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Studies of Electrode Processes of Oxovanadium(IV). IV. Catalytic Reduction of Acetylacetone Coupled with Cathodic Reduction of Bis(acetylacetonato)oxovanadium(IV)

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Acetylacetone was catalytically reduced in the course of the electrolytic reduction of bis(acetylacetonato)-oxovanadium(IV) at a mercury cathode. In acetonitrile solutions the catalytic reduction proceeded at −2.1 V *vs.* Ag/0.01 mol dm^{-3} $AgClO_4$ electrode and the reduction products were hydrogen and acetylacetonate anion, while by the direct electrolysis of acetylacetone at −2.5 V a product with vicinal hydroxyl groups was formed. A steady-state current was observed in the controlled potential electrolysis. A reaction mechanism involving the regeneration of trivalent vanadium by the coupled chemical reaction of divalent vanadium with acetylacetone is proposed.

The electrochemical or photochemical behavior of oxovanadium(IV) complexes has been reported in previous papers.[1-3] Although in acetonitrile solution containing a large excess of acetylacetone (Hacac) a well-defined polarographic cathodic wave of bis(acetylacetonato)oxovanadium(IV), $[VO(acac)_2]$, was developed in a single step with two-electron transfer, only trivalent vanadium was detected in the solution subjected to controlled potential electrolysis at −2.1 V *vs.* Ag/0.01 M $AgClO_4$ electrode (M=mol dm^{-3}). The processes involved therein were postulated as follows:

(1) One-electron transfer to break a V–O bond;

$$[VO(acac)_2] + e^- + \text{Hacac} \longrightarrow [V(acac)_3] + OH^-. \qquad (1)$$

(2) Further one-electron transfer to form divalent vanadium;

$$[V(acac)_3] + e^- \longrightarrow [V(acac)_3]^-. \qquad (2)$$

Reaction 1 proceeded at a more negative potential ($E_{1/2}=-1.93$ V) than Reaction 2 ($E_{1/2}=-1.78$ V) owing to the strong V–O bond and ligand rearrangement. Reactions 1 and 2 may be followed by the reaction of OH^- with Hacac or of $[V(acac)_3]^-$ with $[VO(acac)_2]$, thus forming $acac^-$ or $[V(acac)_3]$. But, the concentration of $acac^-$ was found to increase even after the vanadyl species was depleted completely in the solution, suggesting another route in the reaction sequence.

The evidence for catalytic regeneration of trivalent vanadium by a coupled chemical reaction of divalent vanadium with Hacac is presented in this paper, and the reaction mechanism is discussed.

Experimental

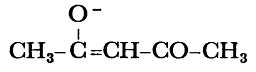
An ordinary polarograph and a potentiostat were used, and the UV and visible absorption spectroscopy and vapor phase chromatography were employed for subsidiary purposes.

For the controlled potential electrolysis a three-compartment cell separated by sintered glass diaphragms was used. A mercury pool cathode was stirred by a magnetic bar, and the solution was agitated by bubbling purified nitrogen through it. For measurements of steady-state current, vigorous agitation was essential in order to obtain reproducible data. The reference electrode was Ag/0.01 M $AgClO_4$ electrode.

Solutions were prepared by using purified acetonitrile, which contained a trace of water. The supporting electrolyte was tetraethylammonium perchlorate (TEAP). The prepared solution was deaerated carefully by bubbling purified nitrogen through it. Experiments were carried out at room temperature.

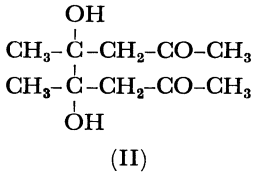
Results and Discussion

Reduction Mechanism of Acetylacetone. Acetylacetone in an acetonitrile solution containing 0.1 M TEAP developed an irreversible polarographic cathodic wave at about −2.3—−2.4 V, the reduction potential being largely shifted with the concentration of Hacac. After the reduction of Hacac by the controlled potential electrolysis at −2.5 V, the polarogram showed an anodic wave at −0.45 V corresponding to the anodic process of $acac^-$. The absorption spectra before and after the electrolysis are shown in Fig. 1. The wavelengths of the absorption maximum, 273 nm for Hacac and 293 nm for $acac^-$, coincide well with Neal and Murray's data.[4] The difference between our results and Neal and Murray's data can be attributed to the difference in reaction mechanisms, as will be described later. Neal and Murray used a thin layer cell for the electrolysis of Hacac in acetonitrile, and confirmed $acac^-$ (I) to be the main reduction product. In addition to $acac^-$, in our case where an ordinary electrolysis cell was used, the existence of vicinal hydroxyl groups was confirmed in the reduction products by means of the periodate titration. It is highly likely that the product is 4,5-dihydroxy-4,5-dimethyl-2,7-octanedione (II). This estimate is supported by the formation of pinacol as a dimeric product of the reduction of 1,3-diphenyl-1,3-propanedione in DMSO as reported by Buchta and Evans.[5] Vapor phase chromatography indicated that an ether extract from the electrolyzed solution contained two dominant species which appeared



