59654-65-8; $(C_6H_5)_3SnMn(CO)_4P(C_6H_{11})_3$, 59654-66-9; $[C_5Me_5Fe(CO)_2]_2$, 35344-11-7; $Hg(S_2CFe(CO)_2C_5H_5)_2$, 59654-68-1; $Cr(S_2CFe(CO)_2C_5H_5)_3$, 59654-67-0; $(C_6H_{11})_3P(CO)_4MnCS_2^-$, 59654-69-2; $Re(CO)_5^-$, 14971-38-1; $Re(CO)_5CS_2^-$, 59654-70-5; CS_2, 75-15-0.

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Chemistry and Electrochemistry of the Vanadium–Carbonyl System

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Received January 22, 1976 AIC60053Z

The chemistry and electrochemistry of the vanadium–carbonyl system are very solvent dependent. In acetone solution, electrochemical studies on the hexacarbonylvanadate(–I) anion show a reversible $V(CO)_6^-/V(CO)_6$ couple. However, chemically synthesized $V(CO)_6$ disproportionates in acetone to V^{2+} and $V(CO)_6^-$ and has no long-term stability in this or other coordinating solvents. By contrast, in dichloromethane solution, $V(CO)_6$ whether generated chemically or electrochemically, is stable and a reversible $V(CO)_6^-/V(CO)_6$ couple is observed using both $V(CO)_6^-$ and $V(CO)_6$ as the starting material. Oxidation of $V(CO)_6$ is irreversible in both solvents and the species $V(CO)_6^+$ appears to have no inherent stability under any of the conditions examined. Interesting redox reactions occur when solutions of $[V((CH_3)_2CO)_6^{2+}][V(CO)_6^-]_2$ are diluted in dichloromethane, or alternatively when the acetone is removed under vacuum, to generate $V(CO)_6$.

Introduction

Hexacarbonylvanadium, $V(CO)_6$, is known to disproportionate in two ways on reaction with ligands. Calderazzo[1] found it reacted with arenes to give $[V(CO)_4\text{arene}^+][V(CO)_6^-]$, i.e., V^+ and V^-, but in contrast Hieber and coworkers[2,3] found that most oxygen and nitrogen donors, including common organic solvents such as acetone, gave products of the type $[VL_x^{2+}][V(CO)_6^-]_2$, i.e., V^{2+} and $2V^-$.

No detailed electrochemical studies on the vanadium–carbonyl system have been reported, although a brief mention of the reduction of $V(CO)_6$ has appeared in a recent publication.[4]

In this paper we present detailed electrochemical data on both $V(CO)_6$ and the diglyme-stabilized sodium salt of $V(CO)_6^-$ in both acetone and dichloromethane solutions. The marked differences in electrochemical behavior between the two solvents led to a study of some interesting redox reactions which occur on changing the solvent.

Experimental Section

Electrochemistry. Polarograms at a dropping mercury electrode (controlled drop time 0.5 s) and cyclic voltammograms at a platinum disk electrode were recorded with a Princeton Applied Research Corp. Model 170 electrochemistry system. A three-electrode system incorporating positive feedback circuitry to minimize the *IR* drop was

Table I. Polarographic Data Obtained for the Vanadium–Carbonyl System[a]

Compd	Electrode process	Acetone		Dichloromethane	
		$E_{1/2}$,[b] V	$\lvert E_{1/4} - E_{3/4}\rvert$, mV	$E_{1/2}$,[b] V	$\lvert E_{1/4} - E_{3/4}\rvert$, mV
$[Na(diglyme)_2][V(CO)_6]$	$V(CO)_6^- \rightleftharpoons V(CO)_6 + e^-$	0.32	56	0.23	56
	Oxidn of $V(CO)_6$			0.9[c]	80[c]
$V(CO)_6$	$V(CO)_6 + e^- \rightleftharpoons V(CO)_6^-$			0.23	56
	Oxidn of $V(CO)_6$			0.9[c]	80[c]

[a] Drop time 0.5 s; temperature 20 ± 2 °C. [b] Measured vs. Ag/AgCl. [c] The electrode process designated as oxidation of $V(CO)_6$ in dichloromethane occurs close to the mercury limit and cannot by characterized accurately.

