Volume 3 Number 9

August 31, 1964

Inorganic Chemistry

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CONTRIBUTION FROM CYANAMID EUROPEAN RESEARCH INSTITUTE, COLOGNY, GENEVA, SWITZERLAND

The Reaction of Hexacarbonylvanadium with Aromatic Hydrocarbons

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Received April 13, 1964

Hexacarbonylvanadium reacts with benzene, toluene, p-xylene, and mesitylene to give the red crystalline $[V(CO)_4(arene)]$ - $[V(CO)_6]$. The corresponding hexafluorophosphates and tetraphenylborates $[V(CO)_4(arene)]X$ (X = PF₆⁻, $[B(C_6H_6)_4]^-$) have been prepared by metathetical reactions in tetrahydrofuran. The infrared spectra of these compounds in the CO stretching region are presented and a mechanism of formation of $[V(CO)_4(arene)][V(CO)_6]$ is proposed.

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Introduction

Aromatic hydrocarbons are known to react with the hexacarbonyls of the group VI metals giving tricarbonylarene metal complexes¹⁻³

$$M(CO)_6 + Ar \rightleftharpoons M(CO)_3Ar + 3CO$$
 (1)

(M = Cr, Mo, W). Several compounds of this class have been synthesized⁴ by this reaction and their chemistry investigated extensively.

Since vanadium gives a stable hexacarbonyl⁵ and stable diarene^{6,7} complexes, V(arene)₂, it was conceivable that a reaction of the type 1 could lead to the still unknown mixed complexes V(CO)₃(arene). However, instead of the expected neutral mixed complexes, the ionic [V(CO)₄(arene)][V(CO)₆] have been obtained from the reaction of hexacarbonylvanadium with aromatic hydrocarbons.

Results

Hexacarbonylvanadium reacts slowly in the absence of light at $20-50^{\circ}$, preferably at 35° , with aromatic hydrocarbons with the evolution of carbon monoxide and precipitation of unattractive solids, whose color varied from red to yellow or green, depending on the conditions and on the aromatic hydrocarbon employed. The reaction has been successfully carried

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out with benzene, toluene, p-xylene, and mesitylene. When the reaction was carried out in the presence of light, the color of the precipitate was black, because of extensive decomposition. The solid reaction products were separated from any soluble or volatile substance as described in the Experimental section. Only unreacted $V(CO)_{6}$ could be detected spectroscopically in the solutions from the above-mentioned reactions. The dry solids are extremely sensitive to air and contain: (a) water-soluble compounds, (b) the waterinsoluble, tetrahydrofuran-soluble $[V(CO)_4(arene)]$ -[V(CO)₆], and (c) small amounts of unidentified decomposition products insoluble in both solvents. Because of their solubility properties the components of the reaction mixture are separated in the order first (a) and then (b), while (c) is left as insoluble residue. The components (a) and (b) will be reported here in their order of separation, rather than in order of importance.

(a).—The water-soluble reaction products, or better their aqueous solutions, were investigated. The solid reaction mixture, from which only the unreacted V-(CO)₆ had been eliminated, usually had a CO content higher than expected for $[V(CO)_4(arene)][V(CO)_6]$. This, despite the fact that the mixture contained some decomposition products (presumably free from bonded carbon monoxide).

On treatment with water, a part of the solid mixture dissolved with simultaneous evolution of hydrogen. In the aqueous solution, vanadium was found as $[V(CO)_6]^-$, and as cation in unknown oxidation states (probably 2 and 3). The ratios between $[V-(CO)_6]^-$ and V^{n+} could be determined and were found to be in the range 1.2–1.5. After treatment with

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water, the mixture of the solids (now consisting of the complexes $[V(CO)_4(arene)][V(CO)_6]$ and the decomposition products) was not particularly sensitive to air, which suggested that the water-soluble products were mainly responsible for the extreme sensitivity of the starting solid reaction mixture toward air.

All these facts suggest that the water-soluble products are $V[V(CO)_6]$ and $V[V(CO)_6]_2$, *i.e.*, the V(I) and V(II) hexacarbonylvanadates, respectively. The relative amount of the two salts probably depends on the reaction conditions: this would explain the erratic values of the ratio $[V(CO)_6]^-/V^{n+}$ in their aqueous solutions.

