yield) was identified as $V(CO)_4[P(OMe)_3]_2$ by its IR [toluene, 2007 (m), 1905 (sh), 1885 (s), 1865 (sh) cm^{-1}] and mass spectrum (*m/e* 411). On standing overnight under nitrogen or under vacuum, the compound acquires a drab green color and some $V(CO)_3[P(OMe)_3]_3$ (*m/e* 508) was detected in the mass spectrum. An elemental analysis of the drab green powder was obtained. Anal. Calcd for $V(CO)_4[P(OMe)_3]_2$: C, 29.2; H, 4.42; P, 15.07. Found: C, 25.7; H, 4.44; P, 15.85.

Acknowledgment. This material is based upon work supported by the National Science Foundation under Grant No. CHE-8210514 and the donors of the Petroleum Research Fund, administered by the American Chemical Society. T.G.R. was the recipient of an NSF predoctoral fellowship, and Q.-Z.S. (Lanzhou University) was supported by the Ministry of Education of the People's Republic of China. We thank Professors John Ellis and Theodore Brown for helpful discussions.

Registry No. $V(CO)_6$, 14024-00-1; PMe_3, 594-09-2; $P(n\text{-}Bu)_3$, 998-40-3; $PMePh_2$, 1486-28-8; $P(O\text{-}i\text{-}Pr)_3$, 116-17-6; $P(OMe)_3$, 121-45-9; PPh_3, 603-35-0; $P(i\text{-}Pr)_3$, 6476-36-4; $AsPh_3$, 603-32-7; $V(CO)_5P(n\text{-}Bu)_3$, 87739-19-3; $V(CO)_5PMePh_2$, 87739-24-0; $V(CO)_5P(O\text{-}i\text{-}Pr)_3$, 87739-25-1; $V(CO)_5P(OMe)_3$, 87739-26-2; $V(CO)_5PPh_3$, 72622-82-3; $[Et_4N][V(CO)_5P(OMe)_3]$, 75009-05-1; *cis*-$V(CO)_4[Ph(OMe)_3]_2$, 87739-27-3.

Supplementary Material Available: Tables of infrared spectral data for the substitution products and observed rate constants as a function of ligand concentration and temperature for all reactions studied (4 pages). Ordering information is given on any current masthead page.

Kinetics and Mechanism of Lewis Base Induced Disproportionation of Vanadium Hexacarbonyl and Its Phosphine-Substituted Derivatives

Thomas G. Richmond, Qi-Zhen Shi, William C. Trogler,*[†] and Fred Basolo*

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. *Received May 2, 1983*

Abstract: Vanadium hexacarbonyl readily disproportionates upon treatment with oxygen and nitrogen Lewis bases. The reaction is first order with respect to Lewis base and $V(CO)_6$. Nucleophilic attack on the metal center appears to be the rate-determining step. Second-order rate constants in dichloromethane decrease in the series py > Et_3N > MeCN > MeOH > acetone > THF > 2,5-Me_2THF > DME > $MeNO_2$ > Et_2O, with a factor of 10^4 separating the first and last members of this group. Activation parameters for disproportionation by THF are in accord with an associative mechanism: $\Delta H^{\ddagger} = 14.2 \pm 1.2$ kcal/mol and $\Delta S^{\ddagger} = -21.5 \pm 4.2$ cal/mol·deg. The structure of the disproportionation product is also dependent on the nature of the Lewis base. For Et_2O, the bridging isocarbonyl complex $[V(Et_2O)_4][O\text{-}C\text{-}V(CO)_5]_2$ can be isolated from $CH_2Cl_2\text{-}Et_2O$ solution. For stronger oxygen and nitrogen bases (B), $[V(B)_6][V(CO)_6]_2$ is the final product. In the case of B = pyridine, a bridging isocarbonyl intermediate can be detected as a kinetic product of the disproportionation process. This intermediate reacts with additional pyridine to afford $[V(B)_6][V(CO)_6]_2$. The observation of an isocarbonyl-bridged intermediate suggests that electron transfer may take place through an isocarbonyl ligand. Phosphine-substituted derivatives of $V(CO)_6$ undergo disproportionation much more slowly than $V(CO)_6$, although the rate-limiting step also appears to be CO substitution by the Lewis base. For example, disproportionation of $V(CO)_5P(n\text{-}Bu)_3$ induced by CH_3CN is five orders of magnitude slower than that of $V(CO)_6$.

Vanadium hexacarbonyl undergoes a disproportionation reaction[1,2] when treated with hard Lewis bases, eq 1. Similar

$$3V(CO)_6 + 6B \rightarrow [V(B)_6]^{2+} + 2[V(CO)_6]^- + 6CO \quad (1)$$

base-induced disproportionation reactions have been observed for the homoleptic carbonyls of manganese, iron, cobalt, and nickel.[3] In addition, photochemical disproportionation of a number of metal carbonyl complexes has been reported.[4] Presumably, these disproportionation reactions involve both ligand substitution and electron-transfer processes. As a complement to our study[5] of the mechanism of ligand substitution of $V(CO)_6$, we have investigated the kinetics and mechanism of the Lewis base induced disproportionation of this molecule. Despite the importance of disproportionation processes in metal carbonyl chemistry, we are aware of only three previous kinetic studies of this transformation.[6] These all involved $Co_2(CO)_8$, and the complex behavior observed[6] tended to hamper the study of the reaction mechanism. In a broader context, the redox behavior of the 17e $V(CO)_6$ species may provide a general model for the base-induced disproportionation of organometallic radicals. A portion of this work has

