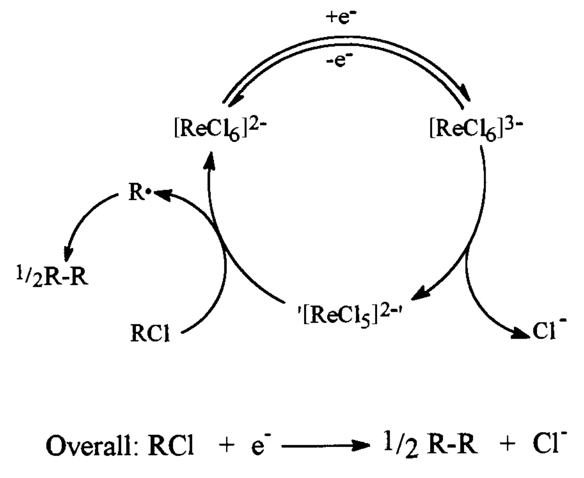
slope of the corresponding linear regression was found to be 0.47, indicating a 94% yield of the organic product in this case.

Whilst the products of the reaction are then consistent with a classical redox catalytic cycle, the position of the reduction couple of complex **1** relative to that of dichloromethane means that this process, though possible, should be glacially slow.[3] One would be obliged to reject this classical mechanism completely in this case if it were to be shown that the chloride produced in the bulk reduction originated from **1** and not from the solvent.

The bulk electrolysis described above was repeated, using a 10 mg sample of ^{36}Cl radiolabelled **1**, to produce 5 molar equivalents of free chloride. This chloride was then oxidised electrochemically to dichlorine and driven into a 77 K trap, containing a Teflon sheathed stirrer bar and a small quantity of zinc dust, using a stream of dinitrogen. The trap was allowed to warm to room temperature and the contents stirred for 10 min whereupon the mixture of zinc and zinc chloride was separated from the dichloromethane by filtration. This solid material was then stirred with 2 ml of deionised water and the supernatant solution of zinc chloride removed by filtration; 0.5 ml of this solution (sample 1) and 0.5 ml of the condensed dichloromethane (sample 2) were tested for activity. In addition, a control experiment was carried out to ensure that there was no possibility of chloride exchange between **1** and either dichloromethane or free chloride. A 10 mg sample of ^{36}Cl radiolabelled **1** was stirred for 1 h in 8 ml of 0.4 mol dm^{-3} [NBu$^n_4$][BF$_4$]–dichloromethane solution containing 4 molar equivalents of [NBu$^n_4$]Cl in the sample compartment of the bulk electrolysis cell. The chloride was then separated by electrochemical oxidation as described above and a 0.5 ml sample of the resulting zinc chloride solution (sample 3) and 0.5 ml of the condensed dichloromethane (sample 4) were tested for activity. A blank (sample 5) was run on 0.5 ml of deionised water that had been stirred with zinc dust. Table 1 shows the activity for each of these five samples.

Table 1 Total activity of samples derived from ^{36}Cl tracer experiments (see text for identity of samples)

Sample	Activity/Bq
1	19.32
2	4.03
3	0.78
4	0.47
5	0.29



Scheme 1 Catalytic cycle proposed for the reduction of complex **1** in chlorinated solvents

The high activity for sample 1 demonstrates unambiguously that the chloride produced in the bulk electroreduction is derived from the radiolabelled rhenium complex. In addition, the low counts for samples 3 and 4 show that there is no significant chloride exchange between **1** and either dichloromethane or [NBu$^n_4$]Cl on the timescale of the experiment, hence the chloride produced in the reduction of **1** cannot be derived from the solvent.

We propose the mechanism shown in Scheme 1, consistent with the above observations, to account for the observed electrochemical behaviour. This mechanism avoids the need for an intermolecular electron transfer, proceeding rather by abstraction of a chlorine atom from the substrate by a highly reactive co-ordinatively unsaturated rhenium(III) intermediate. The mild activity of sample 2 can be explained by a side reaction whereby the radical CH$_2$Cl$^\bullet$ extracts a chlorine atom from complex **1** rather than combining with another radical species.

A reaction proceeding by this mechanism can be treated by classical methods provided that chloride loss from [ReCl$_6$]$^{3-}$ is fast compared with the subsequent reaction of [ReCl$_5$]$^{2-}$ with the solvent. Addition of up to 30 equivalents of chloride failed to change the response of the system, showing that chloride loss is not the rate limiting step. In order to extract kinetic parameters from the system, we carried out digital simulations of voltammograms of complex **1** recorded in 0.4 mol dm^{-3} [NBu$^n_4$][BF$_4$]–dichloromethane at a variety of scan rates, assuming the mechanism shown in equations (1)–(3). The

$$[\mathrm{ReCl_6}]^{2-} + \mathrm{e}^- \underset{}{\overset{k_0}{\rightleftharpoons}} [\mathrm{ReCl_6}]^{3-} \qquad (1)$$

$$[\mathrm{ReCl_6}]^{3-} \xrightarrow{\text{fast}} [\mathrm{ReCl_5}]^{2-} + \mathrm{Cl}^- \qquad (2)$$

$$[\mathrm{ReCl_5}]^{2-} + \mathrm{CH_2Cl_2} \xrightarrow{k_1} [\mathrm{ReCl_6}]^{2-} + \mathrm{CH_2Cl}^\bullet \qquad (3)$$

