

## ELECTROANALYTICAL CHEMISTRY OF VANADIUM COMPLEXES: ELECTROCHEMICAL OXIDATION OF $[V(IV)O(nta)(H_2O)]^-$

Roland MEIER<sup>a</sup>, Gerhard WERNER<sup>b</sup> and Matthias OTTO<sup>c</sup>

<sup>a</sup> Department of Natural Sciences, Technical University of Leipzig,

P.O. Box 66, 7030 Leipzig, G.D.R.

<sup>b</sup> Department of Chemistry, Karl Marx University Leipzig, 7010 Leipzig, G.D.R. and

<sup>c</sup> Department of Chemistry, Bergakademie Freiberg, 9200 Freiberg, G.D.R.

Received January 5, 1988

Accepted April 11, 1988

Electrochemical oxidation of  $[V(IV)O(nta)(H_2O)]^-$  ( $H_3nta$  nitrilotriacetic acid) was studied in aqueous solution by means of cyclic voltammetry, differential pulse polarography, and current sampled DC polarography on mercury as electrode material. In the pH-range under study (5.5–9.0) the corresponding V(V) complex is produced by one-electron oxidation of the parent V(IV) species. The oxidation product is stable within the time scale of cyclic voltammetry. The evaluation of the pH-dependence of the half-wave potentials leads to a  $pK_a$  value for  $[V(IV).O(nta)(H_2O)]^-$  which is in a good agreement with previous determinations. The measured value for  $E_{1/2}$  is very close to the formal potential  $E^{0'}$  calculated via the Nernst equation on the basis of known literature values for  $\log K_{ox}$  and  $\log K_{red}$ , the complex stability constants for the oxidized and reduced form, respectively.

The investigation of the redox chemistry of transition metal oxo complexes by electro-analytical methods has attracted considerable interest in recent years<sup>1–3</sup> (and references cited therein). Most of these studies were done because oxo-metal ion complexes are good candidates for oxygen transfer catalysts that oxidize inorganic and organic substrates as well<sup>4</sup>.

The present study was undertaken as a first step in search for electrochemically reversible V(V)/V(IV) redox couples interesting from several points of view.

Analytically, reversible electrode processes can be used to determine the oxidized and reduced forms of a redox couple by means of DC-polarography<sup>5</sup>.

On the other hand, V(V)/V(IV) couples in coordination environments which allow fast redox reactions may be regarded as model cases with biochemical relevance. It was shown only recently that the interconversion of the complexed V(V)/V(IV) couple in human serum occurs rapidly under physiological conditions<sup>6</sup>. For this, certain structural requirements have to be fulfilled.

In this work a detailed study of the electrochemical oxidation of the  $[V(IV)O(nta).O(H_2O)]^-$  complex was carried out as a candidate redox V(IV)/V(V) couple that shows reversible electrochemical behaviour.

## EXPERIMENTAL

## Materials

The complex  $\text{Na}[\text{V(IV)O}(\text{nta})(\text{H}_2\text{O})] \cdot 2.5 \text{H}_2\text{O}$  was prepared according to the method by Nishizawa and Saito<sup>7a</sup>.

Boric acid and sodium tetra borate tenhydrate (VEB Laborchemie Apolda, G.D.R.) were of analytical grade purity and were used without further purification.

## Methods

All voltammetric measurements were done with the polarographic analyzer PA 3 (Laboratorní přístroje, Prague, Czechoslovakia) in a standard three compartment cell. The static mercury drop electrode SMDE 1 (as a part delivered with the PA 3) was used as the working electrode throughout. Opening times of 160 ms for the magnetic needle valve (which controls the flow rate of mercury and, in this way, the size of the mercury drop) were used in all measurements to ensure a reproducible drop surface.

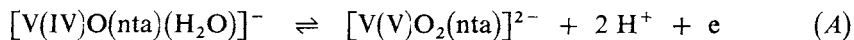
The reference electrode was a commercial  $\text{Ag}/\text{AgCl}/\text{Cl}_{\text{sat}}^-$ -electrode (Forschungsinstitut "Kurt Schwabe" Meinsberg, G.D.R.). All potentials given in this work refer to this electrode, unless otherwise stated. The counter electrode was a commercial platinum wire electrode of the same manufacturer.

pH-values were measured with the micro combination glass electrode EGA 801 N ("Kurt Schwabe" Meinsberg) coupled to a MV 85-pH-meter (VEB Praecitronik, Dresden, G.D.R.). The glass electrode was calibrated with commercial standard buffers of pH 6.86 and pH 9.18.