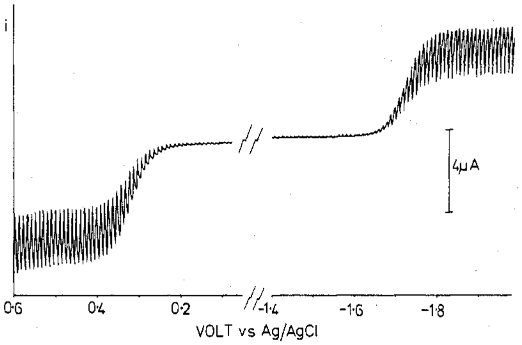

Figure 1. Dc polarogram of $[Na(diglyme)_2^+][V(CO)_6^-]$ in acetone (0.1 M Et_4NClO_4). Reduction wave is the electrode process $Na^+ + e^- \rightleftharpoons Na(Hg)$ and the oxidation wave is the electrode process $V(CO)_6^- \rightleftharpoons V(CO)_6 + e^-$.

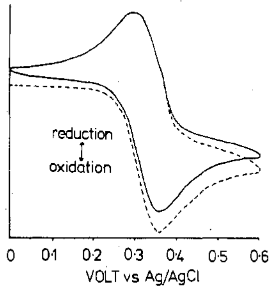

Figure 2. Cyclic voltammogram of the $V(CO)_6^- \rightleftharpoons V(CO)_6 + e^-$ oxidation in acetone (0.1 M Et_4NClO_4); scan rate 200 mV/s: first scan, - - - -; second scan, ——.

used for all measurements. Platinum was used as the auxiliary electrode and Ag/AgCl (0.1 M LiCl, acetone) as the reference electrode in both acetone and dichloromethane solvent systems.

For electrochemistry in acetone, 0.1 M Et_4NClO_4 was used as the supporting electrolyte. The salt bridge separating the reference electrode from the test solution also contained 0.1 M Et_4NClO_4 (acetone). With dichloromethane as solvent the supporting electrolyte was 0.2 M Bu_4NClO_4.

Solutions for electrochemical investigation were prepared in the 5×10^{-4} to 2×10^{-3} M concentration range by adding the solid compound to thoroughly deoxygenated solutions of solvent and supporting electrolyte. All measurements were made under a blanket of argon, in the dark, and at temperatures of 20 ± 2 °C unless otherwise stated. Low-temperature cyclic voltammograms were recorded at −78 °C using dry ice/acetone as a thermostating system and a saturated solution of the appropriate perchlorate salt as the supporting electrolyte.

Chemicals. $[Na(diglyme)_2^+][V(CO)_6^-]$ was obtained commercially (Strem Chemicals) and used without further purification. Hexacarbonylvanadium was prepared by the action of orthophosphoric acid on the hexacarbonylvanadate(−I) and separated by vacuum sublimation.[5] All solvents were of AR standard.

Determination of Volume of Gas Evolved. Direct determinations were made of the number of moles of CO evolved when acetone and diglyme reacted with $V(CO)_6$ in order to confirm the mode of disproportionation. Excess solvent was poured onto a known quantity of $V(CO)_6$ in a small tube by rotating a side arm in the apparatus. The volume of gas evolved was measured directly by collecting the gas over water in a graduated tube.

Results and Discussion

(A) Electrochemistry in Acetone. (i) Polarography of $[Na(diglyme)_2^+][V(CO)_6^-]$. In acetone the sodium diglyme salt of $V(CO)_6^-$ gives two extremely well-defined reversible waves as shown in Figure 1. The reduction wave is attributed to the sodium ion

$$Na^+ + e^- \rightleftharpoons Na(Hg) \qquad (1)$$

and the oxidation to the process

$$V(CO)_6^- \rightleftharpoons V(CO)_6 + e^- \qquad (2)$$

The sodium reduction wave is not of interest in the present work and will be omitted from subsequent discussion. However, since the limiting currents of both waves are almost equal and the sodium wave is known to have an *n* value of 1, this factor combined with the analysis of the wave shape unambiguously defines the oxidation of $V(CO)_6^-$ as being a reversible one-electron step and suggests that $V(CO)_6$ is stable in acetone. Data and electrochemical parameters are summarized in Table I.

