On the Charge Distribution in Complexes: An Electrochemical Study

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The electrochemical behaviour of rhenium dinitrogen complexes and analogues is described in detail, and results are discussed in terms of criteria for a correlation between redox potential and *X*-ray photoelectron spectroscopic measurements.

RECENTLY details of the preparation and properties of a variety of rhenium complexes have been published. Of particular interest here are dinitrogen,[1] carbonyl,[2] nitrosyl,[3] nitrido-,[4] and imido-complexes[5] since little quantitative information is available on how these ligands influence the redox behaviour of the complexes and also because a correlation between *X*-ray photoelectron (*X*-p.e.) spectroscopy measurements and redox potentials has been attempted in the previous paper.[6] This correlation requires that the electrochemical behaviour of the complexes meet certain conditions. This report describes the electrochemical behaviour of the rhenium complexes mentioned above and proves that the requirements for the correlation are satisfied. In particular, the validity of the reversible redox potentials quoted earlier[6] is established. The relative contributions of the metal atomic orbitals and ligand molecular orbitals to the redox orbital are determined which leads to an understanding of the electronic distribution within the complexes.

RESULTS

The electrochemical measurements are summarised in Table 3 of the previous paper (p. 2395) and the Table. The

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[1] J. Chatt, J. R. Dilworth, and G. J. Leigh, *J.C.S. Dalton*, 1973, 612.

[2] J. Chatt, J. R. Dilworth, H. P. Gunz, and G. J. Leigh, *J. Organometallic Chem.*, 1974, **64**, 245.

[3] R. W. Adams, J. Chatt, N. E. Hooper, and G. J. Leigh, *J.C.S. Dalton*, 1974, 1075.

[4] J. Chatt, C. D. Falk, G. J. Leigh, and R. J. Paske, *J. Chem. Soc.* (*A*), 1969, 2288.

[5] J. Chatt, J. R. Dilworth, and G. J. Leigh, *J. Chem. Soc.* (*A*), 1970, 2239.

[6] J. Chatt, C. M. Elson, N. E. Hooper, and G. J. Leigh, preceding paper.

parameter, E', is defined as the formal redox potential (relative to the saturated calomel electrode, s.c.e.) of a reversible redox couple in the electrolyte described below. It was equated to the half-wave potentials determined by polarography [7] or cyclic voltammetry [8] ($E_{\frac{1}{2}} = E_p \pm \frac{29}{n}$ mV). For two of the complexes, $[Re(N_2)(PMe_2Ph)_3(S_2CNEt_2)]$, (XVI), and $[ReCl_2(NO)(PMePh_2)_2]$, (XXV), E' values were determined both by cyclic voltammetry on a vitreous carbon electrode and by polarography at a dropping mercury electrode and found to be in good agreement. To minimise differences in solvation energies between the complexes, the same solvent was used throughout and the standard complexes were selected to be as structurally near to the dinitrogen, carbonyl, and nitrosyl, *etc.* complexes as possible. In some cases one member of the couple was chemically labile and underwent a substitution reaction subsequent to the charge-transfer step. The rate of the substitution reaction was determined using the method of Schwarz and Shain [9] making the usual assumption that the reaction is first (or pseudo-first) order. From the measured rate constant, the half-life of the reaction ($t_{\frac{1}{2}}$) (Table) was calculated. For the experimental conditions used in this study, succeeding chemical reactions having $t_{\frac{1}{2}}$ greater than a few seconds caused only a small shift in E' from the true reversible value. Also listed in the Tables are six electrode reactions that were totally irreversible and E' values were estimated from either cyclic voltammograms at slow scan rates (30 mV s^{-1}) or polarographic half-wave potentials.

Half-lives of some redox products

	E' [a]/V		$t_{\frac{1}{2}}$ [b]/s	
			Product of	
	Reduction	oxidation	reduction	oxidation
$[ReCl(N_2)(py)(PMePh_2)_3]$ (XIII)		+0.015		50
$[ReCl(N_2)(CO)(PMe_2Ph)_3]$ (XIV)		+0.567		4
$[ReCl(CO)(PMe_2Ph)_4]$ (XXI)		+0.410		18
$[ReCl_2(NO)(PMePh_2)_2]$ (XXV)	−0.500 (−0.51)	+0.865 [c]	1	
$[ReCl_2(NO)(PMePh_2)_3]$ (XXVI)		+0.932		17
$[ReCl_4(NO)(PMePh_2)_2]$ (XXX)	−0.173		2	

[a] Relative to the s.c.e.; the value in parentheses was measured at a dropping mercury electrode. [b] Species not cited in this Table, but indicated in the preceding paper, are indefinitely stable. [c] The electron-transfer process was irreversible.

