

**New Molybdenum Systems: Trends in Cyclic Voltammetric Reduction Potentials**

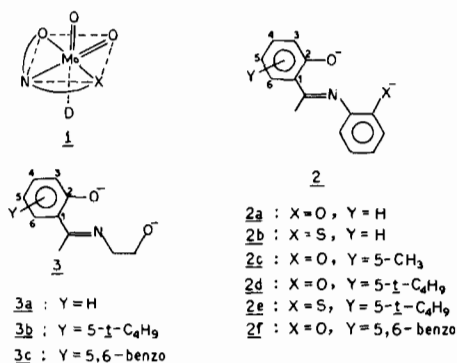
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The function of several redox enzymes is now believed to be dependent on variable valence molybdenum cofactors. Oxygen, nitrogen and sulphur donors have been implicated as ligands. Experiments on relatively small molecules containing molybdenum are being done with the hope of getting some insight into the gross mechanism of enzyme activity [1–3]. In this communication a few preliminary results of our efforts in this area are reported.

By using various dianionic tridentate Schiff base ligands (T) and diverse monodentate ligands D, a large number of molybdenum(VI) systems of the type MoO<sub>2</sub>TD, having structure 1 have been synthesised for using them as models for substrate (D) binding [4, 5]. The present work concerns the systems with T = 2a–2f and 3a–3c and D = dimethylformamide (dmf). The complexes will be specified



by giving the ligand number in parenthesis to 1 e.g., 1(2a) stands for the complex MoO<sub>2</sub>T(dmf) in which T = 2a. The MoO<sub>2</sub> species are readily produced by reacting bis(acetylacetonato)dioxomolybdenum(VI) with the Schiff base in molar quantities. Crystallisation in the presence of dmf yields yellow to orange crystals of MoO<sub>2</sub>T(dmf). Compositions were established by elemental analyses and physical studies. In these complexes dmf is bound through the oxygen end as is evident from the shift of νCO(dmf) to lower frequencies on complexation (representative values of shift are: 1(2a), –31; 1(2c), –28; 1(2d), –35 and

1(2f), –35 cm<sup>-1</sup>). Thermal analyses reveal that MoO<sub>2</sub>T(dmf) complexes endothermically lose all the dmf over a range e.g., 1(2a), 132–175 °C; 1(2c), 123–170 °C; 1(2d), 130–172 °C.

The cyclic voltammetric studies of the complexes at the platinum electrode in anhydrous dmf with tetraethylammonium perchlorate (TEAP) as the supporting electrolyte were made with the equipment described elsewhere [6] used in conjunction with an MP-1502B Electroanalyzer of Pacific Precision Instruments, U.S.A. Each voltammogram displays a characteristic cathodic (reduction) peak (E<sub>pc</sub>) in the range –1.5 to –0.98 V versus saturated calomel electrode (SCE) with no evidence of an oxidation peak on scan reversal (Fig. 1, Table I) showing that the reduction is essentially irreversible. Since the free ligands do not display any reduction in the potential range under consideration electron transfer must occur to molybdenum as in other systems [7, 8]. At potentials more negative to the above peak, one and in some cases two more reduction peaks are observed. These are under further investigation and will not be considered any further here. Preliminary coulometry data suggest that the reduction level corresponding to the –1.5 to –0.98 peak lies within the 1–2e range. Although the exact nature of the reduced product cannot be ascertained at the present time, the data of Table I reveal certain interesting trends.

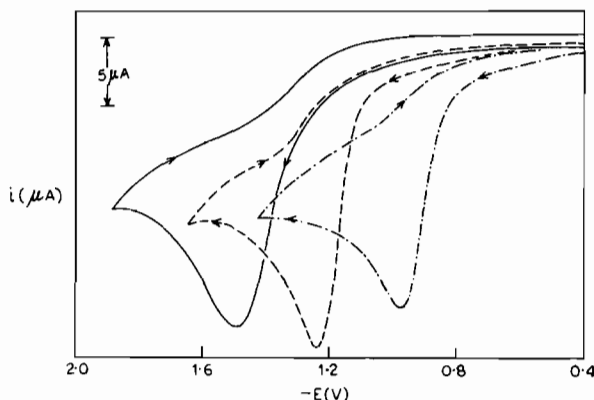


Fig. 1. Cyclic voltammograms of (— · — · —), 1(2b); (— — —), 1(3c); (— — —), 1(3b). E(V) vs. SCE. Conditions are same as those stated in Table I.

It is convenient to define a parameter Δ as,

$$\Delta = (E_{pc})_{\text{complex}} - (E_{pc})_{\text{standard}}$$

The Δ values of Table I are calculated with reference to the standard 1(2a). A negative value of Δ means that the complex is reduced at a potential which is more negative than that of 1(2a); a positive value of the parameter has the opposite significance. From

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TABLE I. Cyclic Voltammetric Data.<sup>a,b</sup>

Compound	E <sub>pc</sub> (V)	(mV)
1(2a)	-1.080 <sup>c</sup>	-
1(2b)	-0.980	+100
1(2c)	-1.120	-40
1(2d)	-1.160	-80
1(2e)	-1.060	+20
1(2f)	-1.040	+40
1(3a)	-1.380	-300
1(3b)	-1.490	-410
1(3c)	-1.240	-160

<sup>a</sup>Conditions are: scan rate, 0.027 Vs<sup>-1</sup>; solute concentration, 3 × 10<sup>-3</sup> M; solvent, dmf with 0.1 M TEAP as supporting electrolyte.

<sup>b</sup>Symbols have meaning as stated in the text.

<sup>c</sup>Literature value [7], -1.155 V (scan rate, 0.100 Vs<sup>-1</sup>; 0.10 M TEACl in dmf).

Table I it is seen that, (i) replacement of one oxygen donor by a sulphur donor leads to positive Δ value, (ii) alkyl substitution at 5-position of the salicylaldehyde ring gives negative Δ and (iii) increased number of aromatic rings in T results in positive values of Δ. Among these (i) is of significance in relation to the presence of sulphur donor in molybdenum enzymes. As is evident from the Δ value, sulphur donors make the metal centre more easily reducible. Trends (ii) and (iii) bring out the interesting result that even when electron density and mobility changes take place primarily in regions not directly linked to the metal ion, substantial modifications in the electron transfer properties at the molybdenum centre can still occur.

Further scrutiny of peak potential data (Table I) reveals the possibility that the substituent effects may be additive. Replacement of O by S (1(2a) → 1(2b); 1(2d) → 1(2e)) leaving the rest of the molecule unchanged decreases the magnitude of E<sub>pc</sub> by 100 mV; similarly substitution by t-C<sub>4</sub>H<sub>9</sub> at 5-position (1(2a) → 1(2d); 1(2b) → 1(2e)) increases the magnitude of E<sub>pc</sub> by 80 mV. When both substituents occur simultaneously (1(2a) → 1(2e)), E<sub>pc</sub> is found to decrease by 20 mV. While such exact additivity is likely to be fortuitous, the observation does call for further scrutiny using a wide variety of substituents.

## References

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