Table I. Second-Order Rate Constants for the Disproportionation of $V(CO)_6$ by Nitrogen and Oxygen Lewis Bases in CH_2Cl_2–Hexane Solution at 25 °C

base	k, M^{-1} s^{-1}	isosbestic points, nm
py	1.22	397, 368
Et_3N	0.765	422
MeCN	0.284	457
MeOH	2.29×10^{-2}	430
acetone	1.93×10^{-2}	414
THF[a]	4.35×10^{-3}	423
2,5-Me_2THF	1.06×10^{-3}	421
DME[b]	2.80×10^{-4}	*c*
$MeNO_2$[d]	1.05×10^{-4}	*c*
Et_2O	9.63×10^{-5}	428

[a] $\Delta H^{\ddagger} = 14.2 \pm 1.2$ kcal/mol; $\Delta S^{\ddagger} = -21.5 \pm 4.2$ cal/mol·deg; uncertainties represent three standard deviations. [b] Temperature = 21 °C. [c] Reaction monitored by FT-IR. [d] Reaction carried out in neat $MeNO_2$; temperature = 21 °C.

[†] Alfred P. Sloan Research Fellow 1983–1985. Address correspondence to this author at the Chemistry Department, D-006, University of California—San Diego, La Jolla, CA 92093.

0002-7863/84/1506-0076$01.50/0

Table II. Infrared Spectral Data for Vanadium Isocarbonyl Bridged Complexes $[V(B)_4][O{-}CV(CO)_5]_2$ in CH_2Cl_2

base	ν_{CO}, cm^{-1}, terminal					isocarbonyl
Et_2O	2032 (w)	1965 (m)	1915 (sh)	1895 (vs)	1860 (sh)	1678 (s)
Et_2O^a	2038 (w)	1960 (m)		1897 (vs)		1684 (s)
Et_2O^b	2032 (w)	1960 (m)		1874 (vs)		1657 (s)
Et_2O^c	2038 (w)	1961 (m)	1942 (sh)	1878 (vs)		1686 (s)
THF	2039 (w)	1960 (m)		1889 (vs)	1860 (s)	1684 (s)
acetone	2030 (w)	1960 (m)		1888 (vs)	1860 (sh)	1680 (m)
py	2037 (w)	1950 (m)		1890 (vs)	1857 (sh)	1680 (s)

[a] Solution spectrum recorded in Et_2O. [b] Solution spectrum of 18% ^{13}CO enriched complex in Et_2O. [c] Solid-state spectrum recorded as a Nujol mull.

been reported in preliminary form.[7]

Experimental Section

General experimental procedures and syntheses of starting materials are detailed[5] in the preceding paper. THF, Et_2O, 2,4-Me_2THF, and DME were dried with sodium benzophenone ketyl, py and Et_3N with BaO, acetone with molecular sieves, CH_2Cl_2 and $MeNO_2$ with P_2O_5, and methanol with $Mg(OMe)_2$. Infrared spectra were recorded on a Niclet 7199 FT-IR or a Perkin-Elmer 283 spectrometer in 0.1-mm CaF_2 cells. Elemental analyses were performed by Galbraith Laboratories Inc., Knoxville, TN.

Kinetic Methods. The rate of disproportionation was determined by monitoring changes in the visible spectra as a function of time. Reactions were inititated by injecting a hexane solution (0.2 mL) of $V(CO)_6$ into a thermostated quartz cell containing a CH_2Cl_2 solution of the Lewis base. Reactions were carried out under pseudo-first-order conditions with respect to base. Isosbestic points were maintained throughout the course of reaction (Table I). Pseudo-first-order rate constants were obtained from the slope of a plot of ln $(A - A_\infty)$ vs. time. Following the completion of the kinetic run, the structure of the product was determined by FT-IR spectroscopy. The reactions could also be monitored by FT-IR, and rate constants obtained by either method were in good agreement. The rate of disproportionation of $V(CO)_5L$ was determined most accurately by absorbance mode IR measurements.

Preparation of $[V(Et_2O)_4][OCV(CO)_5]_2$. Vanadium hexacarbonyl (0.36 g) was stirred with 25 mL of Et_2O for 1.5 h at room temperature. The dark green solid which precipitates from the solution was collected on a glass frit, washed (3 × 10 mL) with hexane, and dried under vacuum. The green powder (0.36 g) was obtained in 83% yield. Anal. Calcd for $C_{28}H_{40}O_{16}V_3$: V, 19.5; C, 42.8; H, 5.14. Found: V, 19.8; C, 41.9; H, 5.21. A sample from an independent preparation also gave a slightly low carbon analysis.

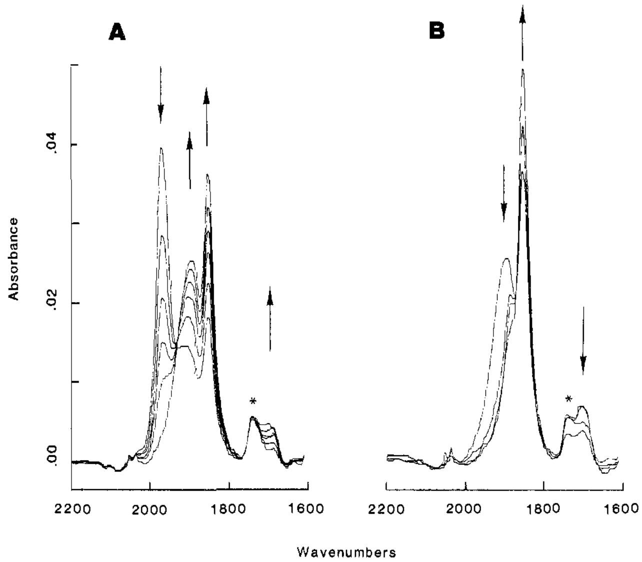


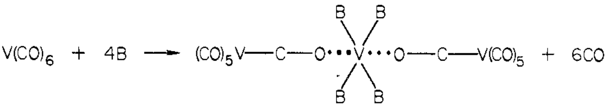
Figure 1. FT-IR spectra of the disproportionation of 1.7 × 10^{-3} M $V(CO)_6$ by 0.14 M py in CH_2Cl_2. (A) Spectra recorded from t = 0 to t = 70 s. (B) Spectra recorded from t = 70 s to t = 1230 s. The peak marked with an asterisk is spurious (see Results section).