Complexes $[ReCl_2(PMe_2Ph)_4]$, (I), $[ReCl_3(PMe_2Ph)_3]$, (II), and $[ReCl_4(PMe_2Ph)_2]$, (III), were studied as reference compounds having rhenium formal oxidation states II, III, and IV, respectively. In two cases, the electrode processes are diffusion controlled, reversible, and involve a single electron. For example, the cyclic voltammogram for reduction of (III) displayed a separation between the cathodic and anodic peaks of 87 mV and a separation between the cathodic peak and half-peak potential of 67 mV. The two theoretical values are $(60/n)$ mV [8] where n is the number of electrons transferred in the electrode process. Differences from the theoretical value of 60 mV could arise from electrode contamination or perhaps from imperfect wetting of the electrode surface. The ratio of the corrected cathodic peak current to the square root of the scan rate $i_{pc}/v^{\frac{1}{2}}$ (in μA V$^{-\frac{1}{2}}$ s$^{\frac{1}{2}}$), was constant for a six-fold change in scan rate and equal to 110 ± 0.5 μA V$^{-\frac{1}{2}}$ s$^{\frac{1}{2}}$. A potential-step chronoamperogram of the same solution demonstrates that the product of the corrected cathodic current and the square root of the time, $it^{\frac{1}{2}}$, (in μA s$^{\frac{1}{2}}$), was constant for the time studied (4 s) and had a value of 25.1 ± 0.2 μA s$^{\frac{1}{2}}$. The constancy of these two quantities indicates that the electrode process is diffusion controlled.[8] Also the Malachesky R factor,[10] $R = i_p/v^{\frac{1}{2}}it^{\frac{1}{2}}$, had a value of 4.38 which is within 11% of the theoretical value of 4.92 for a diffusion-controlled one-electron charge-transfer process. An exception to this behaviour was the irreversible reduction of (II). A cyclic voltammogram of (II) between −0.6 and −1.2 V showed a poorly defined reduction wave (E_{p_c} −1.0 V) with very little decrease in current past the broad peak and no anodic counterpart. The peak current was *ca.* 50% larger than that observed at the same scan rate for reversible one-electron oxidation of the complex at +0.74 V. Also, the polarographic diffusion current for the reduction was *ca.* 2.5 times that predicted from the ratio of the diffusion current to the concentration of the other complexes studied. It seems that reduction of (II) involves a catalytic process whereby the reduced complex is oxidised by the electrolyte to regenerate (II) at the electrode surface and reduce the electrolyte.

Similar interference from the solvent was observed during reduction of $[ReCl_2(N)(PMe_2Ph)_3]$, (V). The reduction of the homologues *cis-* and *trans*-$[ReCl_3(NMe)(PR_2Ph)_2]$, (VI) and (VII) (R = Me or Et), occurred at potentials on the side of the supporting electrolyte discharge wave (−1.5 V) which precluded any measurements being made. Furthermore, the oxidation of (VI) and (VII) took place near the anodic potential limit (+1.2 V). The processes were totally irreversible (no cathodic wave on reverse scan) and were not diffusion controlled. By comparison the oxidation of $[ReCl_2(N)(PEtPh_2)_2]$, (IV), meets all the criteria for a reversible one-electron diffusion-controlled process.

Reduction of all complexes in the series (IX)—(XXII), except one, demonstrated behaviour characteristic of a simple diffusion-controlled reversible one-electron oxidation process. The exception is $[ReCl(N_2)(CO)_2(PPh_3)_2]$, (XV), where the irreversibility can be attributed to a very rapid decomposition step following the charge-transfer process. The behaviour of members of this series is typified by that of $[ReCl(N_2)(py)(PMePh_2)_3]$, (XIII): the separation between the anodic and cathodic peak potentials was 94 mV and the difference between peak and half-peak potentials was 71 mV. The value of the Malachesky R factor, 4.81, is in excellent agreement with the ideal value of 4.92. The reversibility of several couples has been confirmed by preparation of the oxidised forms (see Table and refs. 1 and 2). In the case of complex $[(PhMe_2P)_4ClRe(N_2)MoCl_4(OMe)]$, (XX), $[ReCl(N_2)(PMe_2Ph)_4]$ was also present, possibly due to slow dissociation of the adduct in the electrolyte. None of the dinitrogen or carbonyl complexes was reducible over the potential range −0.1 to −1.5 V in the CH_2Cl_2–MeOH solvent. Complex (XV) was also polarographed in *NN*-dimethylformamide (dmf) (0.1M-tetra-n-butylammonium iodide) and found to be electroinactive between 0 and −2.0 V.

