Electrochemical Reduction of Vanadium Salts under Carbon Monoxide. Synthesis of Tetrabutylammonium Hexacarbonylvanadate(−I)

By **Giuseppe Silvestri,* Salvatore Gambino, Mauro Guainazzi,** and **Raffaele Ercoli,** Istituto di Chimica Industriale, Università di Palermo, Italy

Vanadium(III) complexes can be carbonylated by electrochemical reduction in anhydrous solvents saturated with CO at low and medium pressures. With $V(acac)_3$ as substrate, tetrabutylammonium hexacarbonylvanadate(−I) is obtained in pyridine, with conversion yields of up to 82%. A simplified process to obtain hexacarbonylvanadium is described.

THE synthesis of hexacarbonylvanadate anion $V(CO)_6^-$, a necessary intermediate in the synthesis of hexacarbonylvanadium, can be achieved by the action of strong reductants such as magnesium or sodium on vanadium complex salts in the presence of carbon monoxide under pressure.[1,2] The recovery of pure hexacarbonylvanadates according to the described procedures is rather elaborate, owing to their extreme sensitivity to oxidation.

This paper describes the electrochemical synthesis of $V(CO)_6^-$ suggested in 1967.[3] The method allows better yields of conversion of the vanadium substrate; moreover $V(CO)_6^-$ can be recovered as the stable tetrabutylammonium salt which is easily converted into $V(CO)_6$, following a procedure proposed by Interrante and Nelson.[4]

The synthesis involves electrolysis with an aluminium anode of a solution of vanadium trichloride or vanadium acetylacetonate in an aprotic solvent containing tetrabutylammonium bromide and carbon monoxide. The electrode reactions which are essentially involved in the process are (1) and (2). Reaction (1) is a new way of

$$V^{3+} + 6CO + 4e^- \longrightarrow V(CO)_6^- \text{ (cathode)} \quad (1)$$

$$Al \longrightarrow Al^{3+} + 3e^- \text{ (anode)} \quad (2)$$

obtaining the cathodic reduction of V^{3+} to low oxidation states. Actually, molten-salt electrolysis to obtain the metal and deposition of alloys with low vanadium content in aqueous media are described, but Michimayr and Gutmann [5] have found that in dimethylformamide VCl_3 undergoes a one-electron reduction, and polarographic evidence for further reduction of V^{III} in non-aqueous solvents is reported only for dithioketonate or dithioalcoholate complexes.[6] From this point of view electrochemical carbonylation of vanadium is an example of depolarization of cathodic reduction of transition-metal ions by means of a suitable ligand.

EXPERIMENTAL

VCl_3 (Fluka) was used without further purification; $V(acac)_3$ was prepared according to ref. 7 and recrystallized from ethanol. Bu_4NBr was recrystallized from ethyl acetate and dried at 80 °C *in vacuo*. Carbon monoxide (99%) and solvents were also dried and all the manipulations were made under nitrogen.

The high-pressure electrolytic cell provided with electrodes, stirrer, and thermostatic bath has been described.[8] Glass cells were also employed for pressures slightly above atmospheric. Aluminium anodes were pickled with aqueous HF–HCl mixtures and stainless-steel cathodes were polished with sandpaper. Conditions of electrolysis are dependent on the solvent, substrate, temperature, and pressure of CO in order to obtain the best yields, but they are not critical for the synthesis of $V(CO)_6^-$.

Preparation of $Bu_4NV(CO)_6$.—A solution containing $V(acac)_3$ (10 g) and Bu_4NBr (4 g) in pyridine (90 g), saturated with CO at 114 atm, was electrolysed at 50 mA for 96 h at 21 °C (expt. 7, Table 2). Constant current was maintained by an automatically controlled power supply (Trygon). The pressure dropped to 80 atm and further electrolysis caused no more absorption of CO.

I.r. spectra of the solution showed the presence of $V(CO)_6^-$. On dilution of the solution with 0·5N-NaOH solution (500 ml), containing Bu_4NBr (15 g), the tetrabutylammonium hexacarbonylvanadate(-I) settled out as a yellow precipitate. The precipitate was washed with water and recrystallized from methanol at −80 °C; thus 9·8 g of very pure $Bu_4NV(CO)_6$, m.p. 128 °C, were recovered, corresponding to 75% yield from the substrate [Found: CO, 36·2; C, 57·6; H, 8·0; N, 3·1. Calc. for $Bu_4NV(CO)_6$: CO, 36·4; C, 57·25; H, 7·85; N, 3·25%].

