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Electrochemical Oxidation of $Ru(NO)_2(PPh_3)_2$: an Irreversible Two Electron Process

G. PIAZZA and G. INNORTA

Istituto Chimico 'G. Ciamician', Università di Bologna, Via Selmi 2, I-40126 Bologna, Italy

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$Ru(NO)_2L_2$ ($L = PPh_3$) is oxidized in acetonitrile at a Pt electrode in an irreversible two electron process. The main cause for the activation energy is presumably linked to the slow configuration change from a pseudo-tetrahedral to a planar structure. The latter easily releases two electrons giving a dication which can be reversibly reduced to a monocation, as seen in experiments at low temperature. This dication undergoes homogeneous decomposition via a bimolecular reaction with $Ru(NO)_2L_2$. In the presence of Cl^- it gives a stable product (presumably $RuCl_2(NO)_2L_2$) which can electrochemically regenerate $Ru(NO)_2L_2$.

Introduction

In previous work [1] on the electrochemical reduction of $RuCl(NO)_2(PPh_3)_2^+$ [I], a pentacoordinate Ru(II) complex, it was found that a tetracoordinate Ru(O) compound was invariably formed, *i.e.* $Ru(NO)_2(PPh_3)_2$ [II]. Compound [I] can be considered a product of the oxidative addition reaction of [II] with chlorine, by which the formal oxidation state of Ru goes from O to II. This type of reaction might be a fundamental step in homogeneous catalysis by transition metal complexes.

$Ru(NO)_2(PPh_3)_2$ does not undergo oxidative addition reactions with as wide a variety of substrates as does $Os(NO)_2(PPh_3)_2$ and the mononitrosyl systems $M(NO)(PPh_3)_3$ (M = Rh, Ir) [2]. This observation and the previous results on the electrochemical oxidation of [II] [1] suggested the use of the electrochemical route for the possible selective preparation of oxidative addition compounds. On the other hand, a detailed study of the electrochemical oxidation of [II] might throw light on the nature of transitory species of interest in homogeneous catalytic reactions.

Experimental

$Ru(NO)_2(PPh_3)_2$, a pseudotetrahedral compound, was prepared according to literature [3]. Acetonitrile and all chemicals and apparatus were as described previously [1].

The working electrode was a spherical Pt electrode of 0.12 cm^2 exposed area, as determined with ferrocene ($D = 2.4 \times 10^{-5}$ cm^2 s^{-1} [4]). The nominal radius of the electrode, 9.58×10^{-2} cm, was used for the spherical correction in the voltammetric curves. The electrode was chemically preconditioned with boiling HNO_3 and tested in an aqueous H_2SO_4 0.5 *M* solution prior to every measurement cycle. Upon observation of the typical satisfactory hydrogen and oxygen adsorption peaks, the cell was disconnected at +0.5 V *vs.* NHE, inside the 'double layer' region, and the electrode transferred in acetonitrile for careful washing before its introduction into the measurement cell. After the measurement cycle, the electrode was tested again in the H_2SO_4 solution in order to ascertain if metallic ruthenium or some other insoluble product was deposited on its surface. It was normally found that the electrode was properly regenerated.

Results

The voltammetric curves of [II] show several peaks (Fig. 1). Peak I, the main one, involves an irreversible diffusion controlled two-electron oxidation process. All the others are mainly kinetic, as described in the following.

Peak I

The usual analysis of this peak, in the range of easy solubility of the product (up to 10^{-3} *M*), shows that its height, corrected for the spherical contribu-

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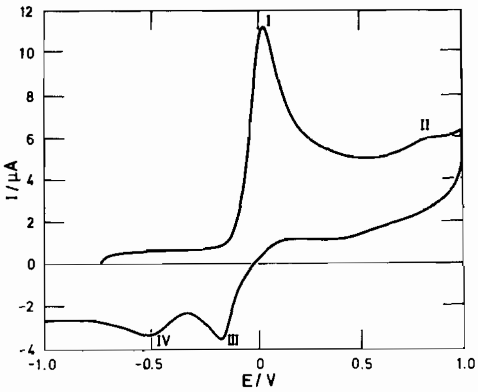

Fig. 1. Voltammetric curve of $Ru(NO)_2(PPh_3)_2$ 1.3 X 10^{-4} *M* in AN; sweep rate, 200 mV s^{-1}.