The final series of complexes examined was the rhenium

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[7] L. Meites, 'Polarographic Techniques,' 2nd edn., Interscience, New York, 1965, p. 214.

[8] R. S. Nicholson and I. Shain, *Analyt. Chem.*, 1964, **36**, 706.

[9] W. M. Schwarz and I. Shain, *J. Phys. Chem.*, 1965, **69**, 30.

[10] P. A. Malachesky, *Analyt. Chem.*, 1969, **41**, 1493.

nitrosyls (XXV)—(XXX). The reversible reduction of the five-co-ordinate complex (XXV) involves one electron and was followed by a chemical reaction ($t_{\frac{1}{2}}$ 1 s) which converts the primary electrode product into a second oxidisable species [anodic peak potential (E_{pa}) -0.10 V, see equations (1)—(3)]. However, when the total sample of (XXV) was electrolysed at -0.60 V the reduced form exhibited an oxidation wave at $+0.29$ V indicating that the reduced species (E_{pa} -0.10 V) undergoes a slow secondary rearrangement. Attempts to isolate and characterise the reduced form (E_{pa} $+0.29$ V) were unsuccessful; however, oxidation of this species did not regenerate the starting material. Complex (XXV) could also be oxidised but the electrode process was totally irreversible and not diffusion controlled, presumably due to solvent participation, and the number of electrons involved in the oxidation process could not be determined. However, controlled-potential electrolysis of (XXV) at $+0.90$ V in the presence or absence of tetraethylammonium chloride produced $[ReCl_4(NO)(PMePh_2)_2]$, (XXX).[3] By comparison, oxidation of the six-co-ordinate nitrosyl $[ReCl_2(NO)(PMePh_2)_3]$, (XXVI), was well behaved (R 4.75) and was followed by a decomposition step ($t_{\frac{1}{2}} \approx 17$ s) involving the oxidised species. The complex $[ReCl_3(NO)(PMePh_2)_2]$, (XXVIII), could be reversibly reduced to form the simple anion $[ReCl_3(NO)(PMePh_2)_2]^-$.[3] Complex (XXX) also accepts one electron in a diffusion-controlled reversible electrode reaction. The product was chemically reactive and converted into an oxidisable form with an anodic peak potential of $+0.15$ V. Attempts to characterise this species have been unsuccessful; however, cyclic voltammetry demonstrated that oxidation of the species with E_{pa} $+0.15$ V is followed by a chemical step to regenerate (XXX). The chemical reactions following reduction of (XXX) and oxidation of the stable reduced form were assumed to involve the phosphine ligands since loss of NO or Cl^- would yield a previously characterised species.

$$[ReCl_2(NO)(PMePh_2)_2] + 1e^- \rightleftharpoons [ReCl_2(NO)(PMePh_2)_2]^- \tag{1}$$

$$[ReCl_2(NO)(PMePh_2)_2]^- \xrightarrow{t_{\frac{1}{2}} = 1\mathrm{s}} \mathrm{Red}'(E_{pa}\ -0.10\ \mathrm{V}) \tag{2}$$

$$\mathrm{Red}' \xrightarrow[\mathrm{slow}]{} \mathrm{Red}''\ (E_{pa}\ +0.29\ \mathrm{V}) \tag{3}$$

DISCUSSION

Rhenium carbonyls can be oxidised to rhenium(II) complexes by chemical agents and by electrochemical methods. The same is true of rhenium dinitrogen complexes. However, these Re^{II} complexes are somewhat unstable and in the case of the carbonyls are easily reduced.[1] To determine the role of the solvent in the chemical reactions which follow the oxidation step (Table), the voltammetric behaviour of $[ReCl(CO)(PMe_2Ph)_4]$, (XXI), was also studied in a dichloromethane (0.1M-tetraethylammonium tetrafluoroborate) electrolyte. The coupled chemical reaction has a rate constant of $(7 \pm 3) \times 10^{-2}$ s^{-1} which is within experimental error of that determined in dichloromethane–methanol [$(4 \pm 3) \times 10^{-2}$ s^{-1}] indicating that reduction of $[ReCl(CO)(PMe_2Ph)_4]^+$ by methanol is not the source of the chemical steps. Therefore chemical reactions following the charge-transfer steps in this series of complexes were assigned to first-order decomposition of the Re^{II} anions *via* loss of N_2 or CO, which justifies the application of Schwarz and Shain's method for the determination of the rate constants.