Preparation of $[V(B)_6][V(CO)_6]_2$. These complexes for B = acetone, py, and CH_3CN were prepared by a modification of the method of Hieber and co-workers.[1b,c] Solid $V(CO)_6$ was added to a toluene solution containing an excess of Lewis base, and the solid precipitate was collected by filtration, washed with toluene, and dried under vacuum. Mull spectra of these complexes exhibited a single broad CO stretch at 1850 cm^{-1} identical with that reported earlier.[1b,c]

Results

Kinetic Measurements. Vanadium hexacarbonyl undergoes facile disproportionation according to eq 1 when treated with nitrogen or oxygen Lewis bases in dichloromethane solution. A table listing the pseudo-first-order rate constants as a function of Lewis base concentration and temperature is available as supplementary material. The rate of disproportionation is first order with respect to both $V(CO)_6$ and Lewis base. The second-order rate constants for several bases are collected in Table I.

Nature of the Disproportionation Products. For tetrahydrofuran (THF) and diethyl ether (Et_2O), an isocarbonyl bridged complex **1** is observed when the reaction is monitored by FT-IR. Thus, the reaction proceeds according to eq 2. Carbonyl stretching



$$3V(CO)_6 + 4B \longrightarrow (CO)_5V{-}C{-}O\cdots V(B)_4\cdots O{-}C{-}V(CO)_5 + 6CO \qquad (2)$$

1

frequencies of these complexes are listed in Table II. For B = Et_2O, complex **1** is stable in the presence of excess Et_2O and can

---

(1) (a) Ercoli, R.; Calderazzo, F.; Alberola, A. *J. Am. Chem. Soc.* **1960**, *82*, 2966–2967. (b) Hieber, W.; Peterhaus, J.; Winter, E. *Chem. Ber.* **1961**, *94*, 2572–2578. (c) Hieber, W.; Winter, E.; Schubert, E. *Ibid.* **1962**, *95*, 3070–3076. (d) Calderazzo, F. *Inorg. Chem.* **1964**, *3*, 1207–1211. (e) Calderazzo, F. *Inorg. Chem.* **1964**, *3*, 810–814. (f) Calderazoo, F. *Inorg. Chem.* **1965**, *4*, 223–227. (g) Behrens, V. H.; Lutz, K. *Z. Anorg. Allg. Chem.* **1968**, *356*, 225–238. (h) Ellis, J. E.; Faltynek, R. A. *J. Organomet. Chem.* **1975**, *93*, 205–217. (i) Ellis, J. E.; Faltynek, R. A.; Rochford, G. L.; Stevens, R. E.; Zank, G. A. *Inorg. Chem.* **1980**, *19*, 1082–1085. (j) Calderazoo, F.; Pampaloni, G.; Vitali, D. *J. Chem. Soc., Dalton Trans.* **1982**, 1993–1997.

(2) Abbreviations: B, Lewis base; L, phosphorous ligand; THF, tetrahydrofuran; 2,5-Me_2THF, 2,5-dimethyltetrahydrofuran; DME, dimethoxyethane; py, pyridine; Et, ethyl; Me, methyl; Ph, phenyl; *n*-Bu, *n*-butyl.

(3) (a) Hieber, W.; Sedlmeier, J.; Abeck, W. *Chem. Ber.* **1953**, *86*, 700–710. (b) Hieber, W.; Sedlmeier, J. *Chem. Ber.* **1954**, *87*, 25–34. (c) *Ibid.* **1954**, *87*, 789. (d) Hieber, W.; Sedlmeier, J.; Werner, R. *Chem. Ber.* **1957**, *90*, 278–286. (e) Hieber, W.; Brendel, G. *Z. Anorg. Allg. Chem.* **1957**, *289*, 324–337. (f) *Ibid.* **1957**, *289*, 338–344. (g) Hieber, W.; Werner, R. *Chem. Ber.* **1957**, *90*, 286–296. (h) Hieber, W.; Wiesboeck, R. *Ibid.* **1958**, *91*, 1146–1155. (i) *Ibid.* **1958**, *91*, 1155–1161. (j) Hieber, W.; Freyer, W. *Ibid.* **1958**, *91*, 1230–1234. (k) Hieber, W.; Kahler, N. *Ibid.* **1958**, *91*, 2223–2233. (l) *Ibid.* **1958**, *91*, 2234–2238. (m) Hieber, W.; Beck, W.; Zeitler, G. *Angew. Chem.* **1961**, *11*, 364–368.

(4) (a) Haines, R. J.; Nyholm, R. S.; Stiddard, M. H. B. *J. Chem. Soc. A*. **1968**, 43–46. (b) Allen, D. M.; Cox, A.; Kemp, T. J.; Sultana, Q.; Pitts, R. B. *J. Chem. Soc., Dalton Trans.* **1976**, 1189–1193. (c) McCullen, S. B.; Brown, T. L. *Inorg. Chem.* **1981**, *20*, 3528–3533. (d) Gard, D. R.; Brown, T. L. *Organometallics* **1982**, *1*, 1143–1147. (e) Stiegman, A. E.; Tyler, D. R. *J. Am. Chem. Soc.* **1982**, *104*, 2944–2945. (f) Steigman, A. E.; Stieglitz, M.; Tyler, D. R. *Ibid.* **1983**, *105*, 6032–6037.

