Inorganica Chimica Acta, 54 (1981) L255–L257

Identification of the Oxidation Product of a Binuclear Mixed-valence Vanadium(IV,V) 8-Quinolinol Complex

MICHELE A. HEPLER* and THOMAS L. RIECHEL**

Department of Chemistry, Miami University, Oxford, Ohio 45056, U.S.A.

Received July 14, 1981

We have reported previously [1] on the chemical and electrochemical syntheses of a binuclear mixed-valence vanadium(IV,V) complex, $[(V^{IV}OQ_2)–O–(V^{V}–OQ_2)]^-$ (Q^- = 8-quinolinol anion). This complex undergoes a reversible one electron per dimer oxidation in acetonitrile. The oxidation product is stable and its solution exhibits a cyclic voltammogram similar to that of $VO(OH)Q_2$. Due to the bond breaking that would be necessary to form $VO(OH)Q_2$, we suggested that the actual oxidation product might be the vanadium(V,V) dimer, $(V^{V}OQ_2)–O–(V^{V}OQ_2)$. This dimer can in fact be formed from the monomer by heating [2, 3]:

$$2VO(OH)Q_2 \xrightarrow{heat} (VOQ_2)–O–(VOQ_2) + H_2O$$

These two species may exist in equilibrium in non-aqueous solvents.

Although spectroscopic data for the (V,V) dimer have been reported [4], its electrochemistry has not been explored. We report here an electrochemical study of $(VOQ_2)–O–(VOQ_2)$ which verifies that it is the principle oxidation product of the mixed-valence dimer.

Experimental

Cyclic voltammetric measurements were made with a Princeton Applied Research Model 173 three-electrode potentiostat and a Model 175 Universal Programmer. The voltammograms were recorded on a Houston Instruments Model 2000 Omnigraphic X–Y recorder. Controlled potential electrolysis was carried out with the above potentiostat and a Princeton Applied Research Model 179 digital coulometer.

The platinum working and auxiliary electrodes, and the Ag/AgCl reference electrode (adjusted to 0.000 V *vs.* SCE) have been described elsewhere [1]. Experiments were carried out either in all glass cell flushed with prepurified nitrogen or in a Vacuum Atmospheres Co. Model HE-43-2 glove box with an HE 493 Dri-train, under a nitrogen atmosphere.

UV–Visible and IR spectrophotometric measurements were made on Cary Model 14 and Perkin Elmer Model 180 spectrophotometers, respectively.

High purity acetonitrile was obtained from Burdick and Jackson Laboratories with a lot analysis for water of 0.003%. As no electrochemical impurities were found, the solvent was used as received. Tetraethylammonium perchlorate (TEAP) was prepared as previously described [1] and was used as the supporting electrolyte. Tetrabutylammonium hydroxide was obtained from MCB as a 25% solution in methanol.

Preparation of Compounds

μ-Oxobis[oxobis(8-quinolinolato)vanadium(V)]

Preparation of $(VOQ_2)–O–(VOQ_2)$ followed the three step synthesis of Henry *et al.* [4]. The first product, $VO(OH)Q_2$, was refluxed in absolute ethanol to give $VO(OCH_2CH_3)Q_2$. This ester was heated at 130 °C for two days to give the dimer.

(Tetra-n-butylammonium){μ-oxo[oxobis(8-quinolinato)vanadium(V)](oxobis(8-quinolinolato)vanadium(IV)]}

$[(n\text{-}Bu)_4N]^+[(VOQ_2)–O–(VOQ_2)]^-$ was prepared from $VO(OH)Q_2$, VOQ_2, and tetrabutylammonium hydroxide as described previously [1].

Results

The electrochemical behavior of the vanadium (V,V) dimer, $(VOQ_2)–O–(VOQ_2)$, is illustrated in Fig. 1. Although the dimer is markedly more soluble than $VO(OH)Q_2$ in acetonitrile, its solubility is somewhat less than 0.5 m*M*. Figure 1a is the cyclic voltammogram for an approximately 0.5 m*M* solution which indicates a major reduction peak at –0.05 V *vs.* SCE and a small reduction peak at –0.55 V. The cyclic voltammogram of $VO(OCH_2CH_3)Q_2$ exhibits a large reduction peak at –0.55 V indicating that some of this precursor is present in the dimer solution*.

Reversing a negative potential scan at –0.30 V indicates that the oxidation process at +0.075 V is coupled to the –0.05 V reduction, but the potential

---

*Present address: Department of Chemistry, Michigan State University, East Lansing, Mich. 48824, U.S.A.

**Author to whom correspondence should be addressed.

*Please for footnote, see overleaf.

