Electronic Structure and Redox Reactions of Vanadium(II) Polypyridine, Isocyanide, and Phosphine Complexes

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Electronic absorption spectra and redox reactions are reported for a variety of vanadium(II) complexes of strong-field ligands. The absorption spectra of $[V(L\text{–}L)_3]^{2+}$ (L–L = polypyridine) are dominated by intense metal-to-ligand charge-transfer (m.l.c.t.) transitions. The m.l.c.t. absorption maxima for $[V(L\text{–}L)_3]^{2+}$, and half-wave potentials for reduction of $[V(L\text{–}L)_3]^{2+}$, are sensitive to substituents in the polypyridine rings. In contrast, the $[V(L\text{–}L)_3]^{3+/2+}$ redox process is primarily metal-localized. Cyclic voltammetry performed on $[V(CNBu^t)_6]^{2+}$ shows that the 0, I, II, and III oxidation states are readily accessible; $[V(dppe)_3][V(CO)_6]_2$ [dppe = 1,2-bis(diphenylphosphino)ethane] exhibits waves attributable to $[V(dppe)_3]^{3+/2+}$, $[V(dppe)_3]^{2+/+}$, and $[V(CO)_6]^{0/-}$ The lowest-energy spin-allowed electronic transitions in $[V(CNBu^t)_6]^{2+}$ are primarily *d–d* in nature, whereas those in $[V(dppe)_3]^{2+}$ contain substantial m.l.c.t. character.

We have recently begun to study the photoredox properties of vanadium(II) complexes, because they should provide entries into the rich redox chemistry of vanadium while retaining the attractive photophysical properties of the isoelectronic chromium(III). Our initial studies have shown that vanadium(II) polypyridine complexes, $[V(L\text{–}L)_3]^{2+}$, are capable of photochemical one-electron oxidation[1] as well as photoinitiated two-electron oxidation.[2] However, the efficiency of these reactions is limited by the very short lifetimes (1—2 ns at room temperature) of the excited states, which are primarily quartet metal-to-ligand charge-transfer (^{4}m.l.c.t.) in character.[3] These photophysical data therefore contrast with those previously documented for chromium(III): in many chromium(III) complexes, the *d–d* excited state ^2E (^2E_g in complexes with full octahedral symmetry) is lowest lying, resulting in excited-state lifetimes well above 1 μs. In vanadium(II) complexes of phosphines and isocyanides, ^{4}m.l.c.t. should be higher in energy, allowing for longer excited-state lifetimes and therefore more efficient photoredox reactions. We now report a spectroscopic and electrochemical study of two such complexes, $[V(CNR)_6]^{2+}$ (R = Bu^t) and $[V(dppe)_3]^{2+}$ [dppe = 1,2-bis(diphenylphosphino)ethane], and a comparison of their properties with those of a series of complexes $[V(L\text{–}L)_3]^{2+}$.

Experimental

All synthetic procedures were carried out under argon in Schlenk apparatus or in a dry-box. Literature procedures were used to prepare the vanadium(II) polypyridine complexes, as their trifluoromethanesulphonate salts (ligand abbreviations: bipy = 2,2′-bipyridine; dmbipy = 4,4′-dimethyl-2,2′-bipyridine; phen = 1,10-phenanthroline; dpphen = 4,7-diphenyl-1,10-phenanthroline; tmphen = 3,4,7,8-tetramethyl-1,10-phenanthroline),[1,3] $[V(CNBu^t)_6][PF_6]_2$,[4] $[V(dppe)_3][V(CO)_6]_2$,[5] and tetrabutylammonium trifluoromethanesulphonate, $[NBu_4][O_3SCF_3]$.[6] Other reagents and solvents were reagent or spectrophotometric grade and were used as received.