The pH-values of the voltammetric sample solutions were measured before and immediately after each voltammetric run inside the electrochemical cell.

## RESULTS AND DISCUSSION

Our attempts to oxidize  $[\text{V(IV)O}(\text{nta})(\text{H}_2\text{O})]^-$  electrochemically were started as a conclusion from a paper of Nishizawa et al<sup>7b</sup>. In this paper, it was demonstrated that the outer-sphere oxidation of  $[\text{V(IV)O}(\text{nta})(\text{H}_2\text{O})]^-$  by chemical one-electron oxidants at pH < 5.5 occurs so fast ( $t_{1/2} < 10$  ms) that kinetic studies by stopped-flow methods were impossible. The following equation for the redox reaction under study was given



Electrooxidation of  $[\text{V(IV)O}(\text{nta})(\text{H}_2\text{O})]^-$  appears to be reversible in the electrochemical and the chemical sense, as well. Table I gives data for the CV's at three different scan rates at pH 6.7: the anodic ( $E_{\text{pa}}$ ) and cathodic ( $E_{\text{pc}}$ ) peak potentials, the difference between anodic and cathodic peak potentials ( $\Delta E_{\text{p}}$ ), and the difference between the anodic peak potential and the potential at half peak height ( $E_{\text{pa}} - E_{\text{pa}/2}$ ), respectively. The anodic peak current parameter  $i_{\text{pa}}v^{-1/2}$  ( $v$  scan rate) is constant with varying scan rate which confirms the diffusion control of the electrode process.

A further check of the reversibility of the electrochemical oxidation of  $[\text{V(IV)} \cdot \text{O(nta)(H}_2\text{O)}]^-$  has been obtained from the slope of the logarithmic plot of the polarographic wave which is close to the theoretical value of 59 mV for a one-electron Nernstian wave also in agreement with cyclic voltammetry yielding the separation of anodic and cathodic peak potentials  $\Delta E_p = 60$  mV).

As a medium boric acid/borate buffer was used in the present study. In a related study, where the redox couple  $[\text{V(V)O(ox)}_2^{3-}]/[\text{V(IV)O(ox)}_2(\text{H}_2\text{O})^{2-}]$  (ox oxalate) was investigated, we made the experience that borate in contrast to phosphate buffer is not able to substitute the coordinated water molecule at the V(IV)-center<sup>8</sup>. Despite of the fact that the buffering capacity of borate is limited in the neutral pH-range, we focused on this medium in order to avoid overlapping equilibria in which ternary complexes of the type  $[\text{V(IV)O(nta)X}]^{n-}$  (X e.g. phosphate) would be involved. To verify the electrode reaction (A), measurements of the half-wave potential  $E_{1/2}$  were made in the pH-range 5.5 to 9.0. At  $\text{pH} < 6.5$ , the  $E_{1/2}$ -values could be measured only by DPP because with decreasing pH the anodic limiting current is increasingly cut by the anodic dissolution limit of mercury. This evaluation is based on the relation

$$E_{1/2} = E_{pa} + \frac{1}{2} \Delta E, \quad (1)$$

TABLE I

Data for CV's of 0.5 mM  $[\text{V(N)O(nta)(H}_2\text{O)}]^-$  in 0.5M  $\text{H}_3\text{BO}_3$ , pH 6.7; SMDE 1, hanging mercury drop mode, different scan rates ( $\nu$ )

$\nu$ mV s <sup>-1</sup>	$E_{pa}$ mV	$E_{pc}$ mV	$\Delta E_p$ mV	$E_{pa} - E_{pa/2}$ mV	$i_{pa} \nu^{-1/2}$ $\mu\text{A mV}^{-1/2} \text{s}^{1/2}$
200	+60	-5	65	64	0.09
100	+60	-5	65	62	0.09
50	+60	0	60	60	0.09