The role of the electrolyte is very pronounced in the redox reactions of complex (XXV). In dmf (0.1M-$[Et_4N][BF_4]$), reduction of (XXV) appears reversible (separation between anodic and cathodic peak potentials = 70 mV) and is followed by a chemical step having a half-life of 20 s (*cf.* $t_{\frac{1}{2}} \approx 1$ s in CH_2Cl_2–MeOH). The reduced form, which is oxidisable at -0.1 V in the CH_2Cl_2–MeOH electrolyte [see equations (1)—(3)], was not observed in dmf. However, the product of controlled-potential reduction in dmf exhibits an oxidation wave at a potential (E_{pa} $+0.36$ V) within 70 mV of the corresponding oxidation process in CH_2Cl_2–MeOH. The oxidation of (XXV) also involves the solvent: in the absence of added Cl^- the product of controlled-potential oxidation of (XXV) is (XXX) where the additional chlorides have presumably been abstracted from the dichloromethane.

Molecular-orbital schemes[11-13] for complexes $[ML_6]$ or $[ML_5X]$ (L = a unidentate ligand and X is different from L) show that the potential redox orbitals (h.o.m.o. or l.e.m.o.) * are degenerate. The redox orbitals of our six-co-ordinate complexes, as shown below, are basically metal non-bonding orbitals. However, since the complexes studied have a lower symmetry than that of $[ML_5X]$, the degeneracy of the non-bonding orbitals will be removed, but their positions relative to the bonding orbitals should remain unchanged. For the dinitrogen complexes there is only a poor correlation between E' and the dinitrogen stretching frequencies[1,14-16] (Figure). Only if the dinitrogen orbitals make a significant contribution to the redox orbital is a good correlation expected (as observed by Masĕk).[17]

Some correlation is expected since the bonding between the ligands and rhenium affects (*i*) the effective nuclear charge felt by the redox electrons (which is reflected in E') and (*ii*) the dinitrogen stretching frequency. A line could be drawn in the Figure from point (XV) to the cluster of values near 0.0 V and 1 900 cm^{-1}, which follows the expected pattern. The points of divergence are (XX), the adduct species, which will have a redox orbital of different composition from the others, and (XVI) where the ligand *trans* to N_2 has changed from halide to one containing sulphur. The dithiocarbamate

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* h.o.m.o. = Highest energy occupied molecular orbital and l.e.m.o. = lowest energy vacant molecular orbital.

[11] F. A. Cotton, 'Chemical Applications of Group Theory,' Interscience, New York, 1974, p. 225.

[12] Yu. G. Borod'ko and A. E. Shilov, *Russ. Chem. Rev.*, 1969, **38**, 355.

[13] P. T. Manoharan and H. B. Gray, *J. Amer. Chem. Soc.*, 1965, **87**, 3340.

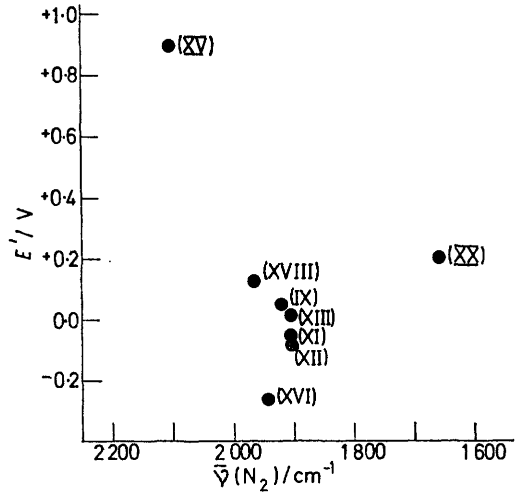
[14] J. Chatt, G. A. Heath, N. E. Hooper, and G. J. Leigh, *J. Organometallic Chem.*, 1973, **57**, C67; J. Chatt, A. A. Diamantis, G. A. Heath, N. E. Hooper, and G. J. Leigh, unpublished work.

[15] M. Mercer, R. H. Crabtree, and R. L. Richards, *J.C.S. Chem. Comm.*, 1973, 808.

[16] J. Chatt, R. H. Crabtree, J. R. Dilworth, and R. L. Richards *J.C.S. Dalton*, 1974, 2358.