The solid vanadium complexes and their solutions were stable for extended periods under an inert atmosphere, except for $[V(CNBu^t)_6][PF_6]_2$ and $[V(dppe)_3][V(CO)_6]_2$, which decomposed in solution over a period of hours even when rigorously degassed. This decomposition made quantitative comparison of the spectral and electrochemical properties of $[V(CNBu^t)_6]^{2+}$ and $[V(dppe)_3]^{2+}$ difficult. Behrens and Lutz[5] reported that $[V(CO)_6]^-$ could be removed from solutions of $[V(dppe)_3][V(CO)_6]_2$ {as solid $[Ni(phen)_3][V(CO)_6]_2$} by addition of $[Ni(phen)_3]^{2+}$ salts. Although we also obtained precipitates under similar conditions, we were unable to isolate tractable $[V(dppe)_3]^{2+}$ salts from the filtrates.

For cyclic voltammetry a 0.1 mol dm^{-3} solution of $[NBu_4][O_3SCF_3]$ in CH_2Cl_2 was degassed by bubbling with N_2. Then the appropriate vanadium complex was added (concentrations 10^{-3}—10^{-2} mol dm^{-3}), and the voltammograms were recorded immediately. The measurements were made with a PAR model 174A polarographic analyzer, using platinum working and counter electrodes and Ag–AgCl (3 mol dm^{-3} aqueous NaCl) as reference electrode. The potential of the ferrocene redox couple was 0.54 V under these conditions. Waves exhibiting peak separations significantly larger than 60 mV but equal anodic and cathodic peak currents were described as quasireversible.

Electronic absorption spectra were recorded using a Cary 219 spectrophotometer. Samples for spectroscopic measurements were prepared by freeze–pump–thaw degassing of the solvents on a high-vacuum line.

Results and Discussion

Electronic Absorption Spectra.—Spectral data for the low-energy intense m.l.c.t. transitions in the vanadium(II) polypyridine complexes are given in Table 1. Compared to that of $[V(phen)_3]^{2+}$, the m.l.c.t. absorption of $[V(dpphen)_3]^{2+}$ appears at significantly lower energy and is noticeably more intense (see absorption coefficients in Table 1). Both of these changes are as expected. The electron-withdrawing phenyl groups should stabilize the m.l.c.t. excited state. Also, delocalization of electron density should be more extensive in the $[V(dpphen)_3]^{2+}$ m.l.c.t. excited state than in that of $[V(phen)_3]^{2+}$, causing the corresponding m.l.c.t. transition dipole moment to increase. Similar effects have also been observed in $[Cu(L\text{–}L)_2]^+$ complexes.[7] The other substitutent we have studied, methyl (L–L = tmphen or dmbipy), has little effect on the position or intensity of the m.l.c.t. absorption bands. This is surprising, since we expected to find at least some blue shift in the bands relative to $[V(phen)_3]^{2+}$. However, methyl substitution also causes only minor spectral changes in iron(II) polypyridine complexes.[8]

Solutions of $[V(CNBu^t)_6]^{2+}$ in degassed CH_2Cl_2 show

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Table 1. Low-energy m.l.c.t. absorptions for vanadium(II) polypyridine complexes

Complex	$\lambda_{max.}$/nm	ε/dm^3 mol^{-1} cm^{-1}
$[V(phen)_3]^{2+}$	640^a	6.2×10^3
$[V(tmphen)_3]^{2+}$	640^b	1×10^4
$[V(dpphen)_3]^{2+}$	685^b	1.4×10^4
$[V(bipy)_3]^{2+}$	650^c	5.7×10^3
$[V(dmbipy)_3]^{2+}$	650^b	7×10^3

[a] In ethanol. [b] In acetone. [c] In water.

