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Preliminary communication

THE USE OF ION-PAIRING PHENOMENA IN THE ASSIGNMENT OF ν(CO) IR BANDS OF $PV(CO)_5^-$

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Summary

The interaction of a sodium cation with the *trans*-CO oxygen of $PV(CO)_5^-$ (P = $P(OPh)_3$, PPh_3, $P(n\text{-}Bu)_3$) had a major effect on the vibrational mode that is primarily comprised of that CO group and removed the accidental degeneracy of A_1^1 and E ν(CO) frequencies.

The assignment of ν(CO) IR bands of monosubstituted phosphine derivatives of vanadium hexacarbonyl is less than straightforward because of overlapping bands, the presence of an ubiquitous impurity, and the possible appearance of a band formally forbidden by IR selection rules. We have used ion-pairing phenomena to rigorously clarify the assignment.

The C_{4v} symmetry of an isolated $V(CO)_5P^-$ anion (P = phosphine or phosphite ligands) leads to the expectation of 3 infrared active CO stretching vibrations of symmetry A_1^2, A_1^1 and E. The E mode is expected to be of greater intensity than either A mode. Forbidden by the selection rules is a B_1 stretching vibration. The ν(CO) IR spectrum of $n\text{-}Bu_3PV(CO)_5^-$ as a salt of a hexamethylphosphoric triamide solvate of sodium, $Na(HMPA)_x^+$, is shown in Fig. 1. To be sure there are 3 bands here, however the band at 1860 cm^{-1} is present in a series of $PV(CO)_5^-$ anions and is at the position of $V(CO)_6^-$, the starting material for the synthesis of these anions [1,2], and/or the possible decomposition product of $PV(CO)_5^-$. Consistent with band assignments for $LM(CO)_5$ derivatives in general [3] the high frequency band at 1964 cm^{-1} is assigned to the A_1^2 vibrational mode. Hence the A_1^1 mode is either degenerate with the E mode at 1809 cm^{-1} or it unfortuitously appears at the precise position of a possible impurity.

Based on arguments presented earlier [4], we predicted that an alkali cation/$LM(CO)_5^-$ contact ion pair interaction should be at the CO oxygen *trans* to the good donor substituent ligand. The stretching motion of this CO group

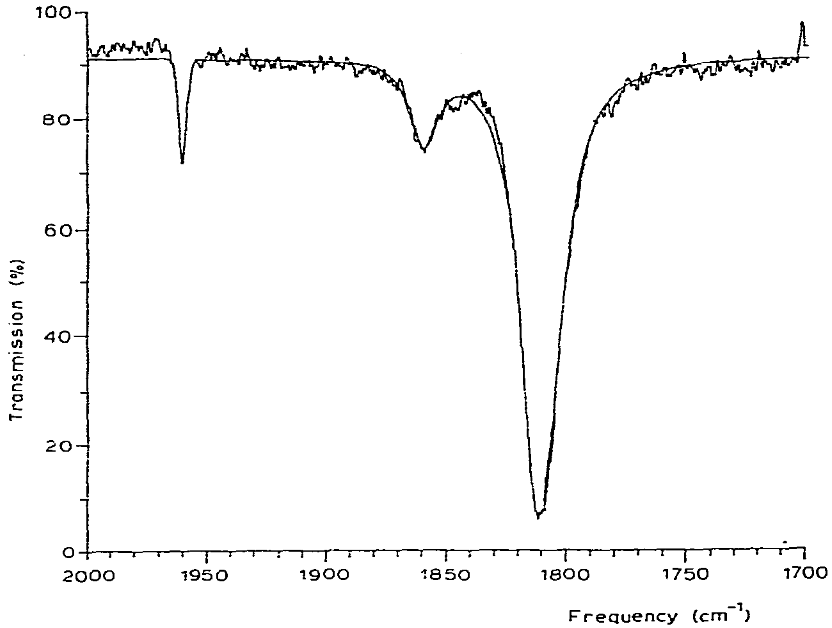


Fig. 1. ν(CO) spectrum of $[Na(HMPA)_x^+][V(CO)_5P(n\text{-}Bu)_3^-]$. A 0.010 *M* solution of $Na^+V(CO)_5P(n\text{-}Bu)_3^-$ to which 10 equivalents of HMPA to each Na^+ has been added. The spectrum was measured in 0.10 mm sealed NaCl cells on a Perkin—Elmer 283B spectrophotometer.

