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Kinetics of Decomposition of a Molybdenum(I) Dinitrogen Complex

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The complex, trans-$[Mo(N_2)_2(Ph_2PCH_2CH_2PPH_2)_2]^+$*, decomposes with the loss of both* N_2 *ligands in tetrahydrofuran–methanol (26% V/V)–0.1N LiX electrolyte* ($X = Cl^-$ *and* ClO_4^-) *via a first order dissociative mechanism. The rate constant of decomposition at 25° C in the presence of lithium chloride is* $2.4 \pm 0.2 \times 10^{-1}$ s^{-1} *and the activation parameters are:* $E_a = 24 \pm 2$ *Kcal* mol^{-1} *and* $\Delta S^* = +19 \pm 5$ *cal* deg^{-1} mol^{-1}*. The kinetic parameters for the perchlorate electrolyte are similar. The molybdenum-containing product of decomposition disproportionates to produce Mo(0) and Mo(II) species which further react, in some cases, with the anions of the electrolyte. All reactions are initiated and monitored by electrochemical techniques.*

Introduction

Recently interest has been focused on the reactions of *trans*-bisdinitrogenbis(1,2-diphenylphosphinoethanc) molybdenum(0), *trans*-$[Mo(N_2)_2dpe_2]$ (A), with organic and hydrogen halides[1], sulfuric acid[2] and on its interaction with iron–sulfur cluster compounds[3]. In our studies of the redox behaviour and X-ray photoelectron spectra of the dinitrogen complexes of tungsten and molybdenum and analogues[4], we confirmed that A could be reversibly oxidized to *trans*-$[Mo(N_2)_2dpe_2]^+$, (A^+)[5]. Furthermore, we established[6] that A did not interact with the ferredoxin-model compound, $[NBu^n{}_4]_2$ $[Fe_4S_4(SEt)_4]$ (where $Et = C_2H_5$ and $Bu^n = nC_4H_9$), nor did acidification of a mixture of the two compounds produce ammonia. This last reaction did demonstrate that iron(III) chloride, derived from the reaction of HCl with the iron–sulfur cluster, oxidised A and under heterogeneous conditions yielded the salt, *trans*-$[Mo(N_2)_2dpe_2][FeCl_4]$. However, the tetrachloroferrate molybdenum(I) compound was never prepared pure and was always contaminated with a non-nitrogen containing species[7] due to chemical decomposition. This report describes the kinetics of decomposition of *trans*-$[Mo(N_2)_2dpe_2]^+$ in a tetrahydrofuran (thf)–methanol (MeOH) solvent and the nature of the decomposition products.

Experimental

The molybdenum(0) dinitrogen complex was prepared by Dr. R.L. Richards. All solvents and lithium salts were dried before use. The electrolyte employed in this study was tetrahydrofuran–methanol (26% V/V) containing 0.1*N* lithium chloride or perchlorate. All solutions were approximately 1m*M* in complex and dissolved air was removed by purging with high purity argon.

The working electrode was either a vitreous carbon electrode (0.46 cm^2) for cyclic voltammetry, 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 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 0.4*M* tetrabutylammonium iodide in mcthanol–water (1 : 1).

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 30 and 500 mV s^{-1} and the chronoamperograms used pluses of 1,3 and 10 s. The current–potential curves were displayed on a Bryans X–Y recorder (model 26000 A3).

The elevated pressure studies were performed in a one-litre rocking autoclave (Baskerville and Lindsay, Manchester) which was connected to cylinders of high purity gases. Electrical contact to the interior of the autoclave was achieved by passing wires through a PTFE gland. The electrolytic cell used in conjunction with the autoclave consisted of a three-necked round bottom flask which was wrapped in cotton wool to provide thermal insulation. The three electrodes, working, counter and reference, were mounted inside the vessel. The sample was flushed three times at pressures of 10 atm prior to the experiments.

Results

The electrochemical techniques of cyclic voltammetry and chronoamperometry were found to be the most

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convenient methods of producing known quantities of *t*-$[Mo(N_2)_2dpe_2]^+$, A^+, and monitoring its disappearance. The reaction scheme can be written:

$$trans\text{-}[Mo(N_2)_2dpe_2]-e^- \rightleftarrows trans\text{-}[Mo(N_2)_2dpe_2]^+ \quad (1)$$

$$trans\text{-}[Mo(N_2)_2dpe_2]^+ \xrightarrow{k} trans\text{-}[Mo(S)_2dpe_2]^+ + 2N_2 \quad (2)$$

where S is a solvent molecule derived from the electrolyte.