While coordinated vanadium(I) is known from the present and previous⁷ studies to be stable in nonaqueous systems, there are no examples known of compounds containing ligand-free vanadium(I), such as the vanadium halides VX. It is, however, predictable that once formed in a water-free medium, they would be promptly oxidized in aqueous solution to V(II) by H⁺. The similar oxidation of V(II) to V(III) is a rather slow process, unless a catalyst is present. The rapid hydrogen evolution obtained on treatment of the solid reaction mixture with water is, therefore, in agreement with the presence of the salt V[V(CO)₆].

(b).—After elimination of the unreacted V(CO)₆ and of the water-soluble products, the compounds $|V(CO)_{4}$ -(arene)][V(CO)₆] could be isolated. They are all red crystalline solids, without definite melting points, decomposing between 80 and 110°, with displacement of the aromatic ligand. In the case of [V(CO)₄-C₆H₃(CH₃)₃][V(CO)₆], spectroscopically pure mesitylene was actually found by thermal decomposition of the complex, thus demonstrating the presence of π bonded aromatic hydrocarbons in this type of compound.

The ionic character of the compounds $[V(CO)_{4}-(arene)][V(CO)_{6}]$ is evidenced by their nonvolatility and their negligible solubility in hydrocarbons. Moreover, the infrared spectra (Table I) show the presence of two distinct groups of bands in the carbonyl stretching region: the two bands at 1895 and 1859 cm.⁻¹ can be assigned^{7,8} to the anion $[V(CO)_{6}]^{-}$. The remaining three bands at higher frequencies are, therefore, attributable to the carbon monoxide groups in the cation $[V(CO)_{4}(arene)]^{+}$. That this assignment is correct is shown by the fact that the hexafluorophosphates and the tetraphenylborates obtained by the metathetical reactions

 $[V(CO)_{4}(arene)][V(CO)_{6}] + Na[B(C_{6}H_{5})_{4}] \longrightarrow$ $[V(CO)_{4}(arene)][B(C_{6}H_{5})_{4}] + Na[V(CO)_{6}]$ $[V(CO)_{4}(arene)][V(CO)_{6}] + NH_{4}PF_{6} \longrightarrow$ $[V(CO)_{4}(arene)]PF_{6} + NH_{4}[V(CO)_{6}] (2)$

show only the carbonyl stretching bands at higher frequencies.

The hexacarbonylvanadates $[V(CO)_4(arene)][V-(CO)_6]$ react violently with pyridine with evolution of 2–2.5 moles of CO. It has been shown that the

carbon monoxide evolved is that contained in the cation, since the same reaction takes place also with the hexafluorophosphate $[V(CO)_4C_6H_3(CH_3)_3]PF_6$. This reaction will be investigated further since there are reasons to believe that a simple solvolysis is not involved in this case, but rather a disproportionation of the cation $[V(CO)_4(\text{arene})]^+$.

Infrared Spectra.---A close similarity exists between the cation $[V(CO)_4(arene)]^+$ and the cyclopentadienyl complex⁹ $V(CO)_4C_5H_5$, since both compounds contain a ring system of six π -electrons and the same number of CO ligands bonded to vanadium in the oxidation state 1+. It is, therefore, reasonable to think that they should also be structurally analogous. The infrared spectra of $V(CO)_4C_5H_5$ were run for comparison in tetrahydrofuran: two bands were found at 2024 (m) and 1919 (s) cm.⁻¹ (reported 2019 and 1919 cm.⁻¹ in CHCl₃ solution¹⁰; 2035 and 1935 cm.⁻¹ in cyclohexane solution,11 with values of the integrated extinction coefficient 5.03 and 17.2 \times 10⁷ cm./mole, respectively). The frequencies in tetrahydrofuran are directly comparable with the data of Table I. Two considerations arise from this comparison, first from the number of bands and second from their position. All the compounds $[V(CO)_4(arene)][V(CO)_6]$ have three bands between 2068 and 1977 cm.⁻¹, attributed to stretching vibrations of the cationic carbonyl groups. However, the band at 2018 cm. $^{-1}$ is very weak and disappears or becomes almost unnoticeable in the hexafluorophosphates and tetraphenylborates. Its position relative to the band at highest frequency and the fact that it is not shifted by the degree of substitution of the aromatic ring (vide infra) would suggest that a ¹³C-O stretching vibration is not involved in this case. However, the intensity of the band is so low that it is reasonable to assume only a slight distortion of the square-pyramidal structure (C_{4v} local symmetry) already proposed¹⁰ for $V(CO)_4C_5H_5$.