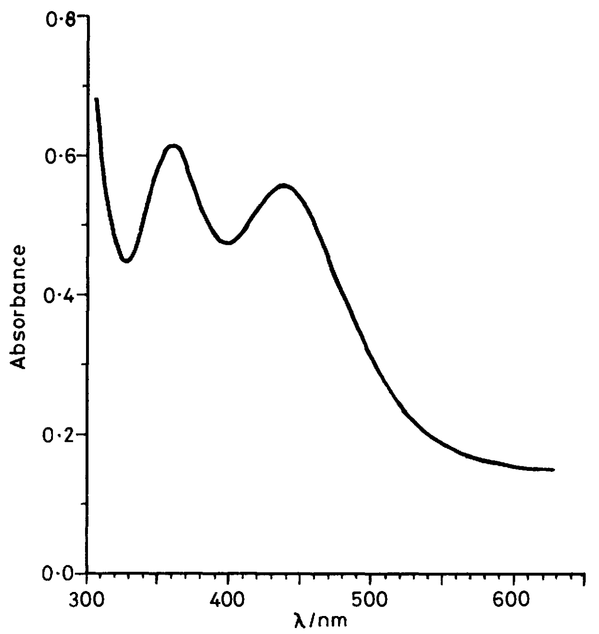

Figure 1. Electronic absorption spectrum of $[V(CNBu^t)_6][PF_6]_2$ (4×10^{-3} mol dm^{-3}) in CH_2Cl_2

bands at 435 and 355 nm, with absorption coefficients of 180 and 200 dm^3 mol^{-1} cm^{-1} respectively (Figure 1). We assign these bands to the $^4A_{2g} \longrightarrow {}^4T_{2g}$ and $^4A_{2g} \longrightarrow {}^4T_{1g}(F)$ *d–d* transitions (O_h). This spectrum is very similar to the spectra of the isoelectronic strong-field complexes $[V(CN)_6]^{4-}$ [*d–d* bands at 450 (120) and 360 nm (150 dm^3 mol^{-1} cm^{-1})][9] and $[Cr(CN)_6]^{3-}$ [*d–d* bands at 375 (80) and 307 nm (55 dm^3 mol^{-1} cm^{-1})].[10]

The spectrum of $[V(dppe)_3][V(CO)_6]_2$ in degassed CH_2Cl_2 shows a small band at 495 nm, a shoulder at *ca.* 400 nm, and a sharp band at 350 nm [Figure 2(*a*)]. The features near 400 and 350 nm are assigned to the characteristic *d–d* ($^1A_{1g} \longrightarrow {}^1T_{1g}$) and m.l.c.t. [$t_{2g} \longrightarrow \pi^*(CO)$] transitions, respectively, of $[V(CO)_6]^-$.[11] Although the band at 495 nm is clearly due to $[V(dppe)_3]^{2+}$, the remainder of the cation spectrum is masked by the strong absorption due to the anion. Although we were unable to prepare salts of $[V(dppe)_3]^{2+}$ without the interfering $[V(CO)_6]^-$ counter ion, we were able to identify additional features due to $[V(dppe)_3]^{2+}$ by placing a solution of $[NEt_4][V(CO)_6]$ of appropriate concentration in the reference beam of the spectrophotometer. The resulting difference spectrum [Figure 2(*b*)] shows three distinct bands with absorption maxima at 495, 435, and 375 nm (ε *ca.* 3 000, 2 000, and 4 000 dm^3 mol^{-1} cm^{-1} respectively). These bands probably contain contributions from *d–d* transitions, but the relatively large absorption coefficients suggest substantial m.l.c.t. character as well.