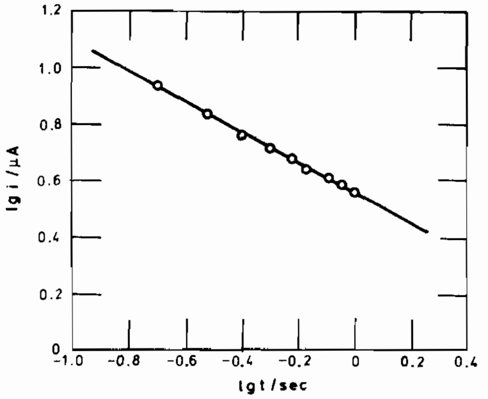

Fig. 2. Log i *vs.* log t at +0.2 V; 1 s impulse; $[Ru(NO)_2(PPh_3)_2]$, 4.3 X 10^{-4} *M.*

tion [5], is a linear function of concentration and $\sqrt{v}$ (v = sweep rate) up to 40 V s^{-1}. For the spherical correction the necessary parameters βn_a, D and n were evaluated as follows: βn_a from the equation [5] $E_p - E_{p/2} = 1.857\ RT/\beta n_a F$. The value found was 0.59 ± 0.02. The evaluation of D, however, required the unambiguous knowledge of n. For this purpose we followed different methods: a) *Coulometry.* The oxidation of [II] at a controlled potential slightly anodic to peak I in order to avoid possible contributions of oxidizable homogeneous reaction products, for about 20% of initial concentration decrease, gave n = 2. The extensive oxidation gave a final value close to one (see below); b) *Chronoamperometry.* The application of a short potentiostatic pulse, in the order of a few hundred milliseconds, to a limit potential value for the rigorous applicability of the Cottrell equation (Fig. 2) allowed

$$i = nFAC\,(D/\pi t)^{1/2}$$

the evaluation of $nD^{1/2}$. From its value, we estimated D, 8.9 X 10^{-6} cm^2 s^{-1} for n = 2. This diffusion coefficient gave, by means of the Stokes–Einstein equation, a value of 0.401 nm for the molecular radius, consistent with the crystallographic structural data [2]. On the contrary, n = 1 would have given D = 4.3 X 10^{-5} cm^2 s^{-1} corresponding to an unacceptable radius of 0.083 nm; c) *Comparison with other substances.* Several compounds of known electrochemical behaviour (*e.g.*, ferrocene, triphenylphosphine, *etc.*) were used for comparison purposes. Allowing for the influence of the different degree of reversibility on the respective peak heights [5], the most consistent value for n was 2.

By means of the previous figures, then, an average value for the ratio i_p(exp.)/i_p(calcd) of 0.97 ± 0.03 was obtained, close to the theoretical 1, in the range of v from 0.01 to 20 V s^{-1}.

Peak II

The origin of this peak was attributed to the irreversible monoelectronic oxidation of the triphenylphosphine ligand produced in the homogeneous decomposition of the primary cation. Its peak potential was comparable to that found in a voltammetric study by Schiavon *et al.* [6], and it perfectly merged with the oxidation peak due to an excess of free ligand added to a solution of [II]. The presence of oxidation peaks between I and II, of as yet unknown origin, prevented a careful study of the ratio $(i_p)_{II}/(i_p)_I$ as function of the experimental parameters. However, it was found that, at constant v, the ratio of the total current at the peak II and $(i_p)_I$ increased with the initial concentration of [II]; while, at constant C, $(i_p)_{II}$ decreased with the increase of v until it almost disappeared above 200 mV s^{-1}. As an excess of free triphenylphosphine in solutions of [II] did not change the general shape and features of the voltammograms it was concluded that the ligand formation reaction might be an irreversible one.

Cathodic Branch

In the cathodic branch two main peaks can be observed, *i.e.*, III and IV. The influence of the sweep rate and of the anodic inversion potential on their relative heights showed that they are complementary to each other. At constant concentration and anodic inversion potential, the ratio $(i_p)_{III}/(i_p)_{IV}$ increased with v about 30% from 0.1 to 1 V s^{-1}. Both peaks were measured toward a common base line, arbitrarily chosen at the inflection point before the foot of peak III. The same ratio, on the other hand, was inverted, at constant v, by shifting the inversion potential increasingly more anodic from 50 to 600 mV with respect to the peak I potential. Finally, no clear evidence of a definite concentration influence on the same ratio was obtained.