For the following arguments, only the two main bands of $[V(CO)_4(arene)]^+$ will be considered. It is interesting to notice that the bands of $V(CO)_4C_6H_6$ at 2024 and 1919 cm.⁻¹ are shifted in $[V(CO)_4C_6H_6]^+$ to 2068 and 1986 cm.⁻¹; this shift is probably related to the localization of an increased positive charge on the central metal atom in $[V(CO)_4C_6H_6]^+$. Another example of such an effect is known in the literature. $Mn(CO)_8C_6H_5$ has infrared carbonyl bands¹⁰ at 2023 and 1939 cm.⁻¹, whereas these bands are shifted¹² to 2083 and 2024 cm.⁻¹ in the related benzene cation $[Mn(CO)_8C_6H_6]^+$.

The infrared bands of $[V(CO)_4(\text{arene})]^+$ show a regular shift to lower frequencies of 2–3 cm.⁻¹ per methyl group with increasing number of methyl substituents on the aromatic ring. Similar effects

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CARBONYL STRETCHING FREQUENCIES OF	$[V(CO)_4(arene)]X (X =$	$(V(CO)_{6}]^{-}, PF_{6}^{-},$	$[B(C_6H_5)_4] =$

- ·				-			
Compound	νco, cm. ⁻¹						
$\left[\mathrm{V(CO)}_{4}\mathrm{C}_{6}\mathrm{H}_{6}\right]\left[\mathrm{V(CO)}_{6}\right]^{a}$	2068 (w)	2018 (vw)	1986 (m)	1895 (wm)	1859 (vs)		
$[V(CO)_4C_6H_5CH_3][V(CO)_6]^a$	2066 (w)	2018 (vw)	1983 (m)	1894 (wm)	1859 (vs)		
$[V(CO)_4C_6H_4(CH_3)_2][V(CO)_6]^a$	2064 (w)	2018 (vw)	1980 (m)	1895 (wm)	1859 (vs)		
$[V(CO)_4C_6H_3(CH_3)_3][V(CO)_6]^a$	2061 (w)	2018 (vw)	1977 (m)	1894 (wm)	1859 (vs)		
$[V(CO)_4C_6H_6PF_6]^b$	2070	\sim 2017 (vvw)	1988				
$[V(CO)_4C_6H_5CH_3]PF_6^b$	2068	• • •	1985				
$[V(CO)_4C_6H_4(CH_3)_2]PF_5^b$	2066	•••	1983				
$[V(CO)_4C_6H_3(CH_3)_3]PF_6^b$	2063	\sim 2015 (vvw)	1979		• • •		
$[V(CO)_4C_6H_3(CH_3)_3][B(C_6H_5)_4]^{a}$	2059	····	1975				
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^a Tetrahydrofuran solution. ^b Acetone solution.

TABLE II

Reactions between $V(CO)_6$ and Aromatic Hydrocarbons

Run no, Reactant		\sim Vanadium (%) found ^a as \sim					
	Reactant	Reaction temp., °C.	Reaction time, hr.	[V(CO)4(arene)]- [V(CO)6]	Water-soluble hexacarbonyl- vanadates	V ratio ^d	
1	Benzene	35	48	8.4			
2	Benzene	40°	8.5	4.3	13.8	3.2	
3	Benzene	50°	6	8			
4	Toluene	20	120	12			
5	Toluene	35	36	10			
6	Toluene	50°	6	16	39.0	2.4	
7	<i>p</i> - Xylene	35	48	17			
8	p-Xylene	50°	3	16			
9	Mesitylene	20	96	28			
10	Mesitylene	35	48	25, 36^{b}	29.0	1.16	
11	Mesitylene	500	3	15			

^a Based on $V(CO)_6$ employed. ^b Based on $V(CO)_6$ disappeared in the reaction. ^c Reactions carried out in an atmosphere of CO. ^d V (as water-soluble hexacarbonylvanadates)/V (as $[V(CO)_4(arene)][V(CO)_6]$).

have been observed^{13,14} for the tricarbonylarenechromium derivatives, $Cr(CO)_{3}$ (arene), and can be explained by the increasing electron density on the aromatic ring through the inductive effect of the methyl groups. The d_{π} - p_{π} bonding between the metal and the CO ligands thus increases, resulting in a higher metal-carbon (carbon monoxide) bond order and a lower C-O bond order.