The solution of $V(CO)_6^-$ showed a sharp band at 1860 cm^{-1} in its infrared spectrum. This combined with the polarographic data confirms the absence of $V(CO)_6$ or other carbonyl species; this result should be compared with subsequent data.

(ii) Polarography of $V(CO)_6$. On addition of blue $V(CO)_6$ to acetone considerable evolution of gas occurs and a yellow solution is obtained. The infrared spectrum of the solution contains only the 1860-cm^{-1} peak for $V(CO)_6^-$ and polarograms are identical with that described above for $[Na(diglyme)_2^+][V(CO)_6^-]$, except of course that the sodium wave was absent. Despite the fact that polarographic data indicate that $V(CO)_6$ is stable in acetone, this is obviously not true under synthetic conditions. The apparent difference between the two sets of data is of course explicable in terms of the different time scales. In the polarographic experiments the time scale is governed by the drop time (0.5 s) and with this time scale $V(CO)_6$ is observed to be stable. Thus, while $V(CO)_6$ is moderately stable, it obviously decomposes under synthetic conditions where a time scale of minutes operates.

Quantitative measurements showed that the limiting current per unit concentration for $V(CO)_6$ was two-thirds that of $V(CO)_6^-$, demonstrating that in acetone the following disproportionation occurs

$$3V(CO)_6 \rightarrow V(II) + 2V(CO)_6^- + 6CO \qquad (3)$$

This is in agreement with previously reported reactions of $V(CO)_6$ with coordinating ligands[2,3] where species such as $[VL_6][V(CO)_6]_2$ (L = acetone, THF) and $[V(L\text{-}L)_3][V(CO)_6]_2$ (L-L = *o*-phenanthroline) have been isolated.

(iii) Cyclic Voltammetry of $[Na(diglyme)_2][V(CO)_6]$. A cyclic voltammogram of the $V(CO)_6^-$ salt in the potential range 0–0.6 V vs. Ag/AgCl is shown in Figure 2. Despite the fact that $V(CO)_6$ does not exist in acetone under preparative conditions, this figure shows unambiguously that the $V(CO)_6^-/V(CO)_6$ couple is chemically reversible with respect

Table II. Cyclic Voltammetry Data for the Vanadium-Carbonyl System[a]

		Acetone			Dichloromethane		
Compd	Electrode process	$(E_p)_{Ox}$	$(E_p)_{Red}$	$E_{1/2}$	$(E_p)_{Ox}$	$(E_p)_{Red}$	$E_{1/2}$
$[Na(diglyme)_2][V(CO)_6]$	Oxidn of $V(CO)_6^-$	0.36	0.30	0.34	0.32	0.22	0.29
	Oxidn of $V(CO)_6$	0.78		0.76	0.96		0.93
	Third (most positive) oxidn process	1.05		1.03	1.12		1.09
$V(CO)_6$	Reducn of $V(CO)_6$				0.32	0.22	0.21
	Oxidn of $V(CO)_6$				0.96		0.93
	Most positive oxidn process				1.12		1.09

[a] Scan rate 200 mV/s; temperature 20 ± 2 °C. All potentials in volts measured vs. Ag/AgCl.

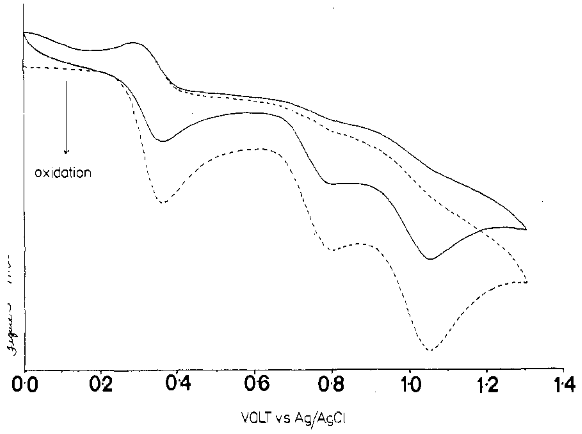

Figure 3. Cyclic voltammogram of $V(CO)_6^-$ showing all oxidation steps in acetone (0.1 M Et_4NClO_4); scan rate 200 mV/s: first scan, - - - -; second scan, ——.

to the time scale of cyclic voltammetry. The $E_{1/2}$ value at platinum (Table II) is very similar to that obtained at the dropping mercury electrode.