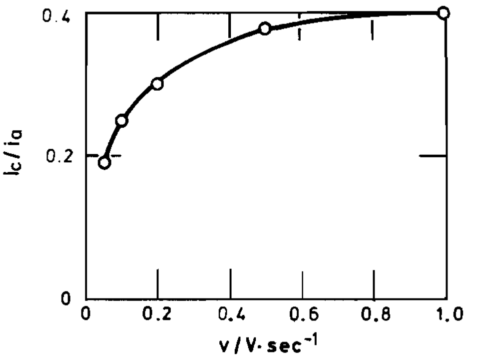

Fig. 3. Effect of the sweep rate on the $(i_p)_{III}/(i_p)_I$ ratio.

These findings suggested that peak III originates directly from the primary dication, and peak IV from a species produced in a homogeneous reaction of the latter. Reasonable confirmations on the origin of peak III came, in addition, from the following experiments:

a) *Effect of Cl⁻ ions.* Increasing amounts of Cl^- ions in a solution of [II] produced the gradual disappearance of peak III and the corresponding increase either of peak IV or of a new one merging to it. In fact, the peak potential of the latter is very close to that for the reduction of $RuCl(NO)_2(PPh_3)_2^+$ [1]. That this was the species formed was confirmed by the shape of the cathodic branch with an excess of Cl^-: very similar to that previously found [1]. As the reaction between Cl^- and the primary dication was fast, it was thought the latter should have had a planar or a quasi-planar configuration in order to allow for both the high activation energy of the electrodic process (see below) and the high homogeneous reaction rate.

b) *Effect of repetitive potential cycling.* Stationary conditions for the production rate of peak III were obtained after almost 20 fast (500 mV s^{-1}) triangular potential cycles between two limits including only peak I and III. This procedure permitted the minimization of the effect of homogeneous reactions and the evaluation of a limiting ratio $(i_p)_{III}/(i_p)_I$ of *ca.* 0.6. When the same ratio was evaluated from the first voltammograms as function of the sweep rate, a limiting value of 0.4 was obtained (Fig. 3). The discrepancy was ascribed to the more pronounced influence of the following homogeneous reaction on the electrode surface concentration of species III in the latter case. The value 0.6 is that expected for the previous ratio if peak III is originated by a reversible monoelectronic reduction of a species with a diffusion coefficient comparable to that of species I. The following experiments at low temperature confirmed, in our opinion, that at peak III the primary dication formed at peak I is reversibly reduced to a monocation with configuration retention.

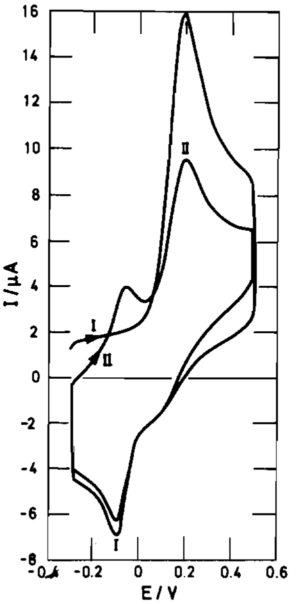

Fig. 4. Voltammetric curves of $Ru(NO)_2(PPh_3)_2$, 1.7 × 10^{-4} *M* in AN, at −20 °C; sweep rate, 500 mV s^{-1}.

c) *Effect of temperature.* Measurements were performed in the range −20 °C–+20 °C, by repetitive cycling in a narrow span in order to avoid interference of the kinetic peaks II and IV still present at the lowest temperature. The main features observed are the following: 1) a shift of $(E_p)_I$ toward anodic values decreasing T with activation parameters comparable to those found in the E_p–v diagrams at 20 °C; 2) $(i_{lim})_I$ decreased with T according to a diffusion controlled process*; 3) starting from the second cycle, an anodic peak corresponding to peak III was observed (Fig. 4). Its peak potential was *ca.* 60 mV anodic to $(E_p)_{III}$, showing that the corresponding process is a reversible monoelectronic one.

