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Redox Reactions of Metal Carbonyls of Group 5A

Fausto Calderazzo* and Guido Pampaloni

Istituto Chimica Generale, Università di Pisa, Via Risorgimento 35, 56100 Pisa, Italy

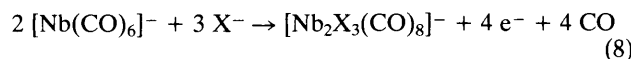
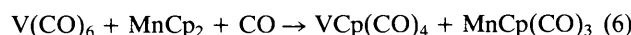
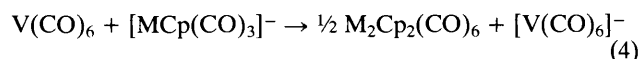
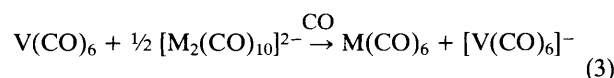
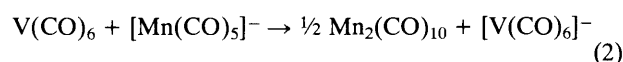
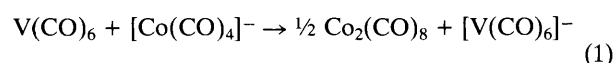
Redox reactions of $V(CO)_6$ with $[Co(CO)_4]^-$, $[Mn(CO)_5]^-$, $[M_2(CO)_{10}]^{2-}$, or $[M(\eta^5-C_5H_5)(CO)_3]^-$ ($M = Cr, Mo, W$), or $Co(\eta^5-C_5H_5)_2$ occur rapidly at 25 °C and lower in hydrocarbons; on the other hand, $V(CO)_6$ is oxidized to $V(\eta^5-C_5H_5)(CO)_4$ by $Mn(\eta^5-C_5H_5)_2$ or $Ni(\eta^5-C_5H_5)_2$ and the two-electron oxidation of $[Nb(CO)_6]^-$ to the $[Nb_2X_3(CO)_8]^-$ anion ($X = Cl, Br, I, \text{acetylacetonato}$), can be carried out using a number of oxidizing agents (Hg^{II} , Cu^{II} , Cu^I , Ag^I , or Fe^{III}).

Hexacarbonylvanadium(0), a 17-electron species, is a long-lived radical,¹ likely to undergo one-electron reduction to the hexacarbonylvanadate(-1) anion. Because of its moderate solubility in hydrocarbons, $V(CO)_6$ offers the unique possibility of studying redox processes in non-aqueous media of low polarity. The oxidizing properties of $V(CO)_6$ have been used in the past for preparing $[VCp(CO)_2]^+$ ($Cp = \eta^5-C_5H_5$) and $[V(\eta^6\text{-arene})_2]^+$ from the $VCp_2/V(CO)_6/CO^2$ and $V(\eta^6\text{-arene})_2/V(CO)_6^3$ systems, respectively.

We have now found new redox reactions involving both $V(CO)_6$ and $[Nb(CO)_6]^-$, occurring *via* outer-sphere and inner-sphere mechanisms. Hexacarbonylvanadium(0) oxidized the carbonyl metallates of cobalt(-1), manganese(-1), and those of the group 6A metals, according to the stoichiometries shown in equations (1)–(4). Although reaction (5) was also found to occur in n-heptane, toluene was used as solvent because of the higher solubility of the reagents as NR_4^+ derivatives. The reactions occurred rapidly (within 5 min) at temperatures ranging from -10 to 25 °C. When reaction (2) was run with $V(^{13}CO)_6^4$ ($\geq 90\%$ enriched, ν_{CO} 1934 cm^{-1} in n-heptane), no labelling was found in the oxidation product and $[V(^{13}CO)_6]^-$ (ν_{CO} 1844sh, 1816vs, 1783w cm^{-1} in tetrahydrofuran; 1817s cm^{-1} in acetone) was the reduction product. This result suggests that the reaction proceeds *via* an outer-sphere mechanism.⁵