Scanning toward more positive potentials reveals the presence of further oxidation waves at platinum as shown in Figure 3. Peak potentials and other data are given in Table II. The $V(CO)_6^-/V(CO)_6$ couple is modified by reaction with the products of the additional oxidation process (cf. Figures 2 and 3). Thus the peak height of the first reverse scan, corresponding to reduction of $V(CO)_6$, is approximately halved and all peak heights subsequent to the first forward scan are markedly decreased in height. After the first cycle, the current–potential curves are almost reproducible. This phenomenon occurs also with scans over the potential range 0–0.9 V vs. Ag/AgCl showing that the distortion of the $V(CO)_6^-/V(CO)_6$ couple emanates from a process occurring in the second oxidation step.

Since the first oxidation wave can be described by eq 2, the second oxidation wave can be written as

$$V(CO)_6 \rightleftharpoons V(CO)_6^+ + e^- \qquad (4)$$
$$\Big\downarrow \text{very fast (loss of CO and substitution by solvent, or disproportionation)}$$
$$\text{products}$$

Under synthetic conditions the final product is[2] $[V((CH_3)_2CO)_6][V(CO)_6]_2$, but on the electrochemical time scale other species are probably present at the electrode surface. A feature of the second oxidation wave was its complete lack of chemical reversibility. Even at temperatures as low as −78 °C and by using scan rates as high as 200 V/s, no reduction was seen on the reverse scan and $V(CO)_6^+$ has no inherent stability in acetone. However, at low temperatures (−78 °C) the anomalous behavior on the second and subsequent scans was no longer evident. In view of the uncertainty of the product of the second oxidation step, the third (most positive) oxidation wave cannot be interpreted satisfactorily at this stage.

The cyclic voltammetry of $V(CO)_6$ dissolved in acetone was essentially identical with that for $V(CO)_6^-$, in agreement with the polarographic data that this species is generated via the disproportionation in eq 3.

(B) Chemistry of $V(CO)_6$ in Acetone. When blue $V(CO)_6$ is dissolved in acetone, a yellow or orange solution (depending on concentration) containing $[V((CH_3)_2CO)_6][V(CO)_6]_2$ is obtained.[2] The infrared spectrum in the carbonyl region shows that $V(CO)_6^-$ is the only carbonyl-containing species present. Quantitative measurements of the amount of CO evolved on dissolution showed that 2 mol is produced for each mole of $V(CO)_6$ in agreement with eq 3.

However, if the acetone solution is evaporated under vacuum, the solution deepens in color (a concentration effect according to *IR* monitoring), but when small volumes of acetone remain, blue $V(CO)_6$ is evolved and can be trapped out with the acetone. The remaining yellowish brown solid is extremely unstable, and after attempts to grind it for infrared spectral examination it suddenly turned deep blue. The infrared spectrum of this material in Nujol showed the presence of $V(CO)_6$, $V(CO)_6^-$, and acetone. If the solid from the acetone solution is warmed under vacuum, it generates further $V(CO)_6$ and the residue is fiercely air sensitive.

If the solid obtained from an acetone solution of $V(CO)_6$ at room temperature is dissolved in dichloromethane and the infrared spectrum is run immediately, it shows the presence of both $V(CO)_6$ (1965 cm^{-1}) and $V(CO)_6^-$ (1860 cm^{-1}). Similarly an acetone solution of $[V((CH_3)_2CO)_6][V(CO)_6]_2$ rapidly generates $V(CO)_6$ on pouring into a large excess of dichloromethane [$V(CO)_6$ exists in CH_2Cl_2—see later].

