One-electron Cyclic Voltammetric Reduction Potentials of Some Molybdo-oxaziridines

Phalguni Ghosh, Pinaki Bandyopadhyay, and Animesh Chakravorty *
Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700032, India

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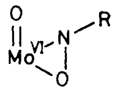
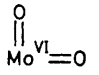
The electrochemistry of $[MoO(S_2CNEt_2)_2(ONC_6H_4X\text{-}p)]$ (X = CH_3, H, or Cl) has been examined voltammetrically. A one-electron cyclic voltammetric reduction peak (E_{pc}) observed near −1.2 V (*versus* a saturated calomel electrode) is assigned to the process $Mo^{VI} \longrightarrow Mo^{V}$. The Mo^{V} species is too unstable for electrochemical detection. The E_{pc} values correlate linearly with Hammett parameters of the substituent X. The reduction peak of $[MoO_2(S_2CNEt_2)_2]$ occurs at −1.03 V. The oxaziridine group is found to be a better donor than the oxo-group.

The electrochemical redox activity of molybdenum complexes of N-, O-, and S-donors is of current interest [1-5] due to their enzymatic and catalytic relevance. The molybdo-oxaziridine group (1) is structurally well characterised [6,7] and acts as an atom-transfer catalyst.[6] But little is known about the electron-transfer properties of (1) and about the relative donor strengths of (1) and dioxomolybdenum(VI) (2), from which (1) is derived [6] *via* the reaction (i).



(1)



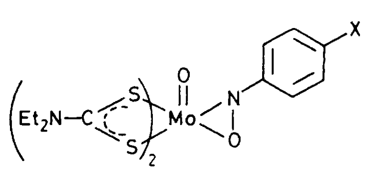
(2)

$$(2) + RNHOH \longrightarrow (1) + H_2O \qquad (i)$$

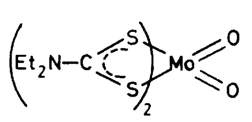
We deal with these two topics in this note.

Results and Discussion

The Complexes.—Three molybdo-oxaziridines of type $[MoO(S_2CNEt_2)_2L]$ [L = η^2-ONC_6H_4X; X = Me (L^1), H (L^2), or Cl (L^3)] (3a)—(3c) were prepared from the dioxa-precursor $[MoO_2(S_2CNEt_2)_2]$ (4). The analytically pure brown complexes display characteristic Mo=O stretches (Table) and are soluble in organic solvents. Although all the complexes reported here are new, the dimethyldithiocarbamate analogues of (3b) and (3c) are known.[6]



(3)



(4)

Electroreduction of $[MoO(S_2CNEt_2)_2L]$.—Cyclic voltammetry (c.v.) and differential pulse voltammetry (d.p.v.) were done in acetonitrile at a platinum electrode in the range 0 to −2.0 V *versus* a saturated calomel electrode (s.c.e.). Each complex displays one reduction peak (E_{pc}) in the range −1.24 to −1.31 V (Table). On scan reversal (c.v.) no anodic peak is observed. On increasing the scan rate (v) the height of the cathodic peak increases as $v^{\frac{1}{2}}$ [Figure (*a*)]. Attempted coulometry at potentials more negative to E_{pc} gave continuous coulomb counts due to unidentified reactions. However, on comparing the observed current height at E_{pc} with those of authentic $1e^-$ reductions studied in this laboratory,[8,9] the reduction of (3) is found to be an $1e^-$ process, equation (ii).

$$[MoO(S_2CNEt_2)_2L] + e^- \longrightarrow [MoO(S_2CNEt_2)_2L]^- \qquad (ii)$$

The lack of the anodic response is evidently due to rapid decomposition of the reduced species $[MoO(S_2CNEt_2)_2L]^-$. Since several monomeric molybdenum(V) chelates have [2,4,10] a single Mo=O group held in the matrix of other ligands, it was considered that $[MoO(S_2CNEt_2)_2L]$ might also yield a stable molybdenum(V) monomer, *i.e.* $[MoO(S_2CNEt_2)_2L]^-$. In practice, however, $[MoO(S_2CNEt_2)_2L]$ behaves much like the complexes of dioxomolybdenum(VI) which on reduction usually give rise [1,3] to unstable and electrochemically non-detectable Mo^{V} species.