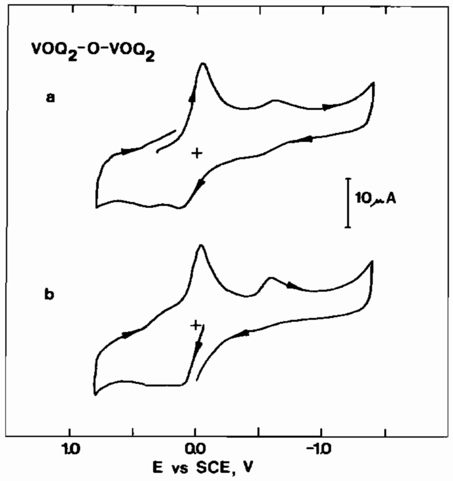

Fig. 1. Cyclic voltammograms in 0.1 *M* TEAP/acetonitrile solution of (a) approximately 0.5 m*M* $(VOQ_2)-O-(VOQ_2)$ and (b) solution (a) after controlled potential reduction at −0.20 V. Scan rate 0.2 V/sec.

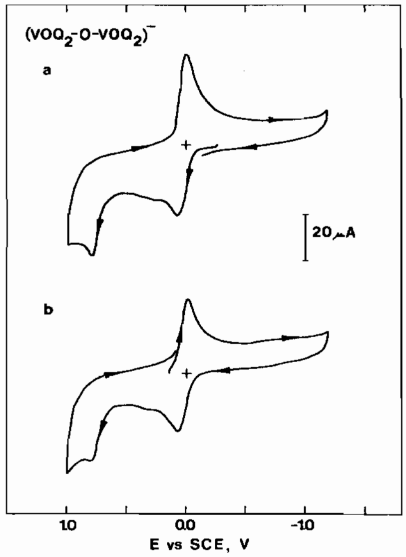

Fig. 2. Cyclic voltammograms in 0.1 *M* TEAP/acetonitrile solution of (a) 0.5 m*M* $[(n\text{-}Bu)_4N]^+[(VOQ_2)-O-(VOQ_2)]^-$ and (b) solution (a) after controlled potential oxidation at +0.25 V. Scan rate 0.2 V/sec.

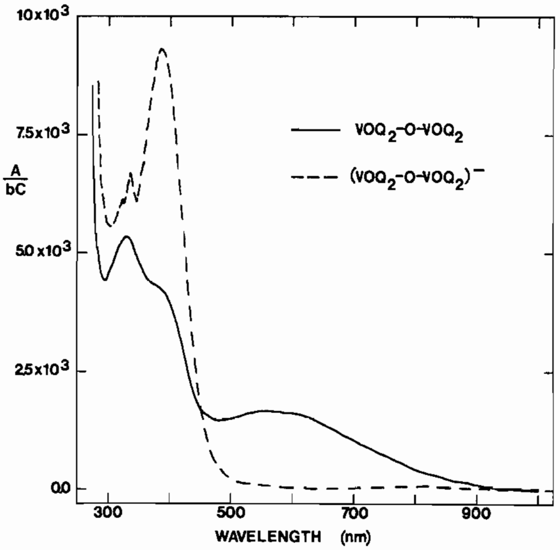

Fig. 3. Absorption spectra of $(VOQ_2)-O-(VOQ_2)$ and $[(n\text{-}Bu)_4N]^+[(VOQ_2)-O-(VOQ_2)]^-$ in acetonitrile.

separation is somewhat larger than the theoretical value of 0.059 V for a reversible one electron process.

The solution resulting from controlled potential coulometry at −0.20 V exhibits the voltammogram shown in Fig. 1b. Since a trace of undissolved dimer remained, meaningful coulometric data could not be obtained. Nonetheless, the resulting voltammogram indicates that the reduction process is essentially complete and that the species oxidized at +0.075 V is the dominant product.

A subsequent controlled potential oxidation at +0.25 V produces a solution whose voltammogram is identical to that of the original solution.

Figure 2a shows a cyclic voltammogram of a 0.5 m*M* solution of $[(n\text{-}Bu)_4N]^+[(VOQ_2)-O-(VOQ_2)]^-$. The positive potential scan reveals a large oxidation peak at +0.075 V and a smaller peak at +0.80 V. The second peak is due to excess hydroxide ion as indicated by a voltammogram of tetrabutylammonium hydroxide.

A controlled potential oxidation of the bulk solution at +0.25 V requires approximately 0.87 electrons per mole and a voltammogram of the resulting solution is given in Fig. 2b. The product of this oxidation exhibits a reduction peak at −0.05 V. A subsequent reduction at a set potential of −0.20 V requires approximately the same number of electrons as the oxidation process, and the voltammogram of this final solution is identical to that of the original solution.

UV–visible spectra have been recorded for the solutions of each redox product described above. Spectra for solutions of $(VOQ_2)-O-(VOQ_2)$, which

---

*Complete conversion of the ester to the dimer is difficult because of the necessity of a stoichiometric amount of water (eqn. 1), while excess water leads to the monomer (eqn. 2):

$$(1)\ 2VO(OCH_2CH_3)Q_2 + H_2O \rightarrow (VOQ_2)-O-(VOQ_2) + 2CH_3CH_2OH$$

$$(2)\ VO(OCH_2CH_3)Q_2 + H_2O \rightarrow VO(OH)Q_2 + CH_3CH_2OH$$

The residual ester does not appear to affect the electrochemical results.

appears black, and $[(\text{n-Bu})_4\text{N}]^+(\text{VOQ}_2)\text{–O–}(\text{VOQ}_2)^-$ (yellow) are shown in Fig. 3. The reduction product of the (V,V) dimer gives a yellow solution and exhibits a spectrum differing from that of the (IV,V) dimer only by a slight absorbance remaining at 560 nm. Subsequent oxidation gives a black solution with a spectrum identical to the original one except that all absorbances have increased proportionally.