Our rationalization for these seemingly perplexing reactions is that $V(CO)_6$ disproportionates in acetone to give $[V((CH_3)_2CO)_6][V(CO)_6]_2$. However acetone is apparently only a weak ligand and may be removed by pumping or by displacement by a diluting solvent. The resulting "V^{2+}" then oxidizes $V(CO)_6^-$ to $V(CO)_6$

$$[V((CH_3)_2CO)_6][V(CO)_6]_2 \xrightarrow{CH_2Cl_2} \text{“}V^{2+}\text{”} + 2V(CO)_6^- + \text{acetone} \qquad (5)$$
$$\text{“}V^{2+}\text{”} + V(CO)_6^- \rightarrow V(CO)_6 + \text{“}V^{+}\text{”}$$

leaving both $V(CO)_6$ and $V(CO)_6^-$ in solution.

An alternative way of considering the above reactions is to consider the two possible disproportionation steps

$$3V(CO)_6 \rightleftharpoons V^{2+} + 2V(CO)_6^- + 6CO \qquad (6a)$$
$$2V(CO)_6 \rightleftharpoons V^+ + V(CO)_6^- + 6CO \qquad (6b)$$

Subtraction of (6b) from (6a) gives

$$V(CO)_6 + V^+ \rightleftharpoons V^{2+} + V(CO)_6^- \qquad (6c)$$

and the thermodynamically favored direction of this reaction can be seen to be governed by the relative free energies of the two disproportionation reactions, which in turn could be very solvent dependent. In acetone, apparently (6a) is the preferred one. However, on addition of CH_2Cl_2 or on decreasing the concentration of acetone by pumping, the reverse of (6c) is postulated to occur. Effectively, this is equivalent to saying that in CH_2Cl_2 eq 6b becomes more favorable than is the case in acetone. It is worth noting that the isoelectronic $Cr(CO)_5I$

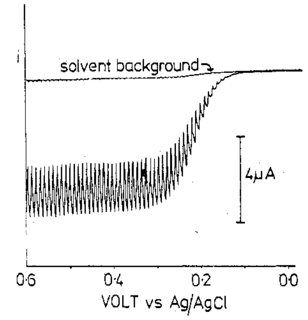

Figure 4. Dc polarogram of $[Na(diglyme)_2^+][V(CO)_6^-]$ in dichloromethane (0.2 M Bu_4NClO_4).

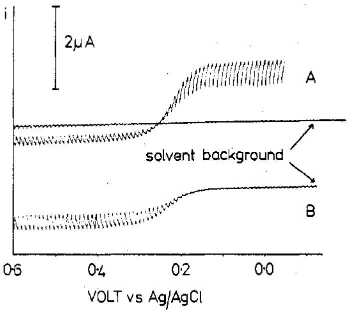

Figure 5. A. Dc polarogram of $V(CO)_6$ in dichloromethane (0.2 M Bu_4NClO_4). B. Polarogram of $V(CO)_6$ in dichloromethane (0.2 M Bu_4NClO_4) after exposure to the air.

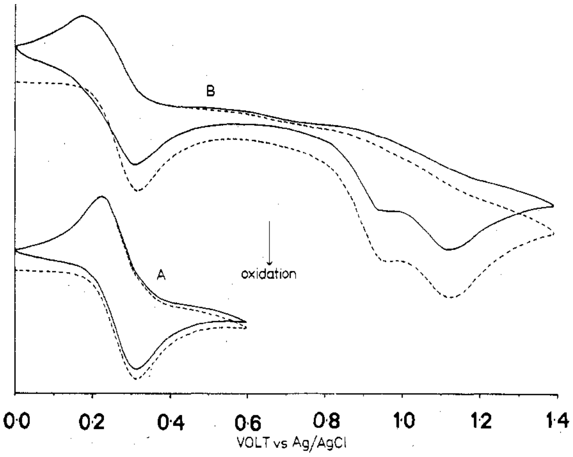

Figure 6. Cyclic voltammogram for oxidation of $V(CO)_6^-$ in dichloromethane (0.2 M Bu_4NClO_4); scan rate 200 mV/s: A, scan of the electrode process $V(CO)_6 + e^- \rightleftharpoons V(CO)_6^-$; B, scan of all processes.

disproportionates in both acetone and dichloromethane in a manner analogous to (6b)[6] and of course the reaction between $V(CO)_6$ and arenes[1] may be rationalized in terms of this equation.