Substituent Effect on Reduction Potential.—Very few systematic studies on remote substituent effects on the $Mo^{VI} \longrightarrow Mo^{V}$ reduction have been reported.[1,5] The $[MoO(S_2CNEt_2)_2L]$ species provide an opportunity for such a study. The E_{pc} of reaction (ii) becomes less cathodic in the order $[MoO(S_2CNEt_2)_2L^1] < [MoO(S_2CNEt_2)_2L^2] < [MoO(S_2CNEt_2)_2L^3]$, *i.e.* in order of increasing electron-withdrawing power of X. The Hammett relationship (iii) is found to hold quite well, as shown in the Figure (*a*) (inset). Here ΔE_{pc} is the shift of E_{pc} from the standard, $[MoO(S_2CNEt_2)_2L^2]$; σ is the substituent constant and ρ is the reaction constant. The observed value of ρ is 0.16 V.

$$\Delta E_{pc} = \sigma\rho \qquad (iii)$$

Relative Donor Strengths of the Oxaziridine and Oxo-groups.—To assess this, the reduction of $[MoO_2(S_2CNEt_2)_2]$ (4) was studied under the same conditions as those used for $[MoO(S_2CNEt_2)_2L]$. A cathodic $1e^-$ response occurs at −1.03 V. On scan reversal a small anodic response is seen at high scan

Table. Microanalytical, spectroscopic, and electrochemical [a] data for the molybdenum(VI) complexes

Complex	E_{pc}/V			Analysis [b] (%)			I.r.
	v/V s^{-1} 0.05	0.10	0.20	C	H	N	ν(Mo=O)/cm^{-1}
(3a) [$MoO(S_2CNEt_2)_2L^1$]	−1.305	−1.310	−1.315	38.4 (38.6)	4.4 (5.1)	8.0 (7.9)	932
(3b) [$MoO(S_2CNEt_2)_2L^2$]	−1.285	−1.295	−1.305	37.0 (37.3)	4.7 (4.8)	8.3 (8.1)	937
(3c) [$MoO(S_2CNEt_2)_2L^3$]	−1.240	−1.250	−1.265	35.1 (34.9)	4.1 (4.4)	7.4 (7.6)	935
(4) [$MoO_2(S_2CNEt_2)_2$]	−1.030	−1.038	−1.045	*c*	*c*	*c*	*c*

[a] All results were obtained in acetonitrile (0.1 mol dm^{-3} [NEt_4][ClO_4]) with Pt working electrode and are referenced to s.c.e. [b] Calculated values are in parentheses. [c] Data are in ref. 14.

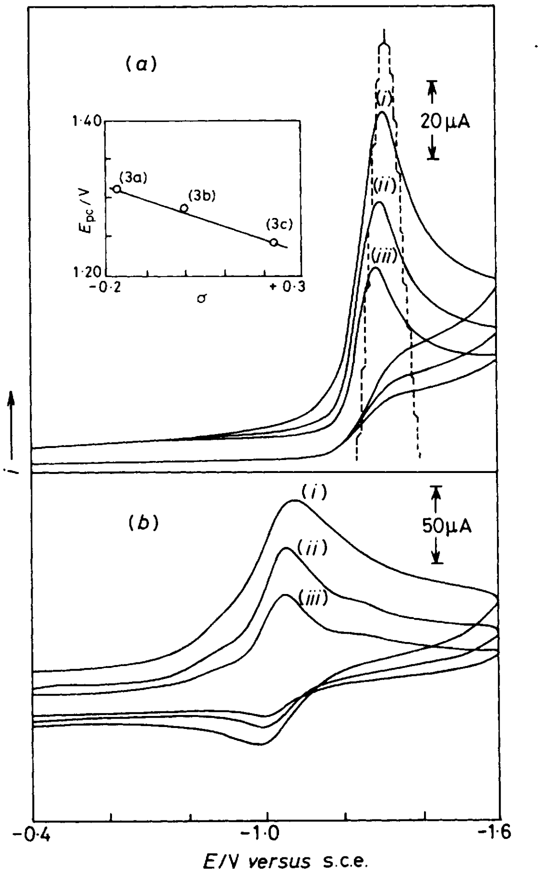


Figure. (*a*) Cyclic voltammogram (——) of (3a) at varying v, (*i*) 0.2, (*ii*) 0.1, (*iii*) 0.05 V s^{-1}; differential pulse voltammogram (— — —) of (3a) at v = 0.025 V s^{-1}, peak-to-peak amplitude 25 mV; inset, plot of E_{pc} *versus* σ for (3). (*b*) Cyclic voltammogram of (4) at varying v, (*i*) 2, (*ii*) 1, (*iii*) 0.5 V s^{-1}