Preparation of $V(CO)_6$.—$Bu_4NV(CO)_6$ (5·4 g) was mixed with 99% H_3PO_4 (20 g) and P_2O_5 (5 g) in a 100 cm³ flask, connected with a vacuum line through a trap at −80 °C. The viscous melt was stirred at 30—35 °C at reduced pressure until the dark blue crystals of $V(CO)_6$, which gradually form according to reaction (3), were completely

$$Bu_4NV(CO)_6 + H_3PO_4 \longrightarrow V(CO)_6 + Bu_4NH_2PO_4 + \tfrac{1}{2}H_2 \quad (3)$$

collected in the trap; the product was then recovered under nitrogen and sealed in a glass tube. The final yield was 2·3 g, corresponding to 90% conversion of the original salt.

RESULTS AND DISCUSSION

Experiments 1—5 (Table 1) show results obtained in the carbonylation of VCl_3 in four solvents. Dimethoxyethane and tetrahydrofuran lead to high cathodic polarization, owing to the formation of solid layers on the electrode, so that, even above 80 °C, cell conductivity drops to very low values at the early stages of the electrolysis. Acetonitrile and pyridine gave good

---

[1] R. Ercoli, F. Calderazzo, and A. Alberola, *J. Amer. Chem. Soc.*, 1960, **82** 2965.

[2] R. B. King *Organometallic Synth.*, 1965, **1**, 82.

[3] R. Ercoli, M. Guainazzi, and G. Silvestri, *Chem. Comm.*, 1967, 927.

[4] L. V. Interrante and G. V. Nelson, *J. Organometallic Chem.*, 1970, **25**, 153.

[5] M. Michimayr and V. Gutmann, *Inorg. Chim. Acta*, 1967, **1**, 471.

[6] D. C. Olson, V. P. Mayweg, and G. N. Schrauzer, *J. Amer. Chem. Soc.*, 1966, **88**, 4876.

[7] A. Rosenheim, E Hilzheimer, and J. Wolff, *Z. anorg., Chem.* 1931, **201**, 162.

[8] M. Guainazzi, G. Silvestri, S. Gambino, and G. Filardo, *J.C.S. Dalton*, 1972, 927.

conductivities throughout the experiments also at room temperature, and consequently the electrolysis can be achieved at constant current.

Since with acetonitrile the yields are poor, pyridine appears the best solvent. Substantially better yields were obtained in pyridine by use of $V(acac)_3$ as substrate (expt. 5, Table 1), so that this system was chosen for further investigation. A maximum of 82% yield was obtained with a 1000 cm^3 cell, stirred by rotation of the entire apparatus around an inclined axis (expt. 7, Table 1). The current efficiency was in this case 42%.

TABLE 1

Influence of the solvent and substrate on the electrochemical synthesis of $Bu_4NV(CO)_6$

Expt.	t/°C	Solvent [a]/g	Substrate/g	Bu_4NBr/g	CO Pressure/atm Initial	CO Pressure/atm Final	10^{-2} × Charge Faraday	$Bu_4NV(CO)_6$ Yield (% substrate)
1	84	DME (90)	VCl_3 (1·6)	3·5	57·8	40·8	8·3	2
2	84	THF (80)	VCl_3 (3·1)	6·5	48·3	15	83	35
3	22	ACN (70)	VCl_3 (1·05)	3·5	53	33	11·8	6
4	22	py (90)	VCl_3 (2·65)	3·5	55·6	36·3	12	40
5	21	py (90)	$V(acac)_3$ (10)	4·0	258	212	19	75
6	20	py (90)	VCl_3 (1·1)	3·5	1·1 *		6·7	5
7	22	py (350)	$V(acac)_3$ (50)	20	117	83	108·7	82

* p Constant throughout the whole expt.