An estimation of the activation energy for the process at peak I was made by means of the equation:

$$E_a^{\neq} = 2.3\,R\left(\frac{\partial \log i}{\partial(1/T)}\right)_{E,C}$$

where i is the current taken in the activation controlled portion of the peak (within 10% of its height); a value of 7.8 Kcal mol^{-1} was evaluated; comparable figures, with the limits on their significance, have been found in cases of bond ruptures before charge transfer [7]. Note that this value is more than twice that found in the limiting current region.

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*The evaluated activation energy, 3.2 Kcal mol^{-1}, was typical for such a process.

Peak IV

The location of this peak in the potential region where compound [I] is reversibly reduced might suggest that it could be originated by a pseudo first-order reaction between $Ru(NO)_2(PPh_3)_2^{++}$ (pseudo planar) and ClO_4^-. However, it was observed even when the supporting electrolyte was $TEAPF_6$. On the other hand, the assumption that it might be originated by a monoelectronic reduction of $Ru(NO)_2(PPh_3)_2^+$ (pseudo planar) formed at peak III seems to be ruled out by the experimental findings previously described. The competition of this peak with III is, in fact, at variance with this assumption.

Coulometric Measurements

Extensive oxidation of [II], in a well stirred solution, at a platinum gauze electrode, was performed at several controlled potentials along the i–E curve. At room temperature, the highest anodic potential was no more than 100 mV anodic to the peak I potential, in order to avoid possible contaminations by the side products. The initial value of n, the number of electrons per molecule of [II] consumed, as estimated by the relative decrease of the substance concentration (discontinuously checked with a stationary electrode) was close to 2. However, its value decreased with the extension of the experiment until a final value of 1.22 was obtained. The logarithm of the stationary current changed linearly with time in the early stages of the experiments. This behaviour looked like that for a bulk reaction between the electrode process product and the parent molecule [8]. Quite similar results were obtained at −15 °C, where the final value of n approached 1. The difference in the value of n at different temperatures was explained mainly on the basis of competing reactions. Presumably, a pseudomonomolecular decomposition of the dication is much less important than its bimolecular reaction with [II] at low temperature. After completion of the oxidation and complete evaporation of the solvent the residue was extracted with hexane; in this portion the presence of $OPPh_3$ and small amounts of PPh_3 was ascertained by mass spectrometry. A brownish non volatile product, containing ruthenium, soluble in acetonitrile and CH_2Cl_2, also resisted analysis by means of field-desorption mass spectrometry. Its UV–Vis (max. abs. at 300 nm) and i.r. (abs. at 1832, 1677 and 1602 cm^{-1}) spectra could not be assigned to any compound of our knowledge.*

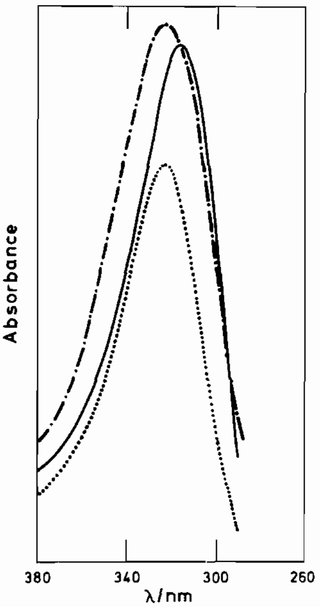

Fig. 5. Qualitative UV spectra in CH_2Cl_2 of: ——— $RuCl(NO)_2(PPh_3)_2^+$; ------ the same solution with excess Cl^- ions; –·–·– the residue of the coulometry of $Ru(NO)_2(PPh_3)_2$ in presence of Cl^- ions.