rates [Figure (*b*)]. The separation between cathodic and anodic peak is *ca.* 60 mV. We thus have the electrode reaction (iv).

$$[MoO_2(S_2CNEt_2)_2] + e^- \rightleftharpoons [MoO_2(S_2CNEt_2)_2]^- \quad \text{(iv)}$$

The smallness of the anodic response shows that [$MoO_2(S_2CNEt_2)_2$]$^-$ is unstable. It is however more stable than [$MoO(S_2CNEt_2)_2L$]$^-$ (no anodic response at all). Our results on [$MoO_2(S_2CNEt_2)_2$] reduction are somewhat at variance with those reported elsewhere.[11] Our value of E_{pc} is more negative and the anodic response is clearly seen by us at $v \geqslant$ 0.5 V s^{-1}. We observe little of the reported [11] dimer response.

The free energy (and hence reduction potential) of an electrode reaction depends on a number of factors.[8] However, when the interest lies only in the *difference between two closely related compounds* of the same metal ion, the entire free energy contribution from the solvation and the entropic part [12] of the free energy of formation may be set aside. The dominant factor [8] is then the heat of formation ($\Delta H_f^\ominus$). The complex with more negative $\Delta H_f^\ominus$ would have the more negative reduction potential. Applying this approach to (3) and (4) we conclude that $\Delta H_f^\ominus$ is more negative for (3). Assuming that the contributions of the ligands common to (3) and (4) are the same in both complexes, it emerges that the oxaziridine ring is a better donor than the oxo-group at least in the present group of complexes. We are at present studying other groups of complexes of (1) and (2) to examine the general applicability of the donor strength order: oxaziridine > oxo.

Experimental

Chemicals and Starting Materials.—Substituted hydroxylamines [13] (RNHOH) and *cis*-bis(*NN*-diethyldithiocarbamato)-dioxomolybdenum(VI) [14] were prepared according to reported methods. Tetraethylammonium perchlorate and acetonitrile for electrochemical work were prepared [9] from commercial materials.

Measurements.—I.r. spectra were recorded (KBr disc) using a Beckman IR-20A spectrophotometer. Electrochemical measurements (c.v., controlled potential coulometry, and d.p.v.) were carried out using a PAR model 370-4 electrochemistry system which includes the 174A polarographic analyzer, 175 universal programmer, RE0074 X–Y recorder, 173 potentiostat, 170 digital coulometer, and 377A cell system. The three-electrode measurements were done with a planar Beckman model 39273 platinum-inlay working electrode, a platinum wire auxiliary electrode, and a saturated calomel electrode. A platinum wire-gauge was used as working electrode in coulometry.

The following σ values [15] for *para* substituents were used: Me, −0.17; H, 0.00; Cl, +0.23.

Synthesis of Compounds.—All complexes of type (3) were prepared using similar methods. Specific details given below for one representative case essentially follow a reported method [6] with some modification.

[$MoO(S_2CNEt_2)_2L^2$]. Phenylhydroxylamine (65 mg, 0.6 mmol) was added to [$MoO_2(S_2CNEt_2)_2$] (200 mg, 0.47 mmol) suspended in dichloromethane (25 cm^3) with stirring. The colour of the solution became deep red. Anhydrous magnesium sulphate (500 mg) was added to it and stirring was continued for 15 min. The mixture was filtered and the filtrate was evaporated to a small volume (5 cm^3). On addition of light petroleum (b.p. 40—60 °C) the solid complex separated out. It was repeatedly recrystallised from a mixture of dichloromethane and diethyl ether (yield, *ca.* 70%).

Acknowledgements

We thank the Department of Science and Technology, New Delhi, Government of India, for financial support.

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Received 14*th June* 1982; *Paper* 2/996