[a] DME = dimethoxyethane; ACN = acetonitrile; py = pyridine; THF = tetrahydrofuran. Initial current: expts. 1—6, 20 mA; expt. 5, 50 mA; expt. 7, 200 mA; cathode: stainless steel, cathodic area 15 cm^2; anode: aluminium (99·9%), anodic area, 100 cm^2. Expt. 7, large-scale experiment, cell geometry as in other experiments; linear dimensions magnified about 1·6 times; cathodic area, 100 cm^2; anodic area, 200 cm^2; 54·2 g of $Bu_4NV(CO)_6$ were obtained.

TABLE 2

Influence of temperature and pressure on electrochemical carbonylation of $V(acac)_3$ in pyridine

Expt.	t/°C	CO Pressure/atm Initial	CO Pressure/atm Final	10^{-2} × Charge Faraday	10^{-2} × CO absd. mol	$Bu_4NV(CO)_6$ obtained g	$Bu_4NV(CO)_6$ obtained Yield (%) substrate
1	84	4·35	2·80	14·9	—	3·2	25
2	84	21·7	9·8	19·1	8·4	5·1	39
3	84	58·7	22·2	22·4	11·4	6·7	51
4	84	264	224	16·0	11·6	7·6	58
5	21	2·35	1·30	17·5	—	1·6	24
6	21	55·5	26·1	17·9	14·5	7·9	60
7	21	114	80	17·9	17·8	9·8	75
8	21	258	212	19·4	18·0	9·8	75

Substrate: $V(acac)_3$ (10 g) (expt. 5 only, 5 g); electrolyte, Bu_4NBr (4 g); solvent, pyridine (90 g); current, 50 mA; cathode, stainless steel, area 15 cm^2; anode, aluminium (99·9%), area 100 cm^2.

When the yields of $V(CO)_6^-$ are poor, other unidentified soluble products of carbonylation are present which, after precipitation of $Bu_4NV(CO)_6$, evolve CO by oxidation with iodine. These products almost certainly contain ligands formed *in situ* by side reduction of pyridine. In fact the very low current efficiencies concurrently observed can hardly be explained otherwise. For instance an anodic reoxidation of $V(CO)_6^-$ must be excluded as the weight loss of aluminium corresponds to reaction (2) within a few percent.

It is noteworthy that the electrochemical synthesis with this system affords yields of 25% at pressures as low as 2—4 atm (expts. 1 and 5, Table 2). An increase of CO pressure has a sharply favourable effect up to 100 atm, whereas higher pressures are of little significance (expts. 1—4 and 5—8, Table 2). Thus the trend with respect to the carbon monoxide pressure is strictly similar to that observed in the electrochemical synthesis of $Cr(CO)_6$.[8]

The opposite is true for the temperature effect as, in this case, lower temperatures give constantly better results, whereas hexacarbonylchromium is best synthesized at 85 °C. This is explained by the existence of various stable Cr^0 pyridine carbonyls, among which $Cr(CO)_5py$ is the main product of chromium carbonylation at room temperature and low pressure.

Regarding the stepwise mechanism of reduction from V^{3+} to V^{-I} it must be recalled that reaction (1) is only an overall balance and does not imply that all the steps involved in the reduction are all really electrochemical. The formation of free $V(CO)_6$ during the reduction appears somewhat unlikely, because hexacarbonylvanadium in such basic solvents (B) as pyridine, methanol, acetone, *etc.*,[9] spontaneously undergoes the disproportionation (4) which is fast and complete at least

$$3V(CO)_6 + 6B \longrightarrow VB_6[V(CO)_6]_2 + 6CO \quad (4)$$

when p_{CO} is 1 atm. Thus it seems reasonable to conceive an electrochemical reduction to some unknown complex of V^I or V^0 containing pyridine and carbon monoxide followed by a spontaneous disproportionation analogous to reaction (4). The carbon monoxide acts as a cathodic depolarizer owing to its outstanding ability to co-ordinate transition elements in their lower oxidation states.

We thank the Consiglio Nazionale delle Ricerche for financial support.

[2/1029 *Received*, 8*th May*, 1972]

---

[9] F. Calderazzo and R. Ercoli, *Chimica e Industria*, 1962, **44**, 990.