(5) (a) Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.*, preceding article in this issue. (b) Shi, Q.-Z.; Richmond, T. G.; Trogler, W. C.; Basolo, F. *J. Am. Chem. Soc.* **1982**, *104*, 4032.

(6) (a) Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 657. (b) Stanghellini, P. L.; Rossetti, R.; Mentasti, E.; Pelizzetti, E. *Inorg. Chim. Acta* **1977**, *22*, 19. (c) Absi-Halabi, M.; Atwood, J. D.; Forbus, N. P.; Brown, T. L. *J. Am. Chem. Soc.* **1980**, *102*, 6248.

(7) Richmond, T. G.; Shi, Q.-Z.; Trogler, W. C.; Basolo, F. *J. Chem. Soc., Chem. Commun.* **1982**, 650–652.

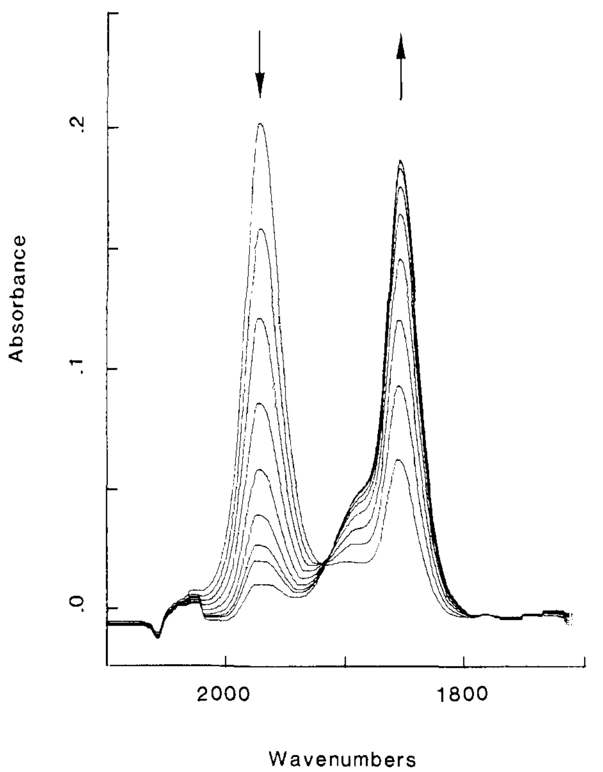


Figure 2. FT-IR spectra of the disproportionation of 4×10^{-4} M $V(CO)_6$ by 1.56×10^{-2} M MeCN in CH_2Cl_2. The final spectrum was recorded at $t = 1543$ s.

be isolated from Et_2O solution and further characterized by its mull IR spectrum and elemental analysis. The strong low-frequency carbonyl stretching band (ca. 1680 cm^{-1}) signals the presence of a carbon- and oxygen-bonded carbonyl. The distorted terminal CO-stretching region indicates ion-paired $[V(CO)_6]^-$. The similarity of the solid-state and solution spectra suggests that the isocarbonyl-bridged structure occurs in both phases. Other workers have reported[11] similar IR spectra for this complex. In the absence of excess Et_2O, $[V(Et_2O)_4][OCV(CO)_5]_2$ is unstable in CH_2Cl_2 and is oxidized over the course of 0.5 h to $V(CO)_6$, which is the only metal carbonyl product detected by IR spectroscopy. Vanadium hexacarbonyl can be isolated in 13% yield from the reaction mixture by vacuum sublimation. When complex **1**, B = THF, is allowed to react with excess THF, $V(THF)_6[V(CO)_6]_2$ slowly precipitates from CH_2Cl_2 solution. The formulation of this product was confirmed by its mull IR spectrum which showed only a broad featureless peak at 1850 cm^{-1}, which is identical with that observed for $[Et_4N][V(CO)_6]$.

In the case of pyridine (py), an intermediate **2** can be detected as a kinetic product of the disproportionation reaction which subsequently reacts with additional pyridine to yield $[V(py)_6][V(CO)_6]_2$. This behavior is illustrated in Figure 1. In the initial stages of the reaction, the intermediate **2** (ν_{CO} = 2053 (w), 1894 (s), 1695 (m) cm^{-1}) grows in as the peak due to $V(CO)_6$ decreases in intensity (Figure 1A). The absorbance at 1894 and 1695 cm^{-1} increase in a constant ratio and are therefore assigned to the same species (**2**). The peak marked with an asterisk does not change in intensity over the course of the experiment until the IR cell is refilled with a fresh sample of the reactant solution and the final spectrum is recorded. This peak may arise from another isocarbonyl species in solution. The relatively high frequency (1740 cm^{-1}) of this peak suggests a weaker isocarbonyl interaction than observed in $[V(py)_4][O{-}C{-}V(CO)_5]_2$. The buildup of **2** continues until all the $V(CO)_6$ is consumed. Concurrently, the intermediate reacts with additional py to afford non-ion-paired $[V(CO)_6]^-$ as the ultimate product of the reaction (Figure 1B).