We have no evidence to suggest that "V^+" and "V^{2+}" are bare cations and they may still be coordinated to acetone or dichloromethane, but the final species $[\text{"}V^+\text{"}][V(CO)_6^-]$ is extremely air and moisture sensitive. It is interesting to note that Calderazzo[1] postulated the formation of $V^+[V(CO)_6^-]$ or $V^{2+}[V(CO)_6^-]_2$ as a product of the interaction of $V(CO)_6$ and arenes. This result would be consistent with our data.

(C) Electrochemistry in Dichloromethane. (i) Polarography of $[Na(diglyme)_2]V(CO)_6$. $V(CO)_6^-$ gives two polarographic oxidation waves in CH_2Cl_2. Figure 4 shows the first reversible one-electron wave corresponding to the reaction $V(CO)_6^- \rightleftharpoons V(CO)_6 + e^-$. This figure shows clearly via reference to the solvent or baseline current that no $V(CO)_6$ is present (cf. $V(CO)_6$—below). The second oxidation wave, not seen in acetone, has a larger limiting current per unit concentration than the first, but its proximity to the mercury oxidation precluded quantitative measurements.

(ii) Polarography of $V(CO)_6$. Blue $V(CO)_6$ dissolves in distilled CH_2Cl_2 to give a yellow solution, usually accompanied by a small amount of gas evolution. Infrared monitoring of the solution shows that the vanadium exists almost exclusively as $V(CO)_6$ with a trace of $V(CO)_6^-$ being present. On exposure to the air, gas is evolved, a brown precipitate forms, and the intensity of the infrared absorption due to $V(CO)_6$ decreases. No growth of the $V(CO)_6^-$ peak occurs, but this is thought to be due to the precipitation of a sparingly soluble $V(CO)_6^-$ salt (see below).

Figure 5A shows the polarographic wave obtained from a freshly prepared solution of $V(CO)_6$ in dry CH_2Cl_2. Reference to the background current shows that while the wave has a majority of reductive component, there is a proportion of oxidative component. This demonstrates that the solution contains some $V(CO)_6^-$ although, unlike in acetone solution, $V(CO)_6$ has a finite existence on the preparative time scale. We believe that the $V(CO)_6^-$ results from disproportionation of $V(CO)_6$ in the presence of moisture unavoidable in the polarographic cell or from diglyme which distills over with the $V(CO)_6$ during its preparation. (Quantitative measurements showed that 2 mol of CO is evolved per mole of $V(CO)_6$ by reaction with diglyme.)

Figure 5B shows the polarogram obtained on the same solution after standing in the absence of the argon purge for about 5 min. This polarogram shows that the solution now contains only $V(CO)_6^-$. Disproportionation is also evident from the limiting current behavior. We postulate that water is behaving in the same manner as described for acetone, that is, disproportionation of $V(CO)_6$ occurs with the formation of $[V(H_2O)_n][V(CO)_6]_2$ and/or $[V(H_2O)_n][V(CO)_6]$, and that it is this product which precipitates on exposure to the air (see above). As expected, an oxidation wave near the mercury limit, as seen for $V(CO)_6^-$, is also observed in the polarography of $V(CO)_6$ in CH_2Cl_2.

Confirmation that the disproportionation reaction for $V(CO)_6$ in CH_2Cl_2 is a direct consequence of the presence of a coordinating species was obtained by the direct addition of each of diglyme, triphenylphosphine, 2,2′-bipyridyl, and bis(diphenylphosphino)methane. All ligands caused $V(CO)_6$ to be converted to $V(CO)_6^-$, although the rates varied substantially. The isolation of $V(CO)_5PPh_3^-$ from addition of PPh_3 to solutions of $V(CO)_6$ in ether[2] suggests that substitution of $V(CO)_6^-$ occurs after disproportionation.