[17] J. Masĕk, *Inorg. Chim. Acta Rev.*, 1969, **3**, 99.

ligand which is strongly basic[6] and also capable of π bonding will exert a stronger *trans* influence on the dinitrogen group than halide. The nett result is to decrease the effective nuclear charge felt by the redox electrons (which lowers E') and also to weaken the σ and π bonds between rhenium and N_2 (which raises the stretching frequency). This is contrary to the linear correlation and shows that the redox potential can vary independently of the dinitrogen stretching frequency.



Plot of redox potential, E', against dinitrogen stretching frequency, $\nu(N_2)$, for rhenium complexes

The redox potentials do not vary significantly with phosphine. This is true of reversible {*cf.* $[ReCl(N_2)(py)(PMe_2Ph)_3]$, (XII), and (XIII)} and irreversible systems [compare (VI) and (VII)] even though there are significant differences in the relative base strengths of the phosphines as reflected in their half-neutralisation potentials.[18,19] In the latter case, the independence of phosphine may be due to the irreversible nature of the electrode reaction, or to the involvement of the supporting electrolyte in the charge-transfer process, or to the presence of configurations such that the more basic dimethylphenylphosphines *trans* to each other partially neutralise their electron-donating abilities. However, the general insensitivity to phosphine appears to be a real effect, and is paralleled by the insensitivity of sub-valence-shell binding energies to phosphine structure.

The participation of the nitrosyl molecular orbitals in the redox orbital of the six-co-ordinate nitrogen oxide complexes can be determined from the ratio of the difference in redox potentials ($\Delta E'$) to the difference in nitrosyl stretching frequencies [$\Delta\nu(NO)$].[17] For the isoelectronic complexes $[ReCl_2(NO)(PMePh_2)_3]$, (XXVI), and $Cs[ReCl_3(NO)(PMePh_2)_2]$, $\Delta E'/\Delta\nu(NO) = 4\,920$ mV per 100 cm^{-1}.[3] This value is more than ten times that calculated from redox potentials and stretching frequencies of free NO^+ and NO [E' for NO^+–NO and NO–NO^- = 1 180 and *ca.* 560 mV, $\nu(NO)$ for NO^+ and NO = 2 275 and 1 876 cm^{-1}, respectively; hence $\Delta E'/\Delta\nu(NO) \sim 425$ mV per 100 cm^{-1}][17] where the electronic charges must, of course, be completely localised on the NO. The interpretation of large $\Delta E'/\Delta\nu(NO)$ values is that the nitrosyl group makes only a small contribution to the redox orbital and, hence, that the orbital is mainly metal in character.

Conclusion.—For the majority of complexes, the electron-transfer reactions were reversible, *i.e.* the rate of electron transfer was rapid and diffusion controlled. Furthermore, the redox orbital was centred on the rhenium atom. Hence the E' values are thermodynamic quantities which reflect the electron density on the metal centre and can be directly compared with the binding energies of the rhenium 4*f* electrons as determined by *X*-p.e. spectroscopy. Such a correlation is unlikely to hold for all complexes in general, and we are at present attempting to determine those for which it is valid.

EXPERIMENTAL

Electrochemical measurements of E' employed a three-electrode cell at 21 °C. The working electrode was either a vitreous carbon electrode (0.46 cm^2) for cyclic voltammetry, a dropping mercury electrode [$m = 1.354$ (mg Hg) s^{-1}, $t = 5.16$ s on open circuit, in methanol–0.1M-tetraethylammonium chloride] for polarography, or a large vitreous carbon plate (14.1 cm^2) for controlled-potential electrolyses. The counter electrode was a piece of platinum foil separated from the sample compartment by a saturated potassium chloride–agar salt bridge and a fritted glass disc. The reference electrode was a saturated potassium chloride–calomel electrode (s.c.e.) separated from the sample by a glass frit and a salt bridge which contained 0.4M-tetrabutylammonium iodide in methanol–water (1 : 1). The experimental error is generally ± 10 mV.

The potential of the working electrode was controlled relative to the s.c.e. by a Chemical Electronics TR 70/2A potentiostat. Potential sweeps and steps were generated by a Chemical Electronics RBI waveform generator. Sweep rates ranged between 3 and 500 mV s^{-1} and the chronoamperogram used pulses of 1, 3, and 10 s. The current–potential curves were displayed on a Bryans X-Y recorder (model 26000 A3).

The solvent used in this study was dichloromethane–methanol (10 : 1) containing 0.1M-tetraethylammonium tetrafluoroborate. All solutions were *ca.* 1mM in rhenium complex and dissolved air was removed by purging the solution with argon.

[4/2596 *Received, 12th December*, 1974]

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