$CH_3\text{-}\overset{O^-}{\overset{|}{C}}\text{=CH-CO-}CH_3$

(I)



$\begin{array}{c} OH \\ | \\ CH_3\text{-}C\text{-}CH_2\text{-CO-}CH_3 \\ | \\ CH_3\text{-}C\text{-}CH_2\text{-CO-}CH_3 \\ | \\ OH \end{array}$

(II)

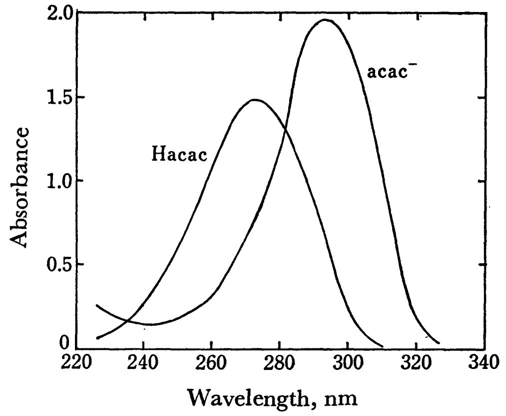


Fig. 1. Absorption spectra of 0.22 mM Hacac in acetonitrile solution before and after controlled potential electrolysis at −2.5 V.

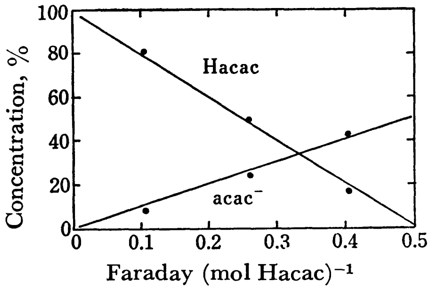


Fig. 2. Relative change in concentrations of Hacac and acac$^-$ in the course of controlled potential electrolysis of Hacac at −2.5 V. Solution: 1 mM Hacac in acetonitrile solution containing 0.1 M TEAP.

at far later stages compared with the retention time of pinacol derived from acetone. Unfortunately, the direct confirmation of these compounds was unsuccessful, owing to their extreme instability and rapid decomposition during the isolation procedure.

The relative concentration changes in both Hacac and acac$^-$ during the course of the controlled potential electrolysis were monitored by using an ordinary polarograph. The result is shown in Fig. 2, where the ordinate and abscissa are expressed in terms of the concentration ratio in % and electricity consumed in Faraday mol^{-1}, respectively. As is seen in Fig. 2, the descending line intersects the abscissa at about 0.5 Faraday mol^{-1}. This indicates that the number of electrons transferred per molecule (n) is equal to 0.5. The increase of the concentration of acac$^-$ was no longer observed after 0.5 Faraday mol^{-1} was consumed. Since the increment of acac$^-$ is exactly one half of the decrement of Hacac, it is concluded that one mol of acac$^-$ is produced from two mol of Hacac. Taking the product with vicinal hydroxyl groups into consideration, the reaction scheme can be expressed as follows:

$$4\ \text{enol–Hacac} + 2e^- \longrightarrow \text{Dimer} + 2\text{acac}^-. \qquad (3)$$

In reaction 3 a proton abstraction by an acetylacetone anion radical from an acetylacetone molecule is assumed to be involved.

This reaction mechanism is consistent with the observed facts, but inconsistent with the result obtained by Neal and Murray,[3] who concluded that the reaction proceeded as follows:

$$\text{Hacac} + e^- \longrightarrow \text{Hacac}^{\overline{\cdot}} \longrightarrow \frac{1}{2}\text{H}_2 + \text{acac}^-. \qquad (4)$$

According to the reaction mechanism of Eq. 4, the stoichiometric molar ratio of Hacac and acac$^-$ is 1 : 1. The difference between Reactions 3 and 4 is clearly shown when we compare the ratio of absorbance of Hacac and acac$^-$ in Fig. 1 of this report and Fig. 1 of Ref. 4. The difference in the reaction mechanisms seems to be attributed to the experimental techniques employed. In the thin layer cell used by Neal and Murray, most of the depolarizer undergoes the electrode reaction without any complication such as proton abstraction or dimer formation, and the reaction intermediate seems to decompose directly to hydrogen and acac$^-$.

Bis(acetylacetonato)oxovanadium(IV) dissolved in the acetonitrile solution containing an amount of Hacac 20 times excess in molar ratio was reduced at a dropping mercury electrode with the half-wave potential of −2.00 V; the reduction product was divalent vanadium, as shown in Eqs. 1 and 2. In polarograms observed *in situ* in solutions subjected to the controlled potential electrolysis at −2.1 V the same anodic wave was observed at −0.45 V as in the case of the direct electrolytic reduction of Hacac. But in this case no dimeric product with vicinal hydroxyl groups could be detected. The relative concentration changes of Hacac and acac$^-$ during the course of the controlled potential electrolysis are shown in Fig. 3. The concentration change of oxovanadium(IV) ions in Fig. 3 was separately measured spectrophotometrically at the wavelength of 700 nm by using 3 mM bis(acetylacetonato)oxovanadium(IV) solution. As shown in Fig. 3, oxovanadium(IV) ions are quickly depleted with a coulombic efficiency of about 1 faraday mol^{-1}. The concentration of acac$^-$ increased steadily even after the oxovanadium(IV) ions were depleted completely. The increment of acac$^-$ at each quantity of electricity consumed was exactly equal to the decrement of Hacac, as shown in Fig. 3, so that the stoichiometric molar ratio of acac$^-$ and Hacac was 1 : 1. The extrapolation of the descending line gives an