(iii) Cyclic Voltammetry of $[Na(diglyme)_2][V(CO)_6]$ in CH_2Cl_2. Figure 6A shows the cyclic voltammogram of $[Na(diglyme)_2][V(CO)_6]$ in CH_2Cl_2 over the potential range 0–0.6 V vs. Ag/AgCl. Figure 6B shows the cyclic voltammogram over the extended range 0–1.4 V vs. Ag/AgCl. The modification of the reversible $V(CO)_6^-/V(CO)_6$ couple on proceeding to the second oxidation wave is clearly revealed by comparing the two scans. The substantial distortion to the $V(CO)_6^-/V(CO)_6$ couple is demonstrated by the observation that the peak to peak separation increased from 85 to 145 mV on extending the switching potential to more positive potentials (scan rate 200 mV/s). This distortion is different from that in acetone. Also different from the acetone solvent system is the fact that the second and third oxidation waves are not completely resolved and the separation in peak potentials between the first and second oxidation waves is considerably larger. This and other comparative data are contained in Table II.

(iv) Cyclic Voltammetry of $V(CO)_6$ in CH_2Cl_2. Figure 7 shows cyclic voltammograms of $V(CO)_6$ in CH_2Cl_2. A chemically reversible one-electron reduction and an irreversible

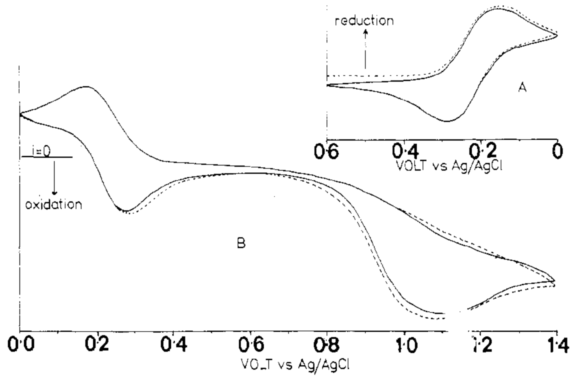

Figure 7. Cyclic voltammogram of $\mathrm{V(CO)_6}$ in dichloromethane (0.2 M $\mathrm{Bu_4NClO_4}$); scan rate 200 mV/s: A, scan of the electrode process $\mathrm{V(CO)_6 + e^- \rightleftharpoons V(CO)_6^-}$; B, scan of all processes.

oxidation wave can be seen. Progressive addition of diglyme caused the oxidation wave to adopt the form obtained from $\mathrm{[Na(diglyme)_2][V(CO)_6]}$ (see Figure 6B). This demonstrates that the $\mathrm{Na(diglyme)_2^+}$ cation dissociates in $\mathrm{CH_2Cl_2}$ and the apparent discrepancies in the electrochemistry of $\mathrm{V(CO)_6}$ and $\mathrm{V(CO)_6^-}$ are partly due to the presence of diglyme. Note also that in the cyclic voltammograms of $\mathrm{V(CO)_6}$ the $\mathrm{V(CO)_6^-/V(CO)_6}$ couple is not perturbed by altering the switching potential. This suggests that a redox reaction between an unidentified vanadium species generated at the electrode surface and $\mathrm{V(CO)_6^-}$ in solution plays an integral role in the electrochemical behavior in both acetone and dichloromethane.

Conclusions

The vanadium–carbonyl system exhibits very solvent-dependent behavior, which is clearly reflected in both the chemistry and the electrochemistry of the system. In noncoordinating solvents $\mathrm{V(CO)_6}$ is completely stable, but since $\mathrm{V(CO)_6^+}$ is extremely reactive toward substitution, a catalytic disproportionation can occur in coordinating solvents to give $\mathrm{V(CO)_6^-}$ and $\mathrm{V(solvent)_x^{2+}}$ so that in acetone and similar solvents $\mathrm{V(CO)_6}$ has no stability at all. The vanadium cation $\mathrm{V^{2+}}$ is only stable when coordinated by solvent or ligand and on removal of the coordinating ligand the equilibrium

$$\mathrm{V(CO)_6} + \text{“}\mathrm{V^{+}}\text{”} \rightleftharpoons \mathrm{V(CO)_6^-} + \text{“}\mathrm{V^{2+}}\text{”}$$

is shifted to the left.