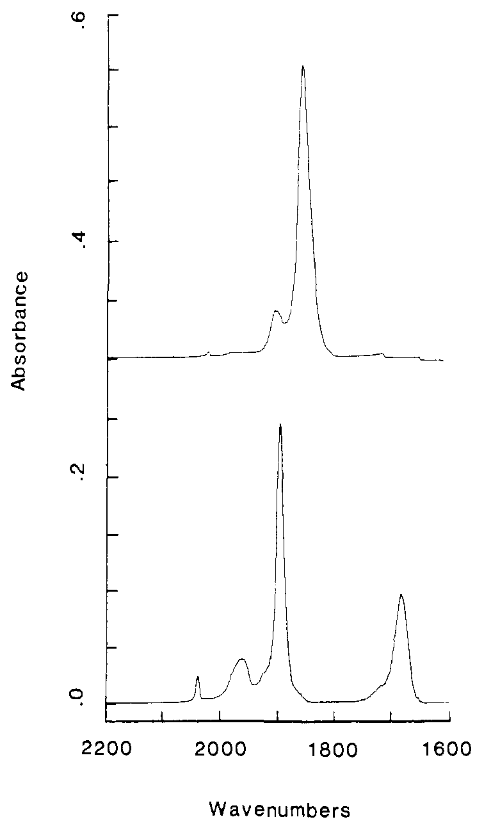
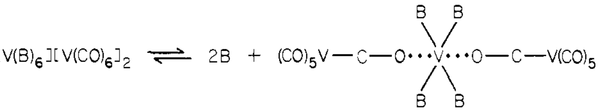


Figure 3. FT-IR of $[V(OEt_2)_4][O{-}C{-}V(CO)_5]_2$ in Et_2O (lower trace). Spectrum recorded in the presence of 0.38 M MeCN (upper trace). The peak at 1900 cm^{-1} (upper trace) arises from unsymmetrical solvation of $[V(CO)_6]^-$ in the low dielectric strength medium.

No intermediates are detected when $V(CO)_6$ is combined with excess acetone, methanol (MeOH), triethylamine (Et_3N), or acetonitrile (MeCN), Figure 2. Isocarbonyl-bridged complexes with B = acetone, py, or THF can be prepared in CH_2Cl_2 solution by dissolution of the appropriate $[V(B)_6][V(CO)_6]_2$ complex, and $[V(B)_4][OCV(CO)_5]_2$ forms according to eq 3 (Table II). When



$$[\mathrm{V(B)_6}][\mathrm{V(CO)_6}]_2 \rightleftharpoons 2\mathrm{B} + \mathrm{(CO)_5V{-}C{-}O}\cdots\overset{\mathrm{B\ \ B}}{\underset{\mathrm{B\ \ B}}{\mathrm{V}}}\cdots\mathrm{O{-}C{-}V(CO)_5} \tag{3}$$

excess py is added to a CH_2Cl_2 solution of $[V(py)_4][O{-}C{-}V(CO)_5]_2$, the frequency of the bridging isocarbonyl band shifts to higher energy. When no residual py is present ν_{CO} = 1664 cm^{-1}, with 2 equiv of py ν_{CO} = 1680 cm^{-1}, and in 0.14 M py ν_{CO} = 1695 cm^{-1}. The non-ion-paired complex $[V(B)_6][V(CO)_6]_2$ is stable to loss of B in CH_2Cl_2 only when B = MeCN. Treatment of the bridging isocarbonyl species **1** (B = Et_2O or THF) with acetonitrile or acetone rapidly cleaves the isocarbonyl linkage to yield free $[V(CO)_6]^-$, Figure 3. The peak at 1900 cm^{-1} in the spectrum of $[V(CH_3CN)_6][V(CO)_6]_2$ in Et_2O is indicative of unsymmetrical solvation of $[V(CO)_6]^-$ in Et_2O solution. Similarly the spectrum of $[Et_4N][V(CO)_6]$ in CH_2Cl_2 exhibits a shoulder at 1900 cm^{-1}. Since the ion pairing observed in these complexes seemed to be a consequence of the relatively low dielectric strength of CH_2Cl_2, nitromethane ($MeNO_2$) was investigated as an alternative polar, noncoordinating solvent. However, $V(CO)_6$ disproportionates in $MeNO_2$ at a similar rate as in Et_2O (Table I). Additionally, the $[V(B)_n][V(CO)_6]_2$ complexes are unstable in $MeNO_2$ and undergo partial oxidation to $V(CO)_6$.

Disproportionation of $V(CO)_5L$. Monosubstituted vanadium carbonyl derivatives $V(CO)_5L$ (L = $P(OMe)_3$, $P(n\text{-}Bu)_3$, and PPh_3) also undergo disproportionation when treated with Lewis bases, eq 4. The rate of the reaction between $V(CO)_5VP(n\text{-}Bu)_3$

$$3\mathrm{V(CO)_5L} + 6\mathrm{B} \rightarrow [\mathrm{V(B)_6}]^{2+} + 2[\mathrm{V(CO)_5L}]^- + 5\mathrm{CO} + \mathrm{L} \tag{4}$$

and THF depends directly on the THF concentration (Table III). New low-frequency carbon monoxide stretches are also observed

Table III. Rate Constants for the Disproportionation of $V(CO)_5L$ in CH_2Cl_2 Solution at 25 °C

L	base	*B*, mol/L	10^5k_{obsd}, s^{-1}	10^6k_2, $M^{-1}\ s^{-1}$
$P(n\text{-}Bu)_3$	THF	6.00	1.60	2.67
		10.30	2.82	2.74
		11.80	3.20	2.71
$P(n\text{-}Bu)_3$	Et_2O	9.53	1.83	1.92
PPh_3	Et_2O	8.38	2.53	3.02

in the reactions of $V(CO)_5P(n\text{-}Bu)_3$ with Et_2O ($\nu_{CO} = 1625\ cm^{-1}$) or THF ($\nu_{CO} = 1634\ cm^{-1}$). In some cases, $[V(CO)_6]^-$ is also observed as a product of eq 2. Indeed, disproportionation of $V(CO)_5P(OMe)_3$ by THF affords only $[V(CO)_6]^-$. Reaction of $V(CO)_5PPh_3$ with Et_2O gives[11] $[V(CO)_5PPh_3]^-$, but reaction with THF also yields some $[V(CO)_6]^-$. The amount of $[V(CO)_6]^-$ obtained is reduced when the reaction is carried out in the presence of added PPh_3. Similarly, $V(CO)_5P(n\text{-}Bu)_3$ and Et_2O or THF afford only $[V(CO)_5P(n\text{-}Bu)_3]^-$, but reaction with MeCN produces both phosphine-substituted and unsubstituted anions in the ratio $[V(CO)_5P(n\text{-}Bu)_3^-]/([V(CO)_6^-] + [V(CO)_5P(n\text{-}Bu)_3^-]) = 0.3$ as determined by quantitative IR measurements of the amount of $[V(CO)_6^-]$ produced. When this reaction is carried out in the presence of 10 equiv of $P(n\text{-}Bu)_3$ per vanadium ($[P(n\text{-}Bu)_3] = 0.4$ M), the above ratio increases to 0.7.