From the cyclic voltammograms, it was established that A underwent a reversible one-electron diffusion-controlled oxidation step[8]: the separation between the anodic peak and half-peak potentials was 65 mV and the separation between the anodic and cathodic peaks was 67 mV (theoretical values = 59/n mV where n represents the number of electrons transferred); also the Malachesky R factor[9] equalled 4.86 (theoretical value = $4.92n^{1/2}$). The one exception to the predicted behaviour was that the cathodic peak current was less than the theoretical value which is characteristic of a chemical reaction succeeding the electron transfer step[8]. The presence of the following chemical reaction was demonstrated by recording cyclic voltammograms at various temperatures (Figure 1). The effects of increasing temperature were: 1) the oxidation peak current, ip_a, increased since the diffusion coefficient increased with temperature; 2) the anodic peak potential, Ep_a, shifted due to differences in reference and junction potentials and 3) the cathodic peak height, ip_c, decreased due to the increased rate of transformation of A^+.

The rate constant of decomposition, k, was determined by the method of Schwarz and Shain[10] assuming that the reaction was first or pseudo-first order. The method employed double-potential step chronoamperommetry (Figure 2). Initially a potential, $E_i = -0.45V$, was chosen at which there was no electrode reaction but which was in the diffusion controlled region for the reduction of the oxidation product, A^+. The potential was then stepped from E_i to a value, $E_f = -0.05V$, in the diffusion-controlled region of the oxidation of A and the oxidation current was recorded against time. After a pre-selected interval, τ, the potential was stepped back to E_i and the oxidised material, A^+, which had not undergone decomposition was reduced. The rate constants were determined from the ratio of the corrected cathodic to anodic currents at various times, t, and from a series of standard curves for various values of τ. The results of the studies in both lithium chloride and perchlorate electrolytes are presented in Table I. Each value was the result of approximately six determinations and the standard deviations were of the same magnitude as found in other studies[11]. The values were reproducible to within the standard deviations.

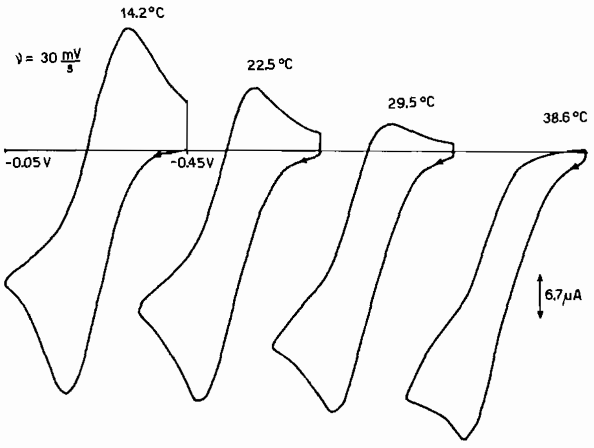

Figure 1. Cyclic voltammograms between –0.45 and –0.05 V of a 1 m*M* solution of *trans*-$[Mo(N_2)_2dpe_2]$ at various temperatures.

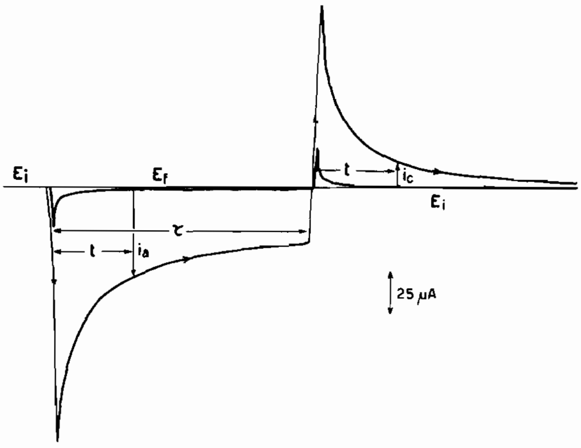

Figure 2. A double potential-step chronoamperogram of a 1 m*M* solution of *trans*-$[Mo(N_2)_2dpe_2]$ between $E_i = -0.45$ V and $E_f = -0.05$ V for $\tau = 3s$ at 22.5° C.