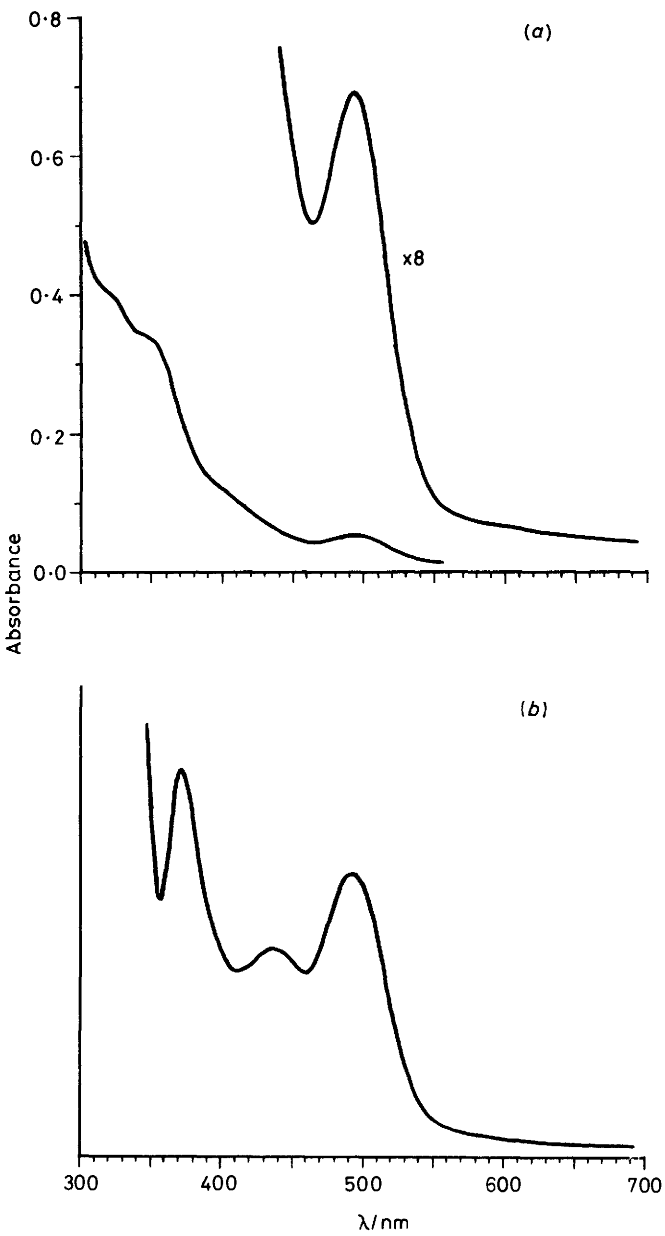

Figure 2. (*a*) Electronic absorption spectrum of $[V(dppe)_3][V(CO)_6]_2$ in CH_2Cl_2. (*b*) Difference spectrum showing bands attributable to $[V(dppe)_3]^{2+}$

The low-energy absorption bands of $[V(CNBu^t)_6]^{2+}$, like those previously recorded for $[Fe(CNMe)_6]^{2+}$,[12] are attributable to *d–d* transitions. However, low-energy transitions in $[V(dppe)_3]^{2+}$, like those in the polypyridine complexes, show substantial m.l.c.t. character. This difference in electronic spectra on changing from isocyanide to phosphine ligands is surprising, since m.l.c.t. transitions generally appear at similar energies in phosphine and isocyanide complexes. In square-planar rhodium(I) species, for example, chelating aromatic[13] and aliphatic diphosphines,[14] as well as aryl[15] and alkyl isocyanides,[16] all lead to intense m.l.c.t. transitions in the 430—480 nm range. In our case, m.l.c.t. transitions appear at low energy in $[V(dppe)_3]^{2+}$ but not in $[V(CNBu^t)_6]^{2+}$.

Electrochemistry.—Cyclic voltammetry data for the complexes are summarized in Table 2 and illustrated schematically

Table 2. Electrochemical data for $[V(L\text{-}L)_3]^z$ from cyclic voltammetry[a]

L-L	z: 0/−	+/0	2+/+	3+/2+
dpphen	−1.53	−1.05	−0.89	0.58
phen		−1.17	−0.97	0.56
tmphen		−1.45	−1.22	0.50
bipy		−1.19	−0.97	0.52[b]
dmbipy		−1.33	−1.12	0.52[c]
$[Cr(phen)_3]^z$ [d]	−1.91	−1.28	−0.725	−0.21

[a] Half-wave potentials for reversible couples, *vs.* Ag–AgCl in CH_2Cl_2, unless otherwise noted. [b] Quasireversible. [c] Irreversible oxidation; the anodic peak potential is given. [d] Data for $[Cr(phen)_3]^z$ in MeCN, from ref. 18*b*, for comparison.