Discussion

Kinetics of Disproportionation. Interaction of hard Lewis bases and $V(CO)_6$ leads to facile disproportionation. The reaction obeys the second-order rate law given in eq 5. The first-order dependence of the rate on the Lewis base concentration suggests that an associative reaction mechanism is operative. This is corroborated by the dependence of the rate on the nature of the base (Table I). Nitrogen bases generally react more rapidly than oxygen bases. The rate of disproportionation increases with the increasing basicity of the nucleophile. Steric factors are also evident since 2,5-Me_2THF[8] reacts five times more slowly than THF. The relatively small activation enthalpy (14.2 ± 1.2 kcal/mol) and large negative entropy of activation (−21.5 ± 4.2 cal/mol·deg) determined for B = THF are also in accord with an associative reaction scheme. Indeed, the activation parameters are strikingly similar to those observed[5] for phosphine substitution in $V(CO)_6$ which proceeds solely by a second-order pathway. Thus, associative attack on vanadium by the Lewis base appears to be the rate-determining step in the disproportionation process.

$$-d[V(CO)_6]/dt = k[V(CO)_6][B] \tag{5}$$

Structure of the Disproportionation Products. The nature of the Lewis base is also critical in determining the structure of the disproportionation product. In the case of weakly coordinating bases such as Et_2O or THF, an isocarbonyl-bridged complex (**1**) is observed as the product (eq 2). For Et_2O, the presence of the bridging isocarbonyl is signalled by the strong, low-frequency (ca. 1680 cm^{-1}) carbonyl stretch in both solution and solid-state IR spectra (Table II). Additionally, the terminal CO stretches are shifted to higher frequency and split because of the reduced symmetry compared to free $[V(CO)_6]^-$.[9] All of the IR bands are shifted to lower frequency when ^{13}CO-enriched $V(CO)_6$ is used to prepare $[V(OEt_2)_4][O{-}C{-}V(CO)_5]_2$. The FT-IR spectrum of **1**, B = THF, is qualitatively similar to the Et_2O adduct. This complex slowly reacts with additional THF in CH_2Cl_2 with precipitation of $[V(THF)_6][V(CO)_6]_2$. Recrystallization of the latter complex from CH_2Cl_2 results in the regeneration of compound **1**, B = THF, which Schneider and Weiss[10] have characterized by single-crystal X-ray diffraction. The structure shows that the V(II) center is octahedrally coordinated by 4 THF molecules and two trans bridging isocarbonyl ligands from $[OCV(CO)_5]^-$. The V–O distances are shorter to the isocarbonyl oxygen (2.08 Å) than to the oxygen atom of THF (2.17 Å).[10] Similar bridging isocarbonyl moieties have been observed in the structures of metal carbonyl anions with hard cations such as in $[Mg(py)_4][OCMo(CO)_2Cp]_2$.[11] Ion pairing of this type is commmon in solutions of metal carbonyl anions and alkali metal cations.[12] Of particular relevance is the recent observation[13] of ion pairing in several $Na[V(CO)_5L]$ (L = phosphorus donor ligand) complexes in THF solution. Similar isocarbonyl-bridged compounds can be prepared for B = py or acetone by dissolution of $[VB_6][V(CO)_6]_2$ in CH_2Cl_2 (eq 3). This transformation does not occur for B = MeCN. Apparently, the ion-paired isocarbonyl-bridged structure is favored because of the relatively low polarity of CH_2Cl_2. Thus, eq 3 is best represented as an equilibrium with the Lewis base B and $[OCV(CO)_5^-]$ competing for the axial coordination sites of the $[V(B)_4]^{2+}$ unit. From these observations the stability of the isocarbonyl-bridged species **1** relative to $[V(B)_6][V(CO)_6]_2$ decreases in the series Et_2O > THF > acetone, py > CH_3CN. The surprising donor ability of $V(CO)_6^-$ to the V(II) center no doubt reflects the importance of electrostatic forces in the low-dielectric solvent.

In contrast, when $V(CO)_6$ is treated with excess acetone, MeCN, or MeOH, no isocarbonyl species are observed, and free $[V(CO)_6]^-$ appears in the solution FT-IR spectrum (Figure 2). Similarly, reaction of $[V(Et_2O)_4][OCV(CO)_5]_2$ with MeCN or acetone rapidly cleaves the isocarbonyl bridge to afford non-ion-paired $[V(CO)_6]^-$, Figure 3.

Evidence for an Isocarbonyl-Bridged Kinetic Intermediate. Sequential FT-IR spectra for the reaction between py and $V(CO)_6$ are recorded in Figure 1. The first series of spectra (Figure 1A) show the decay of the peak arising from $V(CO)_6$ and the appearance of an intermediate (**2**) with spectral characteristics similar (but not identical) to the isocarbonyl-bridged complexes discussed above. Alternative structures for **2** such as $[V(py)_n][O{-}C{-}V(CO)_5]$ where $n \leq 5$ may also be envisioned. The second series of spectra (Figure 1B) show the subsequent decay of **2** to afford free $[V(CO)_6]^-$. These observations suggest that an isocarbonyl-bridged intermediate may be a kinetic product of the disproportionation process.