The activation energies, determined by applying the method of least squares to standard Arrhenius plots

TABLE I. The Rate Constants for Decomposition of *trans*-$[Mo(N_2)_2dpe_2]^+$ at Various Temperatures.

Electrolyte	Temperature (°C)	k × 10 (s^{-1})
thf–MeOH–LiCl	14.2 ± 0.1	0.45 ± 0.05
	22.5 ± 0.1	2.0_1 ± 0.2
	29.5 ± 0.1	5.1_7 ± 0.6
	38.6 ± 0.1	$11._9$ ± 1.0
thf–MeOH–$LiClO_4$	14.0 ± 0.1	0.54 ± 0.05
	20.6 ± 0.1	1.9_4 ± 0.2
	28.5 ± 0.1	6.0_9 ± 0.6
	36.4 ± 0.1	$14._7$ ± 1.5

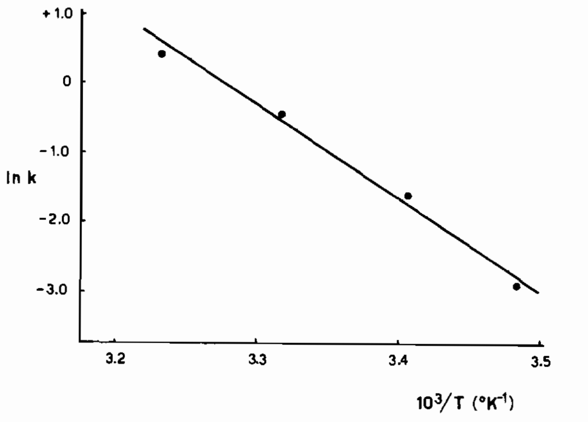

Figure 3. An Arrhenius plot of ln k *versus* 1/T(°K^{-1}) for decomposition of *trans*-[Mo(N$_2$)$_2$dpe$_2$]$^+$ in thf–MeOH–LiClO$_4$.

(Figure 3), were 24 ± 2 and 26 ± 2 kcal mol^{-1} for the chloride and perchlorate electrolytes respectively. The interpolated values of k at 25° C were 2.4 ± 0.2 × 10^{-1} s^{-1} and 3.3 ± 0.3 × 10^{-1} s^{-1} for the same electrolytes which correspond to half-lives of reaction of 2.9 and 2.1 s respectively. The entropy of activation was calculated from the rate constant at 25° C using the theory of Absolute Reaction Rates[12]. The ΔS^* values obtained were + 19 ± 5 and + 26 ± 7 cal deg^{-1} mol^{-1} in the chloride and perchlorate electrolyte respectively.

The cyclic voltammograms and chronoamperograms at the various temperatures were always diffusion controlled. This implied that the chemical reaction following the electrode reaction did not regenerate A. Furthermore, it was found that the rate constant at a given temperature was independent of the concentration of A.

The role of solvent was less clearly defined since restrictions on the composition of the electrolyte were imposed by the solubility and stability of A and the electrochemical method. In solvent mixtures which were greater than 50% V/V MeOH, the dinitrogen complex, A, slowly decomposed and in electrolytes where the MeOH concentration was less than 10% V/V the cyclic voltammograms became distorted and poorly defined. However, using electrolytes which were 26% and 52% MeOH, the rate of decomposition of A$^+$ was found to be approximately 25% slower in the MeOH-rich case.

The decomposition of A$^+$ was also studied at elevated pressures by employing an autoclave. The results of the determination of the rate constant at various pressures of N$_2$ and Ar are given in Table II. The temperatures at which the two sets of data were collected were somewhat different since initial flusing of the autoclave vessel cooled the solutions to different extents. Plots of the logarithm (base 10) of the ratio of the rate constants at elevated pressure to the rate constant at one atmosphere and passing through the origin were non-linear (Figure 4) which precluded further calculations.

TABLE II. The Rate Constants for Decomposition of *trans*-[Mo(N$_2$)$_2$dpe$_2$]$^+$ at Various Pressures in thf–MeOH–LiCl.

