Mechanism of Lewis Base Induced Disproportionation of Vanadium Hexacarbonyl

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Vanadium hexacarbonyl undergoes disproportionation in the presence of several bases (L) (pyridine, tetrahydrofuran, diethyl ether, and acetonitrile) according to a second order rate law $k[V(CO)_6][L]$; Fourier transform i.r. spectroscopic analysis of the reaction for L = pyridine reveals the presence of an isocarbonyl bridged intermediate $[(OC)_6VCOV(L)_4OCV(CO)_5]$ *en route* to the ultimate product $[V(L)_6][V(CO)_6]_2$.

Neutral metal carbonyls often undergo base induced disproportionation.[1] Despite the importance of such reactions, and more generally of redox reactions of organometallics, there have been few quantitative rate studies.[2] We now report measurements for the disproportionation of $V(CO)_6$ which occurs in the presence of several oxygen and nitrogen Lewis bases. The evidence provides the first suggestion of inner sphere electron transfer through an isocarbonyl bridge.

Vanadium hexacarbonyl is known to undergo rapid

associative substitution reactions (S_N2) in the presence of phosphine or arsine ligands;[3] however, oxygen and nitro-
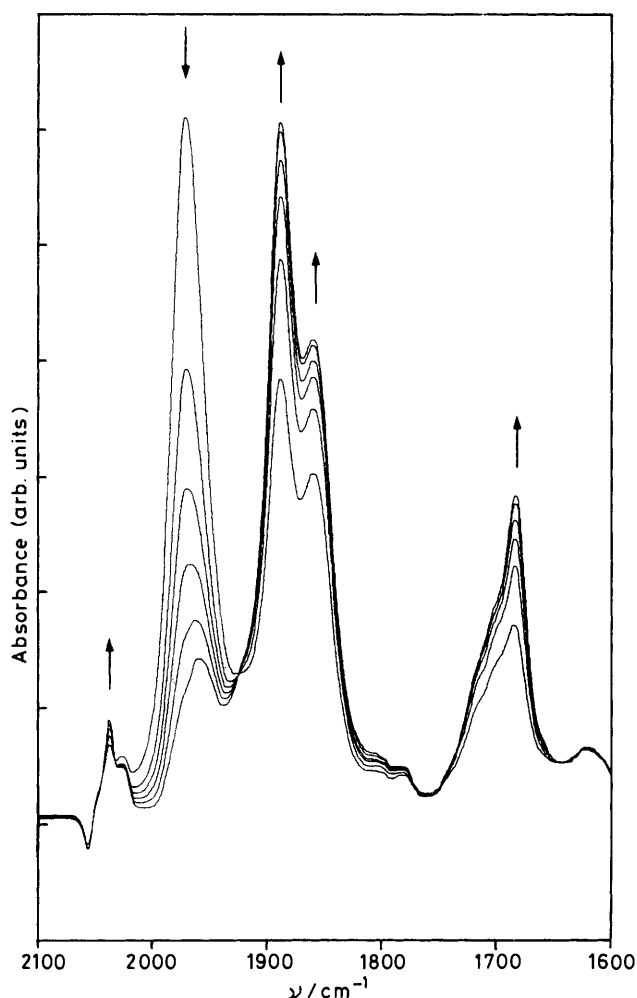
$$(CO)_5V-C\equiv O\cdots V\cdots O\equiv C-V(CO)_5$$

with L ligands above and below the central V.

(1)
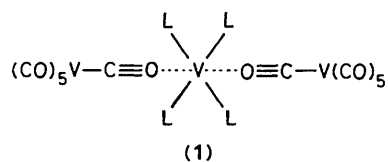
Figure 1. I.r. spectral changes when $V(CO)_6$ (ca. 3 × 10^{-3} mol dm^{-3}) undergoes disproportionation by THF (0.283 mol dm^{-3}) in CH_2Cl_2–hexane solution.

gen donor ligands, L, promote the formation of $[V(L)_6]$-$[V(CO)_6]_2$.[4,5] Even arenes can induce disproportionation.[4] From tetrahydrofuran (THF) solvent, the unusual complex (1; L = THF) has been isolated and, following recrystallization from CH_2Cl_2, characterized by X-ray diffraction.[6] It was not known whether (1) was a kinetic or thermodynamic product and what factors dictated the formation of (1) or $[V(L)_6][V(CO)_6]_2$. Apparently the favourable energetics[7] for the formation of $[V(CO)_6]^-$ provide the driving force for these reactions.

Reactions were performed in CH_2Cl_2–hexane mixtures containing known amounts of Lewis base, and i.r. spectra, obtained by Fourier transform (F.t.) methods, provided a sensitive structural probe. For pyridine (py), THF, and diethyl ether (Et_2O) reaction (1) was observed. The species (1) was

$$3\ V(CO)_6 + 4\ L \xrightarrow{k_d} (1) + 6\ CO \quad (1)$$

$$L = py,\ THF,\ Et_2O$$
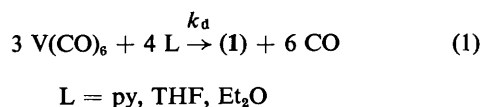
identified by comparison of its i.r. spectrum with those in the literature.[5] In particular, the strong broad 1680—1690 cm^{-1} absorption indicates the presence of the bridging isocarbonyl moiety, and the distorted $[V(CO)_6]^-$ group is evident in the high frequency carbonyl stretching region. Figure 1 illustrates the spectral changes that occur when (1) forms in CH_2Cl_2–

hexane–THF. For L = Et_2O or THF, (1) is stable in CH_2Cl_2. In the case of L = py, the intermediate (1) undergoes further reaction with additional Lewis base according to equation (2).

$$(1) + 2\ py \rightarrow [V(py)_6][V(CO)_6]_2 \quad (2)$$

A key observation is that the isocarbonyl bridged complex (1) appears to be a *kinetic product* when L = py.