The biscyclopentadienyl derivative of d^7 cobalt(II) was also readily oxidized by $V(CO)_6$ to the corresponding cobaltinium cation,⁶ while the d^5 $MnCp_2$ and the d^8 $NiCp_2$ were reduced [equations (5)–(7)] and no reaction occurred with $FeCp_2$. Reaction (5) occurred within the time of mixing the reagents, whereas reactions (6) and (7) required longer times for completion. For example, reaction (6), which was followed by gas volumetry of the CO absorbed (1.02 mol of CO per mol of manganese), had a half-life of *ca.* 15 min at 20.5 °C. This, together with the finding that ligand redistribution occurred, suggests an inner-sphere mechanism for reactions (6) and (7). These were characterized by a high selectivity: the yields of isolated products were *ca.* 85% or higher and no products could be detected spectroscopically in the crude reaction mixtures other than those indicated in the equations. Since the

redox process and the ligand redistribution occur with complexes of both odd and even electronic configurations, it is plausible that the heterometallic intermediate of the reaction is a cyclopentadienyl-bridged⁷ species, possibly containing a metal-metal bond.



$X = Cl, Br, I, \text{acac}$

The hexacarbonylniobate(-1)⁸ anion as its sodium derivative was oxidized to the niobium(I) dimeric anions,⁹ $[Nb_2X_3(CO)_8]^-$, by a number of simple halogeno- and ato complexes of mercury(II), copper(II), copper(I), silver(I), or iron(III), see Table 1, in analogy with the reported reactions of protons⁹ and halogens.¹⁰ The oxidation process, see equation (8), is believed to be mediated by the sodium counter cation.

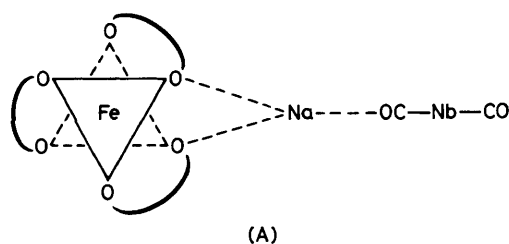


Table 1. Redox processes involving $[\text{Nb}(\text{CO})_6]^-$ and halogeno- and ato complexes of transition metals.^a

$[\text{Nb}(\text{CO})_6]^-$, mmol	Oxidant, mmol	Products, yield/% ^b
0.2	HgCl_2 , 0.22	$[\text{Nb}_2\text{Cl}_3(\text{CO})_8]^-$, N.d. ^c
1.7	CuCl_2 , 1.8 ^d	„ 67
19.6	CuCl , 40.0	„ 72
1.3	CuBr , 2.6	$[\text{Nb}_2\text{Br}_3(\text{CO})_8]^-$, 46 ^e
2.3	CuI , 4.6	$[\text{Nb}_2\text{I}_3(\text{CO})_8]^-$, 26 ^e
0.3	AgCl , 0.6	$[\text{Nb}_2\text{Cl}_3(\text{CO})_8]^-$, N.d. ^c
2.0	FeCl_3 , 4.0 ^d	$[\text{Nb}_2\text{Cl}_3(\text{CO})_8]^-$, 81
2.1	$\text{Fe}(\text{acac})_3$, 4.3 ^d	$[\text{Nb}_2(\text{acac})_3(\text{CO})_8]^-$, 85 ^e

^a Tetrahydrofuran as solvent, 25 °C or below. ^b The yield is for the isolated product. ^c N.d. = not determined, i.r. spectroscopic detection only. The dinuclear anions are characterized by two absorptions in the ranges 2020–2005 cm^{-1} and 1915–1860 cm^{-1} . ^d Stoichiometry of equation (8) verified by gas volumetry. ^e Satisfactory elemental analyses were obtained.

Typical is the case of the $\text{Fe}(\text{acac})_3$ (acac = acetylacetonato)/ $\text{NaNb}(\text{CO})_6$ system of equation (8) in tetrahydrofuran as solvent. When the reaction was attempted under the same conditions as in Table 1, with the sole exception of adding dibenzo-18-crown-6, no change was observed. Also dimethylformamide was found to inhibit the reaction completely. This is taken as evidence that the initial attack is by Na^+ of the $\text{Na}^+[\text{Nb}(\text{CO})_6]^-$ ion pair on the oxygen atoms of the co-ordinated acetylacetonato groups, as indicated in (A). Assistance by alkali cations has been suggested for redox processes involving condensed aromatic hydrocarbons¹¹ and the $[\text{Fe}(\text{CN})_6]^{4-}/[\text{Fe}(\text{CN})_6]^{3-}$ couple.¹²

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