In order to avoid the interference of side reactions, considering that the primary dication might be a quasi-planar species precursor to the generation of the stable $RuCl(NO)_2L_2^+$ with free Cl^- ions, coulometric oxidations were performed in the presence of the latter. Tetrabutylammonium chloride was then purposely added in solution of [II] in the molar ratio 10:1. A much larger value would have drawn the reaction to the final formation of $RuCl_3NOL_2$ [1]. The results showed that the complete oxidation of [II] happened with the exchange of 2 electrons per molecule and with the generation of a reversible cathodic peak at −0.37 V, as ascertained by occasional voltammetric inspections of the electrolyzed solution. This peak is located 130 mV less cathodic than that of [I]. The extensive reduction of the product obtained gave again $Ru(NO)_2L_2$ with the consumption of the same amount of charge. This reversible process might be continued almost indefinitely. Actually some decomposition reactions were operative during repetitive experiments, as was shown by a gradual decrease of the anodic and cathodic peaks. The electrolyzed solution did not give any insoluble product and showed the same spectroscopic (UV and i.r.) features of a solution of $RuCl(NO)_2L_2^+$ with an excess of Cl^- in the molar ratio 1:10. The characteristic band of [I] at 315 nm was replaced by a new one at 328 nm (Fig. 5), the same as that observed in the electrolyzed solution. The i.r. spectrum, in both cases, showed a well defined

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*The reaction of [I] and Ag^+ in acetonitrile gives quantitatively 1 mole of AgCl; the nature of the Ru containing species, mainly formed by successive reactions of the dication $Ru(NO)_2L_2^{++}$, is currently under investigation. Hitherto, two major side products have been found, *i.e.*, N_2O and $OPPh_3$.

band at 1890 cm^{-1} attributable to NO stretching. This band, with a shoulder at higher frequency, is normally observed in the i.r. spectrum of [I]. The latter has also a second NO band at 1624 cm^{-1} in AN. Unfortunately, it was not possible to look in this region, both in the electrolyzed solution and in that of [I] with excess Cl^-, due to a strong interference by the tetrabutylammonium cation. Work is in progress in order to ascertain the nature of the absorbing species which might be $RuCl_2(NO)_2(PPh_3)_2$ with both NO groups bent*.

Conclusions

From the foregoing results, it seems reasonable to conclude that the oxidation of [II], quasi-tetrahedral (C_{2v}), is a slow process since the release of two electrons requires a significant molecular rearrangement to a planar (D_{2h}) isomer. Recently [9] the isomerization $C_{2v} \rightleftarrows D_{2h}$ has been invoked as the first step in ligand substitution reactions of Ru, Os, Rh and Ir complexes of the general formula $M(NO)_2(PPh_3)_2^{n+}$. The coordinatively unsaturated (16 electrons) planar isomer reacts with a ligand molecule through an associative step, followed by the release of a molecule of $OPPh_3$ and one of N_2O. On the other hand, a structural study of [II] supports [2] the view that this compound is a d^{10} system in which the nitrosyl groups are coordinated as NO^+ and the Ru atom has a formal oxidation state of –II. This low oxidation state is stabilized by the two NO^+ groups via strong π-backbonding interactions, explaining in part the relative lack of reactivity of [II] with oxidative addition substrates as compared with $M(NO)(PPh_3)_3$ (M = Rh, Ir) [2]. However, in the same paper it has been reported that [II] undergoes a nitrosyl-transfer reaction with $RuCl_2(PPh_3)_3$. This represents an equilibration reaction between a Ru(II) complex and a Ru(–II) system. All of this information might help in understanding the present electrochemical results. For instance, in the course of the bulk bimolecular reaction between the dication and the present molecule, there might be a ligand transfer with an intramolecular oxygen release from a new ligand N_2O_2 to a PPh_3 molecule to give $OPPh_3$. This sequence of reactions however requires a definite stereochemistry of the electrode reaction, in which the two NO ligands in the planar intermediate are in *cis* position so that, by mutual interaction, a new hyponitrite ligand N_2O_2 (a strong oxidizing agent) may be formed. This *cis* configuration is invoked both in $L_2Pt(N_2O_2)$ [9] formed by reaction of PtL_4 with NO, and in the dimerization reaction of $Ir(NO)_2L_2Cl$ [10]. It is worth noting that $[Ir(NO)_2(PPh_3)_2]^+$ reacts with Cl^- according to a similar mechanism [10], giving a dimer with a bridged hyponitrite ligand, $[Ir(NO)(PPh_3)_2Cl]_2N_2O_2$.

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*From the reaction of [I] with Cl^- in acetonitrile a stable green intermediate has been isolated. Preliminary analytical data suggest the formulation of this compound as $RuCl_2(NO)_2(PPh_3)_2$.