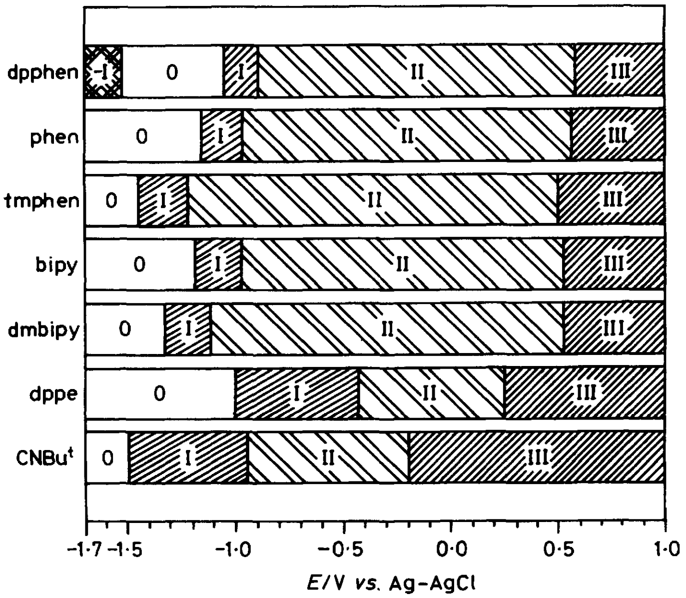

Figure 3. Schematic illustration of half-wave potentials for vanadium complexes (from cyclic voltammetry)

in Figure 3. The half-wave potentials within the polypyridine series change significantly with substitution on the ligand framework, the largest variation occurring in the $[V(L\text{-}L)_3]^{2+/+}$ and $[V(L\text{-}L)_3]^{+/0}$ potentials. With dpphen, the stabilization of the lower oxidation states is so great that the $[V(dpphen)_3]^{0/-}$ couple can also be observed (see Figure 4).

In the absence of specific electronic effects, consecutive electrode potentials in a multistep redox system should be approximately equally spaced. This has been observed, for example, in isocyanide[17] and polypyridine[18] complexes of chromium. Among the vanadium complexes examined here, the $[V(L\text{-}L)_3]^{2+}$ species have the greatest range of stability (see Figure 2). Octahedral d^3 complexes have the stable half-filled $(t_{2g})^3$ electronic configuration, and as a result they should be more difficult to oxidize and reduce than those of adjacent configurations. For example, $[Cr(phen)_3]^{3+}$ (d^3) is more difficult to reduce than $[V(phen)_3]^{3+}$ (d^2); likewise, $[Cr(phen)_3]^+$ (d^5) is more difficult to oxidize than $[V(phen)_3]^+$ (d^4).[18b]

In contrast to $[V(L\text{-}L)_3]^{2+}$, the $[V(L\text{-}L)_3]^+$ species (d^4) are stable only over a small range of potentials. There are two possible explanations for this narrow stability range for vanadium(I). First, the high stability of vanadium(II) (d^3), mentioned above, might be expected to displace the $[V(L\text{-}L)_3]^{2+/+}$ potential to more negative values. However, a similar effect would be expected in the isoelectronic chromium systems, and the stability range of $[Cr(phen)_3]^{2+}$ is not especially small (see half-wave potentials in Table 2).[18b] Thus, the spacing of redox potentials in the vanadium system cannot be attributed entirely to the stability of the d^3 configuration.