Disproportionation of $V(CO)_5L$. The phosphine-substituted derivatives of $V(CO)_6$ undergo disproportionation at a much slower rate than the parent molecule. This parallels the decrease in rate of the second CO substitution step in $V(CO)_5L$ compounds by phosphines.[5] The kinetic data collected in Table III reveal that the reaction is first order with respect to Lewis base. Two products are observed for these reactions depending on the combination of L and B employed. The phosphine-substituted anion $[V(CO)_5L]^-$ is the sole product when weakly coordinating bases (B = THF or Et_2O) are added to solutions of $V(CO)_5P(n\text{-}Bu)_3$. With the more strongly coordinating MeCN, some $[V(CO)_6]^-$ also forms. The relative amount of $[V(CO)_6]^-$ product can be reduced by conducting the reaction in the presence of excess phosphine ligand. Phosphine replacement by CO (liberated during the course of disproportionation) may occur in $V(CO)_5L$ since both phosphines and CO are substitution labile in the 17-electron vanadium carbonyl complexes.[5] Alternatively, phosphine substitution by CO in $[V(CO)_5L]^-$ may occur. It was recently reported that ion pairing of Na^+ to the CO trans to phosphine in $[V(CO)_5L]^-$ promotes phosphine dissociation.[13] The observation of IR bands characteristic of ion pairing to a CO ligand during the disproportionation reaction of $V(CO)_5L$ suggests that this is also a reasonable pathway for phosphine replacement.

Mechanism of Disproportionation. A mechanism for the disproportionation of $V(CO)_6$ is outlined in eq 6–8. The initial and rate-determining step for this reaction is bimolecular substitution

---

[8] Wax, M. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 7028–7030. On the basis of the inductive effect, 2,5-Me_2THF would be expected to be more basic than THF.

[9] Shriver, D. F. *J. Organomet. Chem.* **1975**, *94*, 259–271 and references therein.

[10] Schneider, M.; Weiss, E. *J. Organomet. Chem.* **1976**, *121*, 365–371.

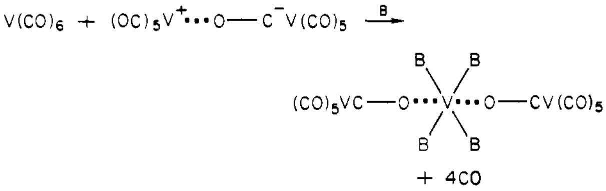
[11] Ulmer, S. W.; Skirstad, P. M.; Burlitch, J. M.; Hughes, R. E. *J. Am. Chem. Soc.* **1973**, *95*, 4469–4471.

[12] (a) Edgell, W.; Chanjamsri, S. *J. Am. Chem. Soc.* **1980**, *102*, 147–155 and references therein. (b) Darensbourg, M. Y.; Jimenez, P.; Sackett, J. R.; Hanckel, J. M.; Kump, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 1521–1530.

[13] Darensbourg, M. Y.; Hanckel, J. M. *Organometallics* **1982**, *1*, 82–87.

$$V(CO)_6 + B \longrightarrow V(CO)_5B + CO \quad (6)$$

$$V(CO)_5B + V(CO)_6 \rightleftharpoons (CO)_5V^{+}\cdots O{-}C{-}V(CO)_5 + B \quad (7)$$



(8)

$$V(CO)_6 + (OC)_5V^{+}\cdots O{-}C^{-}V(CO)_5 \xrightarrow{B} (CO)_5VC{-}O\cdots V(B)_4\cdots O{-}CV(CO)_5 + 4CO \quad (8)$$

of carbon monoxide by the Lewis base B. Thus, the rate of disproportionation depends on the same factors that influence nucleophilic attack on $V(CO)_6$. The slower rate of disproportionation of $V(CO)_5L$ compared to $V(CO)_6$ can be attributed to slower CO substitution in these complexes. The hard Lewis base B would be expected to be very labile[14] in $V(CO)_5B$ by analogy with their 18-electron analogues $[V(CO)_5B]^-$ (B = dimethyl sulfoxide[15] or NH_3[16]) which readily dissociate B. A second CO substitution before electron transfer seems unlikely since this would be expected to be significantly slower than the first CO substitution step (see preceding paper). In addition, disproportionation is not significantly accelerated when the chelating ether DME is employed instead of Et_2O. Formation of $(CO)_5V{-}OCV(CO)_5$ provides a pathway for inner-sphere electron transfer. It is, of course, difficult to eliminate outer-sphere electron transfer as a parallel or competing pathway. Although inner-sphere processes are well known in electron-transfer reactions of Werner complexes,[17] we are aware of no organometallic examples implicating CO in such a fashion. The strong field complex $V(CO)_6$ with a large $10Dq$ and stable t_{2g} orbitals would be expected to be more oxidizing than $V(CO)_5B$, which contains a weak field ligand such as THF that cannot π bond effectively. Substitution of a π-acceptor CO ligand by THF will lead to a destabilization of one of the t_{2g} orbitals. This provides a driving force for eq 7 as well as for the alternative outer-sphere electron-transfer pathway. Similar ligand field effects are evident in electron-transfer reactions of octahedral Werner complexes.[18] We do not favor initial outer-sphere electron transfer between two unsubstituted $V(CO)_6$ molecules; this is known[19] to be a high-energy process. The formation of an isocarbonyl species as a kinetic product of the disproportionation reaction, when B = py, suggests that the isocarbonyl bridge forms prior to electron transfer, at least in this instance. To achieve the second-electron-transfer step, another $V(CO)_6$ apparently must form a second isocarbonyl bridge to a labile V(I) center.[20] The exact sequence of bridge formation and CO substitution is not known; these are combined in eq 8.