By measuring the infrared spectra of the remarkably stable hexafluorophosphates $[V(CO)_4(arene)]PF_6$ it was also possible to observe the characteristic bands of the aromatic hydrocarbons (see Experimental section).

Experimental

Unless otherwise stated, all the operations were carried out in an atmosphere of prepurified nitrogen.

Tetrahydrofuran and diethyl ether were dried over sodium, distilled over lithium tetrahydroaluminate, and used shortly after the distillation. The aromatic hydrocarbons were refluxed over sodium and then fractionated.

Microanalyses are by Dr. K. Eder, Ecole de Chimie, Geneva, Switzerland, and Dr. A. Bernhardt, Mülheim (Ruhr), Germany. The CO content was determined by decomposition of the complexes with iodine in pyridine.

The infrared spectra were recorded on a Perkin-Elmer Model 221 instrument equipped with a grating prism unit. The CO stretching region was recorded on an expanded abscissa scale (5 cm.⁻¹/cm.). Each spectrum was calibrated with CO. The limit of accuracy of the measurements on solution spectra was, therefore, ± 0.5 cm.⁻¹.

(1) Reaction between V(CO)₆ and Aromatic Hydrocarbons.---

The data concerning the reaction between $V(CO)_6$ and aromatic hydrocarbons are in Table II.

A typical reaction between $V(CO)_6$ and mesitylene (run 10 in Table II) is here reported in detail, the procedure being essentially the same for the reactions with the other hydrocarbons.

Hexacarbonylvanadium (3.042 g., 0.0139 mole, 0.708 g. of vanadium) was introduced into a 250-ml. flask protected against light and containing mesitylene (75 ml.). A pressure of about 10 mm. was briefly applied and the flask closed. The mixture was magnetically stirred for 2 days at 35°; during this time the carbon monoxide evolved from the reaction was evacuated three times. The solid formed during the reaction had a color varying from initially orange to brown-green at the end. The solid reaction mixture was filtered, washed several times with heptane. and dried under high vacuum for several hours. The dried solid burns immediately upon contact with air. The filtered solution showed one single infrared band in the carbonyl stretching region at 1974 cm.⁻¹ due¹⁵ to the unreacted V(CO)₆. After decomposition of the hexacarbonyl, the vanadium contained in this solution was determined (0.216 g. of vanadium, corresponding to 0.93 g. of $V(CO)_6).$

In another experiment with p-xylene (run 8 in Table II), the dried solid mixture, after elimination of the unreacted $V(CO)_6$, contained 60.65% of CO determined by decomposition with iodine in pyridine. Calcd. for $[V(CO)_4C_6H_4(CH_3)_2][V(CO)_6]$, 57.38; for $V[V(CO)_6]$, 62.26; for $V[V(CO)_6]_2$, 68.74.

(a) Investigation of the Water-Soluble Products.—The dried air-sensitive solid from the above described reaction with mesitylene was treated with water in a gas-volumetric apparatus under an atmosphere of carbon monoxide. About 20 ml. of gas was rapidly evolved on contact of the solid with water. A sample of the gas phase was collected, passed through a trap at -80° , and analyzed by combustion. From the weight of H₂O obtained and knowing the volume of the reaction apparatus, it was calculated that the gas evolved was mostly hydrogen.

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TABLE III PROPERTIES AND ANALYTICAL DATA OF $[V(CO)_{i}][V(CO)_{i}]$

	A ROLDRIL								
	Dec. pt.,	C, %		——Н, %———		~~~~-V, %~~~~~~		СО, %	
Compound	°C.	Calcd.	Found	Caled.	Found	Calcd.	Found	Caled.	Found
$[V(CO)_4C_6H_6][V(CO)_6]$	107 - 108	41.77	41.32	1.31	1.67	22.14	22.23	60.88	59.25
$[V(CO)_4C_7H_8][V(CO)_6]$	80-82	43.07	42.87	1.70	1.95	21.49	21.33	59.08	58.69
$[V(CO)_4C_8H_{10}][V(CO)_6]$	100 - 102	44.29	44.12	2.06	2.17	20.87	21.06	57.38	56.35
$[V(CO)_4C_9H_{12}][V(CO)_6]$	90-92	45.44	45.05	2.41	2.54	20.29	20.43	55.78	55.20

The solid left after treatment with water was filtered and washed several times with water. The brown-yellow aqueous solution was treated with methylpyridinium iodide (3.4 g.) in water (20 ml.). The red precipitate⁸ of $[C_{\delta}H_{\delta}NCH_{\delta}][V(CO)_{\delta}]$ immediately formed was filtered and washed with water. The amounts of vanadium contained in $[C_{\delta}H_{\delta}NCH_{\delta}][V(CO)_{\delta}]$ and in the filtrate from the latter were separately determined and found to be 0.123 and 0.082 g., respectively; ratio V (as $[V(CO)_{\delta}]^{-})/V^{n+} = 1.5$.