The oxidation of the (IV,V) dimer results in a green solution and a spectrum comparable to that of the (V,V) dimer solution. A final reduction process restores the yellow color and the spectrum of the (IV, V) dimer.

Spectra of the two dimer solutions recorded in long path length cells indicate one further difference. A weak absorbance at 725 nm ($\epsilon = 86\ M^{-1}\ \text{cm}^{-1}$) is observed for the (IV, V) dimer, but not for the (V,V) dimer.

Discussion

The electrochemical data show that $(\text{VOQ}_2)\text{–O–}(\text{VOQ}_2)^-$ is oxidized at +0.075 V by a one electron process giving a stable vanadium(V) product. This product can in turn be reduced back to the (IV,V) dimer at –0.05 V. The direct study of $(\text{VOQ}_2)\text{–O–}(\text{VOQ}_2)$ presented here verifies that it is the vanadium(V) product:

$$(\text{VOQ}_2)\text{–O–}(\text{VOQ}_2)^- \rightleftharpoons (\text{VOQ}_2)\text{–O–}(\text{VOQ}_2) + e^-$$

$$E' = 0.025\ \text{V}.$$

Comparison of this data for the dimer and that presented earlier for VO(OH)Q_2 [1] indicates that in solution these compounds are indistinguishable. Yet two facts substantiate that it is the dimer that predominates in solution. Firstly, the dimer is significantly more soluble. In fact, VO(OH)Q_2 may be soluble only to the extent that it is converted to the dimer. Secondly, although the peak potential separation for the oxidation and reduction processes is greater than predicted for a strictly reversible process, the separation of about 0.1 V indicates that there is no major structural change between the oxidized and reduced forms. Thus, the bimolecular collision that would be required for VO(OH)Q_2 to be reduced to $(\text{VOQ}_2)\text{–O–}(\text{VOQ}_2)^-$ is unlikely.

Examples of mixed-valence complexes of vanadium are rare [5] except for the intermediate oxides between V_2O_3 and V_2O_5 [6]. The distribution of the unpaired electron density in $(\text{VOQ}_2)\text{–O–}(\text{VOQ}_2)^-$ is thus of interest and may give rise to a bent V–O–V bridge. The bridged structure of the (V,V) dimer is well established [2, 4, 7] and stretching frequencies for the V–O–V bridge in $\text{V}_2\text{O}_7^{4-}$, for example, have been reported [8]. A Raman study of the mixed-valence complex may provide structural data that the electrochemistry cannot [9, 10].

In our earlier work [1] we reported various data supporting the mixed-valence nature of the (IV,V) dimer. Another indication for mixed-valence complexes is the presence of intervalence bands in visible absorption spectra [6, 11]. Although such peaks are difficult to identify, peaks at 526 and 625 nm have been assigned to intervalence electron transfers in hydroxobridged vanadium (II, III) complexes with 1,10-phenanthroline or 2,2′-bipyridine [5]. The band at 725 nm revealed by our work only for the (IV,V) dimer may, although weak in intensity, correspond to a similar intervalence process. Our continuing work includes attempts to synthesize other vanadium dimers for comparison.

Acknowledgement

This work was supported by the Research Corporation, The National Science Foundation under grant No. CDP8001911, and the Undergraduate Research Program of Miami University.

References

1 T. L. Riechel and D. T. Sawyer, *Inorg. Chem., 14,* 1869 (1975).
2 A. J. Blair, D. A. Pantony and G. J. Minkoff, *J. Inorg. Nucl. Chem., 5,* 316 (1958).
3 M. Borrel and R. Paris, *Anal. Chim. Acta, 4,* 267 (1950).
4 R. P. Henry, P. C. H. Mitchell and J. E. Prue, *Inorg. Chim. Acta, 7,* 150 (1973).
5 K. S. Murray and R. M. Sheahan, *J. Chem. Soc. Dalton,* 1182 (1973).
6 M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem., 10,* 247 (1967).
7 M. Pasquali, A. Landi and C. Floriani, *Inorg. Chem., 18,* 2397 (1979).
8 R. G. Brown and S. D. Ross, *Spectrochim. Acta, 28A,* 1263 (1972).
9 J. San Filippo, Jr., R. L. Grayson and H. J. Sniadoch, *Inorg. Chem., 15,* 269 (1976).
10 J. San Filippo, Jr., P. J. Fagan and F. J. DiSalvo, *Inorg. Chem., 16,* 1016 (1977).
11 L. J. Boucher and C. G. Coe, *Inorg. Chem., 15,* 1334 (1976).