Pressurising Gas	Pressure (atm)	k × 10^2 (s^{-1})
N$_2$	1 ± 0	3.6 ± 0.4
(T = 12° C)	40 ± 2	6.3 ± 0.6
	80 ± 2	15.$_7$ ± 1.6
	120 ± 2	20.$_3$ ± 2.0
Ar	1 ± 0	3.2 ± 0.3
(T = 11° C)	39 ± 2	10.$_3$ ± 1.0
	81 ± 2	17.$_8$ ± 1.8
	120 ± 2	22.$_3$ ± 2.1
	151 ± 2	27.$_2$ ± 2.5

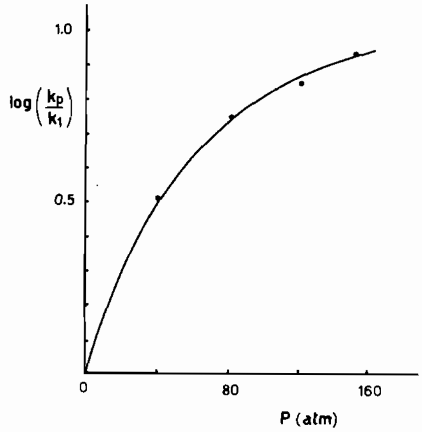

Figure 4. A plot of log(k$_p$/k$_1$) against pressure (atm) for decomposition of *trans*-[Mo(N$_2$)$_2$dpe$_2$]$^+$ in thf–MeOH–LiCl under Ar.

The product of the decomposition reaction was characterised by bulk-scale electrolyses of A. The oxidations of A were performed at 0.0V in both chloride and perchlorate media. In the chloride electrolyte, the oxidation was not well behaved and very prolonged. The resultant solution was reddish pink in colour displaying adsorption bands at 356 and 534 nm and exhibiting a reversible redox couple at Ep$_c$ = –0.16V and Ep$_a$ = –0.10V with both oxidised and reduced forms present. Both these features were characteristic of the couple, *trans*-[MoCl$_2$dpe$_2$]/*trans*-[MoCl$_2$dpe$_2$]$^+$, after allowance was made for the effect of different solvents[4,6]. The product solution when A was oxidised in perchlorate electrolyte was pale yellow and displayed a reversible reduction wave at Ep$_c$ = –0.78V and Ep$_a$ = –0.72V and a further irreversible reduction wave at –1.29V. Recovery of the molybdenum product showed that both N$_2$ ligands had been lost but that OH and ClO$_4^-$ groups were present [IR bands (Nujol) at 1683 and 3500 cm^{-1} and at 1080 cm^{-1}]. When A was dissolved in thf–MeOH–$LiClO_4$ and allowed to stand for several hours, a reversible oxidation wave appeared at Ep_a = –0.71V and Ep_c = –0.79V. Hence, the main products of the gross-scale oxidation of A in perchlorate media were *trans*-$[Mo(S)_2dpe_2]^+$ (where S is a molecule of the electrolyte) and a higher oxidation state molybdenum species.

Discussion

The decomposition reaction involved the loss of the ligating N_2 groups from *trans*-$[Mo(N_2)_2dpe_2]^+$, A^+. The lability of the dinitrogen groups was demonstrated by both the electrolytic oxidation of A in perchlorate media which produced *trans*-$[Mo(S)_2dpe_2]^+$ and by heterogeneous ferric chloride oxidations of A in ethanol which yielded N_2 (0.2–1.0 mol/Mo) and *trans*-$[MoCl_2dpe_2][FeCl_4]$[6]. George and Siebold have also reported that *trans*-$[Mo(N_2)_2dpe_2]I_3$ decomposed in solution with loss of N_2.

The electrochemical behaviour eliminated mechanisms of decomposition involving disproportionation of A^+ or reduction of A^+ by solvent since both these processes would produce A near the electrode surface and it was found that diffusion alone brought A to the electrode. Furthermore, since the reaction obeyed pseudo-first order kinetics and the rate constant was independent of concentration of A, a dimerisation reaction was ruled out.

Volumes of activation could not be calculated from the results of the elevated pressure studies since the applied pressures were insufficient to produce a linear plot of $\log(k_p/k_1)$ *versus* pressure. However, since the same results were obtained with nitrogen and argon gases between 0–150 atm, it was apparent that A^+ was not stabilised by increased pressure of N_2 and that the back reaction (reverse of 2) could be neglected in the kinetic treatment.