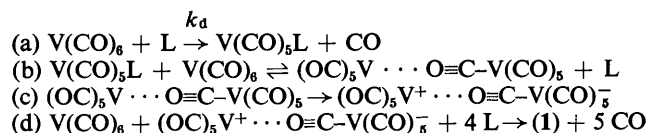$$3\ V(CO)_6 + 6\ MeCN \xrightarrow{k_d} [V(MeCN)_6][V(CO)_6]_2 + 6\ CO \quad (3)$$

For L = MeCN only reaction (3) could be measured. Free $[V(CO)_6]^-$ could be detected in the solution i.r. spectra, and monitoring of the reaction by F.t.–i.r. spectroscopy did not reveal the presence of an intermediate.

Rate determinations of reaction (1) for L = THF establish the second order rate law $k_d[V(CO)_6][THF]$ with $\Delta H^{\ddagger} = 14.8 \pm 2.2$ kcal mol^{-1} and $\Delta S^{\ddagger} = -19.6 \pm 3.5$ cal mol^{-1} K^{-1}.† Second order rate constants for the nucleophiles examined parallel the co-ordinating ability: py, $k_d = 1.22$ dm^3 mol^{-1} s^{-1}; MeCN, $k_d = 0.284$ dm^3 mol^{-1} s^{-1}; THF, $k_d = 4.35 \times 10^{-3}$ dm^3 mol^{-1} s^{-1}; Et_2O, $k_d = 9.63 \times 10^{-5}$ dm^3 mol^{-1} s^{-1}. These data suggest that the rate determining step is equation (4). The rate law for formation of stable complexes such as $V(CO)_5(PPh_3)$ is known[3] to follow second order kinetics with $\Delta H^{\ddagger} = 10.0$ kcal mol^{-1} and $\Delta S^{\ddagger} = -27.8$ cal mol^{-1} K^{-1}.

$$V(CO)_6 + L \xrightarrow{k_d} V(CO)_5L + CO \quad (4)$$

The fact that (1) forms as a metastable intermediate suggests that electron transfer occurs by an inner sphere process through a bridging isocarbonyl ligand. The breakdown of (1) according to equation (2) appears to be dependent on the nature of L. In Et_2O, (1) is stable but it persists only for several minutes in the presence of pyridine (0.14 mol dm^{-3}) and cannot be detected when MeCN is present. For example, the addition of MeCN to an Et_2O solution of (1) resulted in its rapid (i.e., <5 min) reaction according to equation (2).

A mechanism that accounts for the observations is shown in steps (a)—(d) of Scheme 1. Formation of an inner sphere isocarbonyl-bridged complex is the key step (b). Although such processes are well known in electron transfer reactions of Werner complexes,[8] we are aware of no organometallic examples. The strong field complex $V(CO)_6$ would be expected to be more oxidizing than $V(CO)_5L$, which contains a weak field ligand such as THF or Et_2O. This provides the driving force for step (c). Similar ligand field effects are evident in electron transfer reactions of octahedral Werner complexes.[9]

$$\text{(a)}\ V(CO)_6 + L \xrightarrow{k_d} V(CO)_5L + CO$$
(b) $V(CO)_5L + V(CO)_6 \rightleftharpoons (OC)_5V \cdots O{\equiv}C{-}V(CO)_5 + L$
(c) $(OC)_5V \cdots O{\equiv}C{-}V(CO)_5 \rightarrow (OC)_5V^+ \cdots O{\equiv}C{-}V(CO)_5^-$
(d) $V(CO)_6 + (OC)_5V^+ \cdots O{\equiv}C{-}V(CO)_5^- + 4\ L \rightarrow (1) + 5\ CO$

Scheme 1

To achieve the second electron transfer step, another $V(CO)_6$ radical apparently must form a second isocarbonyl bridge to the labile V^I centre. Since the exact sequence of bridge formation and CO substitution is not known, these are combined in step (d). An important aspect of the mechanism is rapid attack at vanadium [step (b)] when L is an N or O donor species. It should be noted that even the normally sub-

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† 1 kcal = 4.18 kJ.

stitution-inert complexes $[V(CO)_5L]^-$ are quite labile when $L = NH_3$[10] or dimethyl sulphoxide.[11]

It seems possible that transfer of an electron *via* a bridging isocarbonyl will prove to be a general feature of electron transfer reactions of metal carbonyls. In this context, we note the facile disproportionation reactions observed[12] for photochemically generated organotransition metal radicals. We also note the recent interest in isocarbonyl bridged structures with regard to CO activation.[13]

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