It is interesting to compare the behavior of the 17-electron $\mathrm{V(CO)_6}$ with the isoelectronic $\mathrm{Cr(CO)_5I}$ (which also disproportionates at ambient temperature in acetone[6]) and also with $\mathrm{Cr(CO)_6^+}$ which exhibits similar behavior in a range of coordinating solvents.[4] In each case it would appear that the 17-electron species undergoes a disproportionation to generate a stable 18-electron carbonyl compound and a very reactive 16-electron carbonyl species which rapidly reacts further to give as the final product a non-carbonyl-containing compound. The substitution of the 16-electron intermediate would now appear to be the driving force in the disproportionation.

The electrochemical data on $\mathrm{V(CO)_6}$ briefly reported by Pickett and Pletcher[4] would now appear to be incorrectly interpreted in view of our findings. In our hands, infrared studies in tetrahydrofuran and acetonitrile (the two solvents used by these workers) demonstrated that, as in acetone and diglyme, $\mathrm{V(CO)_6}$ disproportionates to give $\mathrm{V(CO)_6^-}$. In addition, others[2,7] have reported the disproportionation of $\mathrm{V(CO)_6}$ in THF. These workers would therefore appear to have been describing the electrochemistry of $\mathrm{V(CO)_6^-}$ rather than $\mathrm{V(CO)_6}$. Furthermore, the degree of reversibility for the $\mathrm{V(CO)_6^-/V(CO)_6}$ couple was found to be far higher in the present work and the additional waves corresponding to oxidation of $\mathrm{V(CO)_6}$ were not reported by them. The reason for this last discrepancy is not clear to us, but it does seem very probable that the data of Pickett and Pletcher cannot be those for $\mathrm{V(CO)_6}$.[8]

Registry No. $\mathrm{[Na(diglyme)_2][V(CO)_6]}$, 12110-22-4; $\mathrm{V(CO)_6}$, 14024-00-1.

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(8) Since submitting this work for publication, a private communication from D. Pletcher confirms that in the work of Pickett and Pletcher[4] the data in tetrahydrofuran and acetonitrile have been incorrectly ascribed to $\mathrm{V(CO)_6}$ and that the electrochemistry they report is valid only in dichloromethane.

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Electrochemical Evidence for Reversible Five-Membered Electron Transfer Chains in Octahedral Chromium Complexes

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Received July 17, 1975 AIC50509X

A voltammetric (dc and ac polarography, cyclic voltammetry, and controlled potential electrolysis) study of complexes of chromium(II) and chromium(III) with the ligands bipyridine, terpyridine, and phenanthroline in acetonitrile has shown that in complexes with all three ligands chromium forms reversible, five-membered redox chains with the metal in formal oxidation states of 3+, 2+, 1+, 0, and 1−. Further examination of the redox behavior indicates that in the first three redox couples for each complex (3+ → 2+, 2+ → 1+, 1+ → 0), the ligands help to stabilize the addition of electrons to molecular orbitals which are primarily metal centered, while for the last couple (0 → 1−) the metal helps to stabilize the addition of an electron to a ligand-centered molecular orbital.

Considerable interest has been shown in recent years in the study of complexes which exhibit what have been termed "electron-transfer chains", that is, a series of one-electron, reversible charge transfers between a number of formal oxidation states of the complex. Most of this work has been done on square-planar complexes of two general classes of ligand, the dithiolenes[1,2] and macrocycles.[3-7]

A few such electron-transfer chains have been reported for octahedral complexes of first row transition metals.[8-12] The work was invariably done in a nonaqueous solvent, such as acetonitrile, which reduces and oxidizes with much more difficulty than water, and thus yields a much larger potential