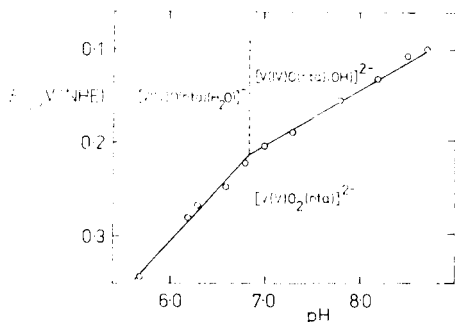


FIG. 1

Plot of the measured half-wave potentials vs  $\text{pH. Ag/AgCl/Cl}_{\text{sat}}^-$  vs NHE = +0.197 V (ref.<sup>15</sup>)

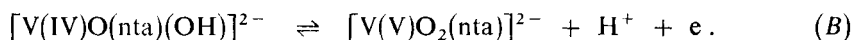
where  $E_{pa}$  is the peak potential of the DPP-peak when anodic pulses are used.  $\Delta E$  is the pulse amplitude and has a positive sign in this case<sup>9</sup>.

The DPP-measurements over the whole pH-range gave  $W_{1/2}$ -values ( $W_{1/2}$  potential separation at half peak height) which were close to the theoretical value of 90.5 mV for a Nernstian one-electron process<sup>9</sup>. The same was true for the slopes in the log plots of the current sampled DC polarography and the CV- $\Delta E_p$  values.

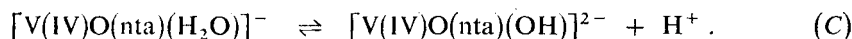
To establish the  $E_{1/2}$  vs pH-diagram in Fig. 1, values gained by all of the three voltammetric techniques mentioned were used. For individual pH-values, these  $E_{1/2}$ -values agree within  $\pm 5$  mV. From the data in Fig. 1 two segments with different slopes were obtained.

The slope of the line at pH < 6.84 is -114 mV/pH, i.e. the  $E_{1/2}$ -value is shifted in the cathodic direction with increasing pH. The value of 114 mV is close to the theoretical value of 118 mV for the case when a one-electron process is coupled with a two-proton transfer. In this way, the correctness of Eq. (A) was confirmed.

At pH > 6.84 a slope of -60 mV was obtained. This corresponds to the following electrode reaction:



The inflection point in the diagram of Fig. 1 is identical with the  $\text{p}K_a$  value of the coordinated water molecule in  $[\text{V(IV)O(nta)(H}_2\text{O)}]^-$ ,



The value of  $\text{p}K_a = 6.84$  agrees well with previously determined values by pH-potentiometry ( $\text{p}K_a = 6.9$ )<sup>7b</sup> and pH-titration with observation by EPR-spectroscopy<sup>10</sup>.

From the diagram in Fig. 1 no information can be gained in view of the actual concentration ratio of the species resulting from the equilibrium (B). It is quite clear that under our conditions even at pH < 6.84 considerable amounts of  $[\text{V(IV)O(nta)(OH)}]^{2-}$  are present in the bulk of the solution.

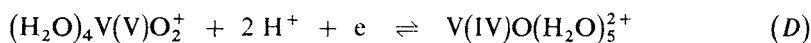
So, from our results no conclusions are possible with respect to the findings in ref.<sup>7b</sup> that the hydroxo-V(IV) complex is oxidized considerably faster than the aquo-V(IV) complex.

The unambiguity of the  $E_{1/2}$ -values determined in this work can be proved in the following way:

The formal potential of the  $[\text{V(V)O}_2(\text{nta})]^{2-}/[\text{V(IV)O(nta)(H}_2\text{O)}]^-$  couple can be calculated via the Nernst equation<sup>8,12</sup> as follows:

$$E_c^{0'} = E_{\text{aquo}}^{0'} - 0.059/n \log \frac{K_{\text{ox}}}{K_{\text{red}}} ; \quad (2)$$

$E_c^{0'}$  is the formal potential of the electrode reaction as defined in Eq. (A).  $E_{\text{aqu}}^{0'}$  is the formal potential of the electrode reaction of uncomplexed V(V) and V(IV) at pH 0:



The value is +1.00 V vs NHE (ref.<sup>8</sup>).  $K_{\text{ox}}$  and  $K_{\text{red}}$  are the complex stability constants as defined in Eqs (3) and (4)

$$K_{\text{ox}} = \frac{[\text{V}(\text{V})\text{O}_2(\text{nta})^{2-}]}{[\text{V}(\text{V})\text{O}_2^+][\text{nta}^{3-}]}, \quad K_{\text{red}} = \frac{[\text{V}(\text{IV})\text{O}(\text{nta})\text{H}_2\text{O}^-]}{[\text{V}(\text{IV})\text{O}^{2+}][\text{nta}^{3-}]} \quad (3), (4)$$