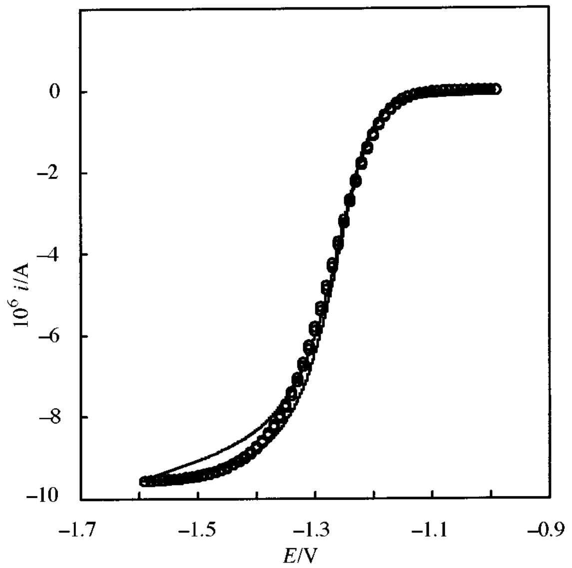


Fig. 5 Real (line) and simulated (open circles) voltammograms for 3.9 mmol dm^{-3} complex **1** in 0.4 mol dm^{-3} $[NBu^n_4][BF_4]$–dichloromethane recorded at a scan rate of 0.1 V s^{-1}

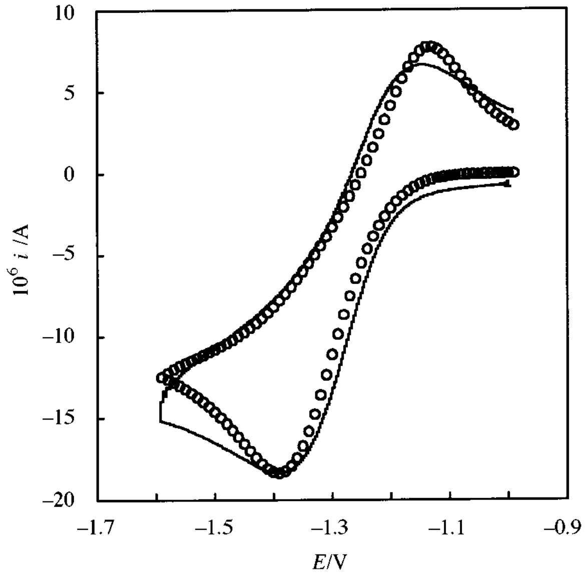


Fig. 6 Real (line) and simulated (open circles) voltammograms for 3.9 mmol dm^{-3} complex **1** in 0.4 mol dm^{-3} $[NBu^n_4][BF_4]$–dichloromethane recorded at a scan rate of 25.6 V s^{-1}

Table 2 Cathodic current maxima for the reduction of complex **1** from experiment and simulation

	i_{max}/μA	
Scan rate/V s^{-1}	Experimental	Simulated
0.1	9.51	9.56
0.2	9.70	9.57
0.4	9.80	9.57
0.8	9.99	9.58
1.6	10.23	9.59
3.2	10.57	9.73
6.4	11.40	11.11
12.8	14.23	13.91
25.6	18.41	18.39

Table 3 Catalytic rate constants ($dm^3\ mol^{-1}\ s^{-1}$) for the regeneration of $[ReCl_6]^{2-}$

Solvent	Catalytic rate constant ($dm^3\ mol^{-1}\ s^{-1}$) at 298.2 K
Dichloromethane	3.0
1,2-Dichloroethane	2.5
1,2-Dichlorobenzene	0.3

diffusion coefficient for **1** was measured to be $5.5 \times 10^{-6}\ cm^2\ s^{-1}$ by cyclic voltammetry[4] of the oxidative $[ReCl_6]^{2-/-}$ couple and the concentration of dichloromethane was assumed to be 12 mol dm^{-3}. Simulation of voltammograms recorded at scan rates high enough for the following reaction to have no effect on the wave shape allowed k_0, the rate constant for heterogenous electron transfer, to be refined at 0.009 cm s^{-1}, with $\alpha = 0.45$ (where α is the transfer coefficient). Using these values we were able to simulate voltammograms over a range of scan rates, the two extremes of which are shown in Figs. 5 and 6. A value of 3 $dm^3\ mol^{-1}\ s^{-1}$ for k_1, the rate constant for chlorine atom abstraction, was found to give the best agreement between experiment and simulation. Table 2 shows values for the cathodic current maxima (peak or plateau) for both experimental and simulated values as a function of scan rate. Using a similar procedure kinetic parameters were obtained for this system in 1,2-dichloroethane and 1,2-dichlorobenzene, these solvents having yielded results qualitatively identical to those detailed above for dichloromethane. The data, presented in Table 3, are easily rationalised if the rate limiting step in the reaction is the abstraction of a chlorine atom from a solvent molecule. The C–Cl bond is known to be about 70 kJ mol^{-1} stronger for aromatic systems than for aliphatic ones[5] which would slow the reaction, consistent with our findings, although a greater difference between these two solvent types might have been expected.