In a similar reaction of V(CO)₆ with benzene (run 2 in Table II) the $[V(CO)_6]^-$ contained in the aqueous solution was separated from the cationic vanadium by treatment with sodium hydroxide and extraction with diethyl ether as NaV(CO)₆, followed by precipitation⁵ as $[Ni(1,10\text{-phen})_8][V(CO)_6]_2$; ratio V (as $[V(CO)_6]^-)/V^{n+} = 1.2$.

Anal. Caled. for $C_{48}H_{24}N_8NiO_{12}V_2$: C, 55.58; H, 2.33; N, 8.10. Found: C, 55.46; H, 2.52; N, 8.03.

(b) Isolation of the Compounds $[V(CO)_4(\text{arene})][V(CO)_6]$.— In the reaction of $V(CO)_6$ with mesitylene, the solid left after the treatment with water described in (1a) was dried *in vacuo* and then dissolved in tetrahydrofuran. The red-brown solution so obtained was filtered to eliminate the insoluble decomposition products. On addition of diethyl ether, the red crystalline hexacarbonylvanadate $[V(CO)_4C_6H_3(CH_3)_3][V(CO)_6]$ separated out and was filtered, washed with diethyl ether, and dried *in vacuo* (0.88 g., 25.2% based on $V(CO)_6$ employed, 36.4% on $V(CO)_6$ consumed).

The physical and analytical data of the hexacarbonylvanadates are in Table III. The hexacarbonylvanadates are all very soluble in tetrahydrofuran and acetone, but solvolysis reactions take place slowly with replacement of the ligands from the cation. The solubility in diethyl ether is very low. The compounds are moderately stable in air in the dry state, but not in solution. They are oxidized rapidly by iodine with quantitative evolution of the bonded carbon monoxide.

(2) Preparation of the Compounds $[V(CO)_4(\text{arene})]PF_6$.---NH₄PF₆ (0.1 g.) in tetrahydrofuran (5 ml.) was introduced into a solution of 0.112 g. of $[V(CO)_4C_6H_6][V(CO)_8]$ in tetrahydrofuran (10 ml.). The red-orange precipitate immediately formed was filtered, washed with tetrahydrofuran, and dried *in vacuo* (0.09 g., 95.7%). $[V(CO)_4C_6H_6]PF_6$, dec. 158-160°, is an orange microcrystalline substance, insoluble in hydrocarbons, sparingly soluble in tetrahydrofuran and diethyl ether, and slightly soluble in acetone. It is remarkably stable in air in the dry state (apparently unchanged after 15 min. of exposure). The infrared spectrum of the filtrate from the preparation of the hexafluorophosphate showed the two bands at about 1895 and 1859 cm.⁻¹ due to the anion $[V(CO)_6]^-$. Anal. Calcd. for $C_{10}H_6F_6$ - O_4PV : C, 31.11; H, 1.57; F, 29.53. Found: C, 31.76; H, 1.69; F, 29.14.

The infrared spectra of this and the following compounds were measured as KBr disks. Carbonyl stretching frequencies (for them, see Table I) and PF_6^- bands are not reported. Infrared bands at: 3100 (m), 3035 (mw), 2930 (w), 2850 (w), 1540 (w), 1465 (m), 800 (w), 745 (w), and 680 (w) cm.⁻¹.

The following hexafluorophosphates were prepared similarly. The properties are similar to those already reported for the benzene derivative; only the solubilities in acetone appear to be higher.

 $[V(CO)_4C_7H_8]PF_6$, orange, microcrystalline, dec. 150–152°. Anal. Calcd. for $C_{11}H_8F_6O_4PV$: C, 33.02; H, 2.01; F, 28.49. Found: C, 33.18; H, 2.27; F, 28.71. Infrared bands at: 3100 (m), 3070 (w), 3010 (w), 2920 (w), 2850 (w), 1555 (m), 1485 (s), 1455 (m), 1350 (w), 1215 (w), 1045 (w), 790 (mw), and 740 (w) cm.⁻¹.