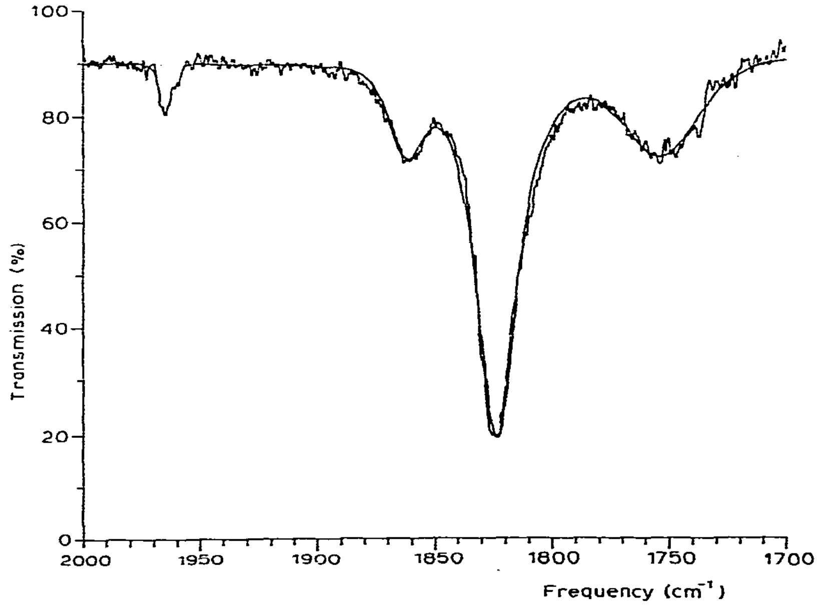
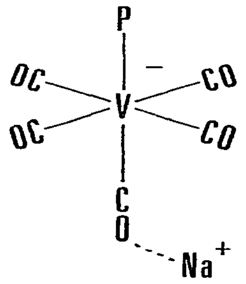


Fig. 2. ν(CO) spectrum of $Na^+V(CO)_5P(n\text{-}Bu)_3^-$, 0.01 *M* in THF. The small shoulder at 1957 cm^{-1} is indicative of the presence of some solvent-separated ion pairs $[Na^+(THF)_y][V(CO)_5P(n\text{-}Bu)_3^-]$ estimated by band fitting analysis (the composite of which is shown in the solid line overlay [6]) to be at a level of ca. 14%.

is the major component of the A_1^1 vibrational mode. The conversion of a CO group into a (CO···Na$^+$) ligand should significantly modify its π-acceptor ability [4], its bond order, and as a result, its ν(CO) position. Figure 2 shows the ν(CO) IR spectrum of the sodium salt of $V(CO)_5P(n\text{-}Bu)_3^-$ in tetrahydrofuran, a solvent of low dielectric constant in which extensive contact ion pairing has been observed [4,5]. The presence of a low frequency band at the expense of the intensity of the band at 1809 cm^{-1} as well as the lack of effect on the 1860 cm^{-1} band suggested the following rationale. The spectrum of the contact ion-paired form of $Na^+V(CO)_5P(n\text{-}Bu)_3^-$ is consistent with the preservation of C_{4v} symmetry for the carbonylate. The A_1^1 band is now clearly distinguishable from the E band, which is itself now shifted to 1820 cm^{-1}. The A_1^2 band is similarly slightly shifted to higher wavenumbers. The combined band areas of the A_1^1 + E are roughly equal to the band area of the 1809 cm^{-1} band of Fig. 1 for solutions of identical concentration. (There is a small intensity loss on going from the symmetrically solvated $PV(CO)_5^-$ to the contact ion-paired $PV(CO)_4(CO^-\cdots Na^+)$. The structure of the contact ion pair is that shown below, with the sodium ion interacting at the unique CO oxygen:



(I)

Incremental addition of the cation solvating agent HMPA gradually diminished the intensity of the low frequency band shown in Fig. 2 and enhanced the intensity of the 1820—1809 cm^{-1} band. Six to eight equivalents of HMPA were required to completely convert the contact ion pairs to solvent-separated ion pairs [4].