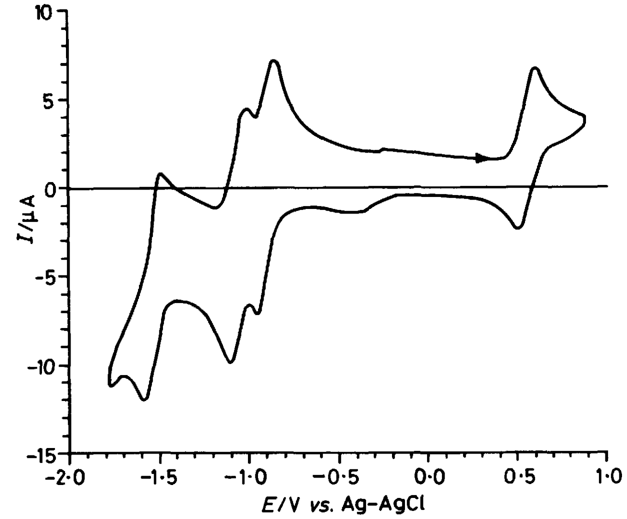

Figure 4. Cyclic voltammogram of $[V(dpphen)_3][O_3SCF_3]_2$ in CH_2Cl_2 (scan rate 500 mV s^{-1})

An alternative explanation for the irregular sequence of potentials relies on a splitting among the 't_{2g}' orbitals in the $[V(L\text{-}L)_3]^+$ complexes. Low-spin octahedral vanadium(I) complexes (d^4) should have two unpaired electrons; this is true of $[V(bipy)_3]^+$.[19] However, under the D_3 symmetry of the polypyridine complexes, the 't_{2g}' orbitals are formally split into e and a_2 sets. The d^4 complex $[Ti(bipy)_3]$ is diamagnetic;[20] this observation has been interpreted in terms of such a splitting, with the e orbitals substantially lower in energy than the a_2. (Similar splittings have also been inferred for ruthenium(II) polypyridine complexes,[21] with the e orbitals stabilized by π interaction with the polypyridine ligands.) The splitting is apparently not large enough in vanadium(I) to make $[V(L\text{-}L)_3]^+$ diamagnetic. However, it could still have a substantial effect on the $[V(L\text{-}L)_3]^{+/0}$ redox potential: a paramagnetic $[V(L\text{-}L)_3]^+$ complex, with electronic configuration $(e)^3(a_2)^1$, might be relatively easy to reduce because of the vacancy in the lower-lying e orbitals. The principal cause of the narrow stability range of the vanadium(I) complexes, then, may be that the $[V(L\text{-}L)_3]^{+/0}$ potential has been displaced in the positive direction. Still, more information concerning redox processes and electronic structure in these and related complexes may be needed before a complete explanation can be given.

Substituent effects on the $[V(L\text{-}L)_3]^{3+/2+}$ half-wave potentials in our complexes are smaller than those mentioned above for the reduction of $[V(L\text{-}L)_3]^{2+}$. This suggests that the redox process in the $[V(L\text{-}L)_3]^{3+/2+}$ couple is primarily localized on the metal centre, whereas the added electrons in the more reduced species (oxidation states −I, 0, and I) are increasingly delocalized on the polypyridine ligands. This trend may also be viewed as indicating more extensive π back bonding in the reduced species. Data for corresponding couples $[M(L\text{-}L)_3]^{3+/2+}$ for other metals are inconsistent: although tmphen complexes of Ru^{II} and Cr^{II} are easier to oxidize than isoelectronic phen complexes, as expected, dpphen also seems to stabilize the higher oxidation state slightly.[22]

In addition to the reversible redox couples described above, small irreversible cathodic and anodic waves are also observed

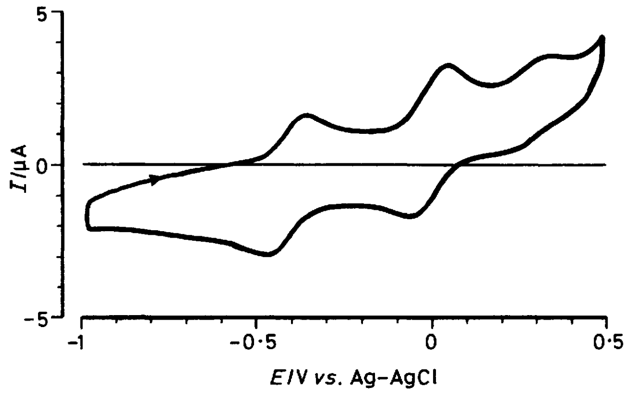

Figure 5. Cyclic voltammogram of $[V(dppe)_3][V(CO)_6]_2$ in CH_2Cl_2 (scan rate 500 mV s^{-1})