 $[V(CO)_4C_8H_{10}]PF_6, \text{ red, crystalline, dec. } 148-150^\circ. Anal. Calcd. for C_{12}H_{19}F_6O_4PV: C, 34.80; H, 2.43; F, 27.53. Found: C, 35.27; H, 2.54; F, 27.29. Infrared bands at: 3080 (m), 3030 (w), 2920 (w), 2850 (w), 1565 (ms), 1500 (s), 1460 (m), 1350 (w), 1230 (w), 1200 (w), 1180 (w), 1110 (w), 1040 (m), 920 (m), 775 (w), and 730 (w) cm.^{-1}.$

 $[V(CO)_4C_6H_3(CH_3)_5]PF_6$, red, crystalline, dec. 102–104°. It reacts rapidly with pyridine at room temperature with evolution of about 2.3 moles of CO. *A nal.* Calcd. for $C_{13}H_{12}F_6O_4PV$: C, 36.47; H, 2.82; CO, 26.17; F, 26.63. Found: C, 36.20; H, 2.98; CO, 25.76; F, 26.46. Infrared bands at: 3120 (w), 3080 (m), 2985 (w), 2940 (w), 2855 (w), 2755 (w), 2490 (w), 2465 (w), 2430 (w), 1570 (m), 1555 (s), 1470 (s), 1350 (w), 1310 (m), 1170 (w), 1120 (w), 1050 (s), 960 (wm), 775 (wm), and 740 (wm) cm.⁻¹.

(3) Preparation of the Compounds $[V(CO)_4(arene)][B(C_6H_5)_4]$. $-[V(CO)_4C_6H_4(CH_3)_2][V(CO)_6]$ (0.10 g.) dissolved in tetrahydrofuran (7 ml.) was treated with Na $[B(C_6H_5)_4]$ (0.2 g.) in methanol (10 ml.). The precipitate formed was filtered, washed with methanol, and dried *in vacuo*. An almost quantitative yield of the tetraphenylborate was obtained. This is an orange crystalline substance, insoluble in hydrocarbons, slightly soluble in methanol and tetrahydrofuran, and moderately stable in air in the dry state. *Anal.* Caled. for C₃₆H₃₀BO₄V: C, 73.49; H, 5.14. Found: C, 72.79; H, 5.25.

 $[V(CO)_4C_6H_8(CH_3)_8][B(C_6H_5)_4]$ was prepared by a similar procedure. It is orange and moderately stable in air in the dry state. *Anal.* Calcd. for $C_{37}H_{32}BO_4V$: C, 73.77; H, 5.35. Found: C, 74.05; H, 5.63.

(4) Thermal Decomposition of $[V(CO)_4(\text{arene})][V(CO)_6]$. (a) In the Dry State.—The mesitylene derivative contained in a Schlenk tube equipped with a cold finger was heated to $80-100^{\circ}$ at about 5×10^{-2} mm. A trap at Dry Ice-acetone temperature was inserted between the tube and the vacuum line. At 95° the hexacarbonylvanadate became black. No sublimate was observed on the cold finger. In the trap, traces of $V(CO)_6$ and pure 1,3,5-trimethylbenzene were detected by infrared spectroscopy. The black residue was not soluble in water.

(b) In the Presence of Aromatic Hydrocarbons.— $[V(CO)_4-C_8H_{10}][V(CO)_6]$ (0.148 g.) was introduced in a 100-ml. flask and suspended in *p*-xylene (50 ml.), previously saturated with carbon monoxide. A pressure of about 10 mm. was briefly applied; the flask was closed and its contents magnetically stirred for 3 hr. at 45°. The brown solid was filtered and dried *in vacuo*. In the dry state the solid was extremely sensitive to air oxidation. By addition of water, it dissolved partially. In the aqueous solution $[V(CO)_6]^-$ was precipitated as $[C_6H_6NCH_3][V(CO)_6]$. The vanadium present in the aqueous solution was 40% of that introduced. The solid left after treatment with water was unchanged starting material.