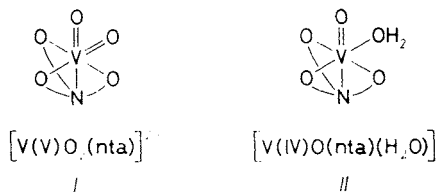
The values used were  $\log K_{\text{ox}} = 13.80$  and  $\log K_{\text{red}} = 10.82$  (ref.<sup>13</sup>). In this way, the formal potential of the complexed couple at pH 0 was calculated as  $E_c^{0'} = 0.824$  V vs NHE. With the known pH-dependence of the electrode reaction (Eq. (A)) the  $E_c^{0'}$  value is calculable according to

$$E^{0'}(\text{pH}) = +0.824 - 0.118 \text{ pH (V)}, \quad (5)$$

e.g. for pH 6 the value obtained was  $E_c^{0'}(\text{pH } 6.0) = +0.116$  V vs NHE. It agrees well with the measured value which is  $E_{1/2}(\text{pH } 6.0) = +0.105$  V vs NHE.

From the present results and our experience from related studies<sup>8</sup> it seems clear that reversible interconversion of V(IV) and V(V) can occur only when the appropriate V(IV) complex has a coordinated water molecule in *cis*-position to the V(IV)-oxo oxygen. Only in such cases highly structural similarity between the V(V) and V(IV) complexes is given. In this respect it should be borne in mind that V(V) occurs in its complexes (with only a few exceptions) in a *cis*-dioxo unit. When the *cis*-position in the V(IV) complex of concern is occupied by a donor atom of a chelate ligand, then the oxidation to V(V) is sterically hindered and the electron transfer is much slower. This was demonstrated for the  $[\text{V}(\text{IV})\text{OEDTA}]^{2-}/^{2-}\text{V}(\text{V})\text{O}_2\text{EDTA}]^{3-}$  couple<sup>14</sup>.

Assumed structures of the complexes involved in the electrode reaction studied are such as depicted by I and II.



In a forthcoming report we will show how electrode reactions of the type described here can be used for a parallel determination of V(V) and V(IV) by current sampled DC polarography on a static mercury drop electrode<sup>11</sup>.

## REFERENCES

1. Lahr S., Finckle H. O., Schultz F. A.: *J. Electroanal. Chem.* **163**, 237 (1984).
2. Pipes D. W., Meyer T. J.: *Inorg. Chem.* **25**, 3256 (1986).
3. Dobson J. C., Takeuchi K. J., Pipes D. W., Geselowitz D. A., Meyer T. J.: *Inorg. Chem.* **25**, 2357 (1986).
4. Meyer T. J.: *J. Electrochem. Soc.* **131**, 221C (1984).
5. Bond A. M.: *Modern Polarographic Techniques in Analytical Chemistry*. M. Dekker, New York 1980.
6. Chasteen N. D., Grady J. K., Holloway C. E.: *Inorg. Chem.* **25**, 2754 (1986).
- 7a. Nishizawa M., Saito K.: *Inorg. Chem.* **19**, 2284 (1980).
- 7b. Nishizawa M., Sasaki Y., Saito K.: *Inorg. Chem.* **24**, 767 (1985).
8. Meier R.: *Thesis*. Karl Marx University, Leipzig 1985.
9. Bard A. J., Faulkner L. R.: *Electrochemical Methods*. J. Wiley, New York 1980.
10. Meier R., Werner G., Stach J., Kirmse R., Dunsch L.: *Z. Chem.* **28**, 370 (1988.)
11. Meier R., Werner G., Otto M.: Unpublished results.
12. Meites L.: *Polarographic Techniques*, 2nd ed., p. 279. J. Wiley, New York 1965.
13. Anderegg G.: *Pure Appl. Chem.* **54**, 2693 (1982).
14. Sasaki Y., Okazaki K., Nagasawa A., Saito K.: *Inorg. Chem.* **24**, 772 (1985).
15. Ackermann G. (Ed.): *Komplexes Lehrwerk Chemie-LB 5: Elektrolytgleichgewichte und Elektrochemie*, p. 93. VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1977.