Electron transfer via a bridging isocarbonyl may prove to be an important feature of redox reactions of metal carbonyls. In this context, we note the disproportionation of photochemically generated organo-transition-metal radicals[4] and the current interest in isocarbonyl-bridged structures with regard to CO activation.[21]

Conclusions

Associative carbon monoxide substitution occurs when $V(CO)_6$ is treated with either soft or hard Lewis bases and at rates that are enhanced greatly when compared to electronically saturated analogues. For soft Lewis bases such as phosphines, stable phosphorus-substituted vanadium carbonyl derivatives are formed as described in the preceding paper. In the case of hard oxygen or nitrogen bases, B, kinetic evidence points to the transient formation of $V(CO)_5B$ which undergoes further reaction to afford disproportionation products. Two factors are important in the further reactions of $V(CO)_5B$. First, in contrast to phosphorus donor ligands, B is expected to be very labile in $V(CO)_5B$, thus enabling isocarbonyl bridge formation to occur. In addition, destabilization of a t_{2g} orbital by the weak-field base provides a driving force for electron transfer to ultimately afford the stable 18-electron vanadium hexacarbonyl anion and V(II). This tendency to disproportionate in the presence of hard donor bases can be contrasted with the behavior of the 18e $M(CO)_6$ (M = Cr, Mo, W) systems.[22] The mechanistic study of $V(CO)_6$ thus illustrates two general reaction types available to 17e carbonyls, ligand substitution or ligand substitution followed by rapid electron transfer.

Acknowledgment. We thank the National Science Foundation (Grant No. CHE-8210514) for financial support. Q.-Z.S. is on leave from Lanzhou University and thanks the Ministry of Education of the People's Republic of China for support. T.G.R. is the recipient of an NSF Predoctoral Fellowship. We thank Prof. John Ellis for helpful comments and Prof. David Tyler for a preprint of reference 4f.

Registry No. 1 (B = Et_2O), 87761-49-7; **1** (B = THF), 61625-19-2; **1** (B = acetone), 87761-50-0; **1** (B = py), 87761-51-1; $[V((CH_3)_2CO)_6][V(CO)_6]_2$, 87739-12-6; $[V(py)_6][V(CO)_6]_2$, 87739-14-8; $[V(CH_3CN)_6][V(CO)_6]_2$, 87739-16-0; $[V(THF)_6][V(CO)_6]_2$, 87739-18-2; $V(CO)_5P(n\text{-}Bu)_3$, 87739-19-3; $V(CO)_5PPh_3$, 72622-82-3; $V(CO)_6$, 14024-00-1; py, 110-86-1; Et_3N, 121-44-8; MeCN, 75-05-8; MeOH, 67-56-1; THF, 109-99-9; 2,5-Me_2THF, 1003-38-9; DME, 110-71-4; $MeNO_2$, 75-52-5; Et_2O, 60-29-7; acetone, 67-64-1.

Supplementary Material Available: Table of pseudo-first-order rate constants and conditions for the Lewis base induced disproportionation of $V(CO)_6$ (1 page). Ordering information is given on any current masthead page.

---

[14] Brown, T. L. *Ann. N.Y. Acad. Sci. U.S.A.* **1980**, *333*, 80–89.

[15] Ihmels, K.; Rehder, P. *J. Organomet. Chem.* **1982**, *232*, 151–154.

[16] Fjare, K. L.; Ellis, J. E. *Organometallics* **1982**, *1*, 1373–1378.

[17] Taube, H. "Electron Transfer Reactions of Complex Ions in Solution"; Academic: New York, 1970.

[18] Marzilli, L. G.; Salerno, J. G.; Epps, L. A. *Inorg. Chem.* **1972**, *11*, 2050–2053.

[19] Holland, G. F.; Manning, M. C.; Ellis, D. E.; Trogler, W. C. *J. Am. Chem. Soc.* **1983**, *105*, 2308–2314.

[20] Electrochemically generated $[V(CO)_6]^+$ is very unstable and decomposes with loss of CO within seconds at −78 °C. We suspect that electrostatic interactions in the low dielectric solvent system hinder displacement of the $(OC)V(CO)_5^-$ ligand relative to the neutral CO ligands from the V^+ center. Bond, A. M.; Colton, R. *Inorg. Chem.* **1976**, *15*, 2036–2040.

[21] (a) Shriver, D. F. *Adv. Chem. Ser.* **1981**, *152*, 1–18. (b) Berry, D. H.; Bercaw, J. E.; Jircitano, A. J.; Mertes, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 4712–4715. (c) Tilley, T. D.; Anderson, R. A. *J. Chem. Soc., Chem. Commun.* **1981**, 985–986. (d) Tilley, T. D.; Anderson, R. A. *J. Am. Chem. Soc.* **1982**, *104*, 1772–1774. (e) Hamilton, P. M., Jr.; Willis, W. S.; Stucky, G. D. *Ibid.* **1981**, *103*, 4255–4256. (f) Marsella, J. A.; Huffman, J. C.; Caulton, K. G.; Longato, B.; Norton, J. R. *Ibid.* **1982**, *104*, 6360–6368. (g) Merola, J. S.; Gentile, R. A.; Ansell, G. B.; Modrick, M. A.; Zentz, S. *Organometallics* **1982**, *1*, 1731–1733.

[22] Slow reaction of $M(CO)_6$ (M = Cr, Mo, W) with hard Lewis bases such as $PhCH_2NH_2$ takes place at elevated temperatures to afford the monosubstituted products $M(CO)_5B$. Pardue, J. E.; Dobson, G. R. *Inorg. Chim. Acta* **1976**, *20*, 207–212.