Conclusion

The results presented show that the electrogenerated species has a quite remarkable reactivity, able to abstract chlorine from both aromatic and aliphatic media after having ejected a chloride ion. This, or a similar cycle, might prove useful in the degradation of polychlorinated biphenyls and highly chlorinated pesticides such as the hexachlorobenzenes, which is a pressing environmental problem. Alternatively, the system could be imagined as a convenient and quantitative means of generating radicals from organic chlorides which could either serve in dimerisation reactions, in a way analogous to the Kolbe reaction,[6] or act as initiators for polymerisation.

Experimental

Electrochemical experiments were performed using a DELL 466 DL personal computer running GPES 4.2 software (Eco Chemie) to drive an Autolab PGSTAT20 potentiostat, the ohmic drop compensation facility of which was used in all voltammetric experiments, the potential scan rate for all voltammograms reported being 100 mV s^{-1} unless otherwise stated. All potentials are quoted relative to an Ag–AgCl–0.05 mol dm^{-3} $[NBu^n_4]Cl$, 0.45 mol dm^{-3} $[NBu^n_4][BF_4]$–dichloromethane reference electrode that gave a ferrocenium–ferrocene couple at +0.43 V. The working electrode for voltammetric studies was a platinum microdisc of diameter 0.5 mm, whilst that for bulk electrolysis experiments took the form of a large platinum basket. A platinum wire or gauze counter electrode was used as appropriate. Bulk electrolyses were carried out in a classical 'H' cell fitted with two glass frits. Solutions were routinely purged with a stream of solvent saturated argon (BOC Gases) except when a 77 K trap was used to condense the exit vapours. In this case a stream of dry, oxygen free dinitrogen (BOC Gases) was used. The cell was thermostatted at 293.2 ± 0.2 K unless otherwise indicated. Simulations of voltammetric experiments were carried out using a DCS personal computer equipped with a Pentium-S CPU running ANTIGONA 32 software written by Dr. Loïc Mottier of the Università di Padova, available from the World Wide Web at http://www.chemistry.unipd.it.

Gas chromatograms were recorded at 313 K using a Shimadzu GC-17A instrument equipped with a Supelco SPB-1 capillary column. The activity of radioactive samples was determined using a Packard Tri-Carb 2100TR Liquid Scintillation Analyser. Samples were mixed with 4 ml of Ultima Gold scintillant cocktail (Packard) and the activity between 5 and 720 keV determined over 10 min for each sample.

Dichloromethane (HPLC grade, Prolabo) was stored over potassium hydroxide pellets for a week before being refluxed over and distilled from phosphorus pentaoxide. 1,2-Dichloroethane (HPLC grade, BDH), 1,2-dichlorobenzene (HPLC grade, Aldrich) and zinc dust (Fisons) were used as supplied. The salt $[NBu^n_4][BF_4]$, prepared by the neutralisation of tetrabutylammonium hydroxide with tetrafluoroboric acid (both Fluka), was recrystallised twice from water–methanol (1:1) and dried at 343 K *in vacuo* for 48 h prior to use; $[NBu^n_4]Cl$ (Aldrich) was dried in an identical manner and handled under an atmosphere of dry argon. The salt K_2ReCl_6 (Johnson Matthey) was metathesised to $[NBu^n_4]_2[ReCl_6]$ by addition of a saturated solution of $[NBu^n_4]Cl$ to a solution of the metal salt in 6 mol dm^{-3} hydrochloric acid, the pale green precipitate being collected and dried *in vacuo*. This solid was recrystallised by the judicious addition of trichloromethane (Prolabo) to a concentrated solution of the salt in dichloromethane to yield mint green crystals which were again dried *in vacuo*. Chlorine-36 labelled $[NBu^n_4]_2[ReCl_6]$ was synthesized using a modification of the procedure of Watt and Thompson.[7] Potassium perrhenate (Johnson Matthey, 50 mg), aqueous $H^{36}Cl$ (22 µl, 0.96 MBq; ICN Pharmaceuticals, Inc.), 50% hypophosphorous acid, H_3PO_2, (125 µl, Aldrich) and 18 mol dm^{-3} aqueous HCl (2.5 ml, Prolabo) were combined in a round-bottomed flask and heated to 95 °C for 2 h, whereupon a solution of $[NBu^n_4]Cl$ (0.4 g) in aqueous 6 mol dm^{-3} HCl (3 ml, Polabo) was added to the hot solution, which was allowed to cool and the pale green precipitate collected. This was then treated as above to yield crystals (85 mg, 53% yield) of the radiolabelled product, whose purity was checked electrochemically.

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