The similarities in the activation energies and entropies determined in chloride and perchlorate electrolytes indicated that the same mechanism was operative in both media. Also, since the rate constants at 25° C in the two electrolytes differed by only 30%, it was concluded that the rate determining step did not involve the attack of anions on A^+. Therefore, the N_2 ligands were replaced by solvent molecules. It was not possible to distinguish whether thf or MeOH was the entering group since the rate constants determined in the 26% and 52% MeOH electrolytes differed by only 25%. However, the infrared spectrum of the products of the bulk-scale oxidation of A in perchlorate media was consistent with the formulation, *trans*-$[Mo(MeOH)_2dpe_2][ClO_4]$ which suggested that methanol was the entering group but satisfactory elemental analysis could not be obtained.

The reaction was envisioned as proceeding in two steps: the first step was rate determining and involved the dissociation of one of the coordinated N_2 groups; subsequently, the second N_2 ligand was very rapidly replaced. Such a mechanism was supported by cyclic voltammetry which detected only *trans*-$[Mo(N_2)_2dpe_2]^+$ and *trans*-$[Mo(S)_2dpe_2]^+$ between +1.0 and –1.0V. Moreover, a dissociative pathway was predicted by the large positive entropies of activation and by the decreased rate in the 52% methanol electrolyte. Transition states which are less polar than the reactants are implicated when the rate constant decreases as the dielectric constant of the medium increases[13]. Since coordinated dinitrogen has been found to be negatively charged when bound to rhenium[14] and molybdenum[4], an activated complex of reduced polarity was expected when a molybdenum–dinitrogen bond was cleaved. By comparison, attack of a solvent molecule (MeOH or thf) in an associative mechanism would have preserved or enhanced the polarity of the transition state.

The controlled potential oxidations of A at 0.0V produced *trans*-$[MoCl_2dpe_2]$ and *trans*-$[MoCl_2dpe_2]^+$ in chloride media and *trans*-$[Mo(S)_2dpe_2]^+$ and a higher oxidation state molybdenum complex in the perchlorate electrolyte. Therefore, it appeared that the initial product of the decomposition reaction, *trans*-$[Mo(S)_2dpe_2]^+$, disproportionated relatively slowly:

$$2\ trans\text{-}[Mo(S)_2dpe_2]^+ \rightarrow trans\text{-}[Mo(S)_2dpe_2] + trans\text{-}[Mo(S)_2dpe_2]^{2+} \quad (3)$$

In the lithium chloride electrolyte, the molybdenum(II) dication reacted with chloride ions to generate the known complex, *trans*-$[MoCl_2dpe_2]$. It was unlikely that chloride reacted directly with *trans*-$[Mo(S)_2dpe_2]^+$ since chloride was not involved in the decomposition step and, since reduction of *trans*-$[MoCl_2dpe_2]$ did not yield a stable Mo(I) chloro complex but, instead, *trans*-$[Mo(S)_2dpe_2]$ was produced[4]. The dichloride complex was oxidisable at –0.13V and was, therefore, converted under the electrolysis conditions to *trans*-$[MoCl_2dpe_2]^+$. Furthermore, the other disproportionation product, *trans*-$[Mo(S)_2dpe_2]$ (Ep_a = –0.72V), was oxidised to regenerate *trans*-$[Mo(S)_2dpe_2]^+$. Such a reaction sequence accounted for the prolonged electrolyses and the production of some *trans*-$[MoCl_2dpe_2][FeCl_4]$ when *trans*-$[Mo(N_2)_2dpe_2]$ was oxidised under homogeneous conditions[6] by *one* equivalent of ferric chloride. In the perchlorate media, *trans*-$[Mo(S)_2dpe_2]^+$ could have been formed either directly from the decomposition of A^+ or by oxidation of the disproportionation product, *trans*-$[Mo(S)_2dpe_2]$. However, since a molybdenum complex in an oxidation state greater than one was observed, disproportionation also occurred in the perchlorate electrolyte. The failure to produce stable Mo(I) species by reduction of *trans*-$[MoCl_2dpe_2]$ further supported the disproportionation scheme.

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