between 0 and -0.8 V for all of the polypyridine complexes. These partially reversible waves are observed only if the electrode is first brought to sufficiently positive potentials to cause oxidation from $[V(L\text{–}L)_3]^{2+}$ to $[V(L\text{–}L)_3]^{3+}$. In our previous study of $[V(phen)_3]^{2+}$,[2] we attributed the waves to a vanadium(III)–vanadium(IV) couple possibly connecting species such as $[V(phen)_2(OH)(H_2O)]^{2+}$ and $[VO(phen)_2]^{2+}$. Analogous species are likely to form with the other polypyridine ligands as well.

Cyclic voltammograms of $[V(CNBu^t)_6]^{2+}$ show one reversible wave and one quasireversible wave. We assign the reversible wave ($E_{\frac{1}{2}} = -0.95$ V) to the $[V(CNBu^t)_6]^{2+/+}$ couple and the quasireversible wave ($E_{\frac{1}{2}}$ *ca.* -1.5 V) to $[V(CNBu^t)_6]^{+/0}$. Two irreversible oxidation waves at -0.2 and 0.4 V are also observed; they may be attributed to further oxidation of $[V(CNBu^t)_6]^{2+}$, possibly to vanadium(III) and vanadium(IV).

In solutions of $[V(dppe)_3][V(CO)_6]_2$, one quasireversible wave and one reversible one-electron wave are attributed to $[V(dppe)_3]^{3+/2+}$ ($E_{\frac{1}{2}}$ *ca.* 0.25 V) and $[V(dppe)_3]^{2+/+}$ ($E_{\frac{1}{2}} = -0.43$ V) respectively (see Figure 5). The reversible wave near the centre of the voltammogram ($E_{\frac{1}{2}} = -0.02$ V) is attributed to the $[V(CO)_6]^{0/-}$ couple: its amplitude increases when solid $[NEt_4][V(CO)_6]$ is added to the solution. Voltammograms recorded using an expanded scan range reveal irreversible reduction (E_{pc} *ca.* -1.0 V) and oxidation waves (E_{pa} *ca.* 0.7 V), which are probably due to reduction of $[V(dppe)_3]^+$ and further oxidation of $[V(CO)_6]$ respectively. The features we attribute to $[V(CO)_6]^-$ are similar to those described by Bond and Colton[23] for $[V(CO)_6]^-$ in acetone. The relative ease of reduction of $[V(dppe)_3]^{2+}$ suggests that the additional electrons in $[V(dppe)_3]^+$ and $[V(dppe)_3]$ are substantially delocalized on the ligands; this is consistent with the partial m.l.c.t. character of the $[V(dppe)_3]^{2+}$ absorption bands.

The lowest-energy spin-allowed electronic transitions, both *d–d* and m.l.c.t., appear at higher energies in $[V(CNBu^t)_6]^{2+}$ and $[V(dppe)_3]^{2+}$ than in the polypyridine complexes. This should result in ^2E (or ^2E_g) being the lowest-energy excited state, thereby leading to a sufficiently long excited-state lifetime for carrying out the desired photoredox chemistry. Thus, the broad range of oxidation states observed in cyclic voltammetry, in combination with the expected long-lived lowest excited state, should make it possible to carry out photoinitiated multielectron redox reactions in these and related systems. The decomposition of these two ions in solution has interfered so far with measurements of their excited-state properties. Therefore, we are also exploring the use of chelating di-isocyanides, such as those synthesized by Plummer and Angelici,[24] and less bulky phosphines {as in the known zerovalent complex $[V(Me_2PCH_2CH_2PMe_2)_3]$[25]}, in stabilizing vanadium(II) complexes for photochemical reactions.

Acknowledgements

This work was supported by grants from Research Corporation, Monsanto Company, and the Biomedical Research Support Grant Program, Division of Research Resources, National Institutes of Health.

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Received 18*th September* 1986; *Paper* 6/1860