Note that the shift of the band at 1809 to 1820 cm^{-1} and of the band at 1957 to 1964 cm^{-1} on changing the conditions from those of Fig. 1 to those of Fig. 2 is also consistent with the existence of the contact ion pair structure I, in pure THF solution. As indicated above, the displacement to lower frequency for the cation-contacted CO group is indicative of the better π-withdrawing ability of the CO···Na$^+$ group, which concurrently induces a shift to higher frequencies for those CO groups which do not interact with the counterion and hence compete less effectively for metal d-electrons. In contrast the band at 1860 cm^{-1} is independent of ion pairing status. It has been shown that the ν(CO) IR of pure $V(CO)_6^-$ in THF is independent of counterion [6].

Similar results were obtained for analogous $P(OPh)_3$ and PPh_3 derivatives and ν(CO) IR results for those anions in a symmetrical solvent environment as

TABLE 1

ν(CO) IR SPECTRAL DATA FOR SALTS OF P-LIGAND SUBSTITUTED VANADIUM CARBONYLATES IN THF SOLUTION[a]

Salt[b]	ν(CO) Active modes			Forbidden B_1 mode[c,d] found (calcd.)
	A_1^2	E	A_1^1	
$Na[V(CO)_5P(n\text{-}Bu)_3]$	1964	1820	1749	1858 (1866)
$[Na(HMPA)_x][V(CO)_5P(n\text{-}Bu)_3]$	1957	1809	1809[e]	1850 (1855)
$Na[V(CO)_5PPh_3]$	1970	1832	1764	[d] (1876)
$[Na(HPMA)_x][V(CO)_5PPh_3]$	1965	1823	1823[e]	[d] (1867)
$Na[V(CO)_5P(OPh)_3]$	1987	1850	1801	~1890 (1893)
$[Na(HMPA)_x][V(CO)_5P(OPh)_3]$	1984	1843	1843[e]	1880 (1886)

[a] These spectra were measured on 0.01 *M* solutions in 0.1 mm sealed NaCl infrared cells using a Perkin—Elmer 283B infrared spectrophotometer and calibrated on the water vapor bands at 1942.6 cm^{-1}. [b] A symmetrical solvent environment about the carbonylate was assured in the HMPA solvates by the addition of 10 equivalents of HMPA. This was ca. 43.5 μl of HMPA in a total THF sample volume of 2.5 ml [c] Calculated as described in the text. [d] Partial overlap of the B_1 with either the E mode or the $V(CO)_6^-$ at 1860 cm^{-1} made resolution and detection difficult. [e] See discussion in text:

well as contacted by Na$^+$ are shown in Table 1*. Consistent with the electron-donating abilities of the P-donor ligands, ν(CO) IR shifts of the A_1^1 bands when contacted by Na$^+$ are not as dramatic for the $P(OPh)_3$ and PPh_3 derivatives as for the $P(n\text{-}Bu)_3$ derivative. A detailed study of spectral and chemical properties of $PV(CO)_5^-$ salts which will be published shortly contains a restricted force field CO stretching force constant analysis [6]. In that study the positions of the B_1 vibrational modes were calculated and are presented in Table 1 along with those observed. Note that the B_1 position is not fixed but varies, as do the IR active bands, with the substituent ligand as well as the state of ion-pairing. Frequently however the very weak B_1 band appears as a shoulder on the $V(CO)_6^-$ band and is difficult to resolve.

The major curiosity of this study is that the A_1^1 band is invariably degenerate with the E band for the three different P-donor ligand substituents. A similar situation exists for isonitrile derivatives [8]. It should be noted that the width of the E band could mask positional shifts of the A_1^1 of possibly 10 cm^{-1} within the band envelope without inducing major asymmetry of the band.

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*The sodium salts of $V(CO)_5P(n\text{-}Bu)_3^-$ and $V(CO)_5PPh_3^-$ were prepared by literature methods [2] and $V(CO)_5P(OPh)_3^-$ was prepared by ligand exchange with $Na^+V(CO)_5(PPh_3)^-$. Full details will be reported [6]. The $P(OPh)_3$ derivative was previously reported as a member of a large series of $LV(CO)_5^-$ anions, however the ν(CO) infrared assignments and Cotton—Kraihanzel force constants reported are incorrect [7].

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