Discussion

An interesting problem is the mechanism of formation of the complexes $[V(CO)_4(arene)][V(CO)_6]$. It has been shown in previous papers that hexacarbonylvanadium-behaves as an oxidizing agent toward dicyclopentadienylvanadium¹⁶ and dimesitylenevana-

(16) F. Calderazzo and S. Bacciarelli, Inorg. Chem., 2, 721 (1963).

dium,⁷ forming the hexacarbonylvanadates of the corresponding oxidized complexes.

$$V^{II}(C_{\delta}H_{\delta})_{2} + V^{0}(CO)_{\theta} \xrightarrow{2CO} [V^{III}(C_{\delta}H_{\delta})_{2}(CO)_{2}][V^{I-}(CO)_{\theta}]$$

$$[V^{0}(C_{\theta}H_{\theta}(CH_{3})_{\theta})_{2} + V^{0}(CO_{\theta}) \longrightarrow [V^{I}(C_{\theta}H_{\theta}(CH_{3})_{\theta})_{2}][V^{I-}(CO)_{\theta}]$$
(3)

These reactions are very fast.

By analogy with eq. 3, the precipitation of $[V(CO)_4$ -(arene)] $[V(CO)_6]$ is probably preceded by the formation of a soluble substitution product of $V(CO)_6$, which is then oxidized to the final complex by a second molecule of $V(CO)_6$. The intermediate could be $V(CO)_8$ (arene), for which the occurrence of the following oxidationreduction reaction is predictable.

$$\frac{V^{0}(CO)_{3}(arene) + V^{0}(CO)_{6} + CO \longrightarrow}{[V^{I}(CO)_{4}(arene)][V^{I-}(CO)_{6}]}$$
(4)

In the soluble products of the reactions between $V(CO)_6$ and aromatic hydrocarbons, only unreacted $V(CO)_6$ could be detected spectroscopically. A possible interpretation of this fact could be that $V(CO)_3$ -(arene) is removed from the solution by the excess $V(CO)_6$ as soon as it is formed, according to the presumably very fast reaction 4. However, an alternative and probably more convincing explanation is that $V(CO)_3$ (arene) is not an intermediate product in the formation of $[V(CO)_4(arene)][V(CO)_6]$. It is in fact unlikely that the aromatic hydrocarbon substitutes three carbon monoxide groups from $V(CO)_6$ at the same time. It is more reasonable to assume that the CO groups are replaced one after the other, presumably at decreasing reaction rates.

$$V(CO)_{\delta} + \operatorname{arene} \xrightarrow{-CO}_{+CO} V(CO)_{\delta}(\operatorname{arene}) \xrightarrow{-CO}_{+CO} V(CO)_{\delta}(\operatorname{arene}) \xrightarrow{-CO}_{+CO} V(CO)_{\delta}(\operatorname{arene}) \quad (5)$$
II III

The excess $V(CO)_6$ would then directly oxidize I or II

giving the final product, with or without the evolution of CO, respectively. Stage III would never, therefore, be reached.

It has been shown that the water-soluble hexacarbonylvanadates are most probably $V[V(CO)_6]$ and $V[V(CO)_6]_2$, which arise from $[V(CO)_4(arene)][V-(CO)_6]$ by a thermal treatment in the presence of the free aromatic hydrocarbon. The formation of the water-soluble hexacarbonylvanadates is mainly responsible for the low yields of $[V(CO)_4(arene)][V-(CO)_6]$ obtained.

From the data of Table II, it is seen that by increasing the degree of substitution of the aromatic hydrocarbons, the yields of the desired products also increase. This is probably due to the two combined effects of higher reaction rates and lower tendency of the formed $[V(CO)_4(arene)][V(CO)_6]$ to decompose to the watersoluble vanadium hexacarbonylvanadates. Probably the second effect is predominant as shown by the ratio water-soluble products/ $[V(CO)_4(arene)][V(CO)_6]$ decreasing from benzene to mesitylene. This is also confirmed by a study¹⁷ of the reactions between $Mo(CO)_6$ and aromatic hydrocarbons, where it was shown that the rate of evolution of CO from the hexacarbonyl was only slightly influenced by the nature of the hydrocarbons used.

Attempts are now being made to prepare $V(CO)_{3}$ -(arene) by reduction of the compounds described in this paper. The magnetic susceptibility measurements of the complexes are also being carried out.¹⁸

Acknowledgment.—The author is greatly indebted to Mr. R. Schopfer and Mr. Jean Moser for their help in carrying out the experimental part of this work, to Dr. K. Noack for helpful discussions on the infrared spectra, and to Miss I. Höflinger for measuring the infrared spectra.

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(18) By Prof. R. Cini of the University of Florence, Italy.