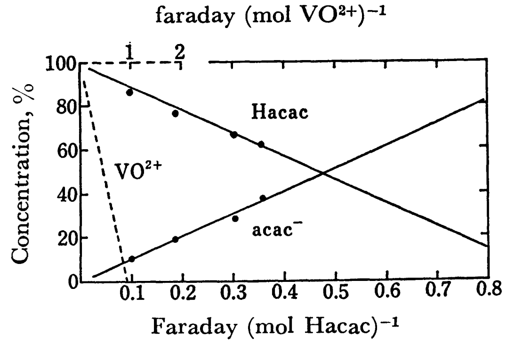


Fig. 3. Relative change in concentrations of VO^{2+}, Hacac and acac$^-$ in the course of controlled potential electrolysis of VO^{2+} at −2.1 V. Solution: 1 mM [VO(acac)$_2$] and 20 mM Hacac in acetonitrile solution containing 0.1 M TEAP. (Refer to the text in relation to the concentration change of VO^{2+}.)

intercept at about 1 F mol^{-1}. This result indicates that the value of *n* is unity. It is noteworthy that this result coincides well with Neal and Murray's result. In view of these findings the following reaction mechanism is deduced:

$$[V(acac)_3]^- + Hacac \longrightarrow [V(acac)_3] + Hacac^{\cdot}, \quad (5)$$

$$Hacac^{\cdot} \longrightarrow \frac{1}{2}H_2 + acac^-. \quad (6)$$

Reaction 2 is coupled with Reaction 5, so that Hacac is catalytically reduced by a regenerative cycle of vanadium(II). This mechanism is also supported by the fact that the limiting current of oxovanadium(IV) ion shows the characteristics of kinetic current, as shown previously in Ref. 2. The formation of a dimeric product by Reaction 3 does not seem to be involved in this case.

Steady-state Current in Controlled Potential Electrolysis. When a solution containing a known quantity of oxovanadium(IV) ion and 20 times excess of Hacac was electrolyzed at −2.1 V, the electrolytic current decreased gradually and attained a steady-state value in a few minutes. The plot of the steady-state current, i_{st}, *versus* the concentration of oxovanadium(IV), C_y, is shown in Fig. 4, where i_{st} is linearly proportional to C_y up to the concentration of 0.6 mM. As described in the previous paper,[2] the color of the electrolyzed solution turned to greenish yellow and finally to dark green. The dark green color indicates the existence of divalent vanadium in the solution bulk, but it promptly fades to yellow on being left to stand in a nitrogen atmosphere. The yellow solution was cathodically reduced to form divalent vanadium at −1.78 V. Therefore, it is concluded that the oxidation of divalent vanadium by Hacac proceeds fairly rapidly, and thus the concentration of trivalent vanadium in the bulk solution is kept practically constant. Under this condition, the electrolytic current flowing through the cell can be expressed by the following equation:

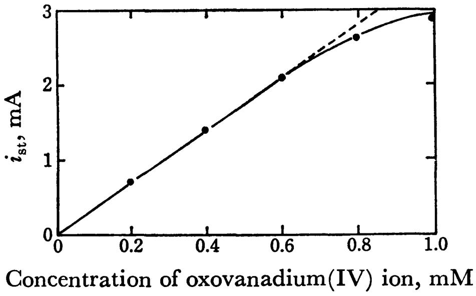


Fig. 4. Dependence of steady-state current on concentration of oxovanadium(IV) ion.

$$i_{st} = nFADC_y/\delta, \quad (7)$$

where A is the surface area of the mercury cathode, the concentration of trivalent vanadium in the bulk solution is practically equal to C_y, δ is the thickness of the diffusion layer, C_y/δ the concentration gradient of trivalent vanadium in the diffusion layer, and the other symbols have their usual meanings. It is noteworthy that in the ordinary case C_y is time deptendent, but in this special case C_y can be treated as a constant.

By introducing numerical data in Eq. 7 ($i_{st}/C_y = 3.5 \times 10^3$ amp mol^{-1} cm^3, $n = 1$, $A = 12.6$ cm^2, and $D = 6 \times 10^{-6}$ cm^2 s^{-1}), we obtain the value of δ to be about 3×10^{-3} cm. This value seems to be reasonable in view of the controlled potential electrolysis with vigorous stirring of the solution.

At the final stage of the controlled potential electrolysis at −2.1 V the steady-state current decreased, and the electrolyzed solution gave no more cathodic wave. This indicates that the regenerative cycle of trivalent vanadium by the coupled chemical reaction ceases owing to the depletion of Hacac.

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