3 yields a limiting rate constant equal to k_6 and predicts that excess leaving group (P) will have no effect on this limit. This is indeed found to be the case. With a large excess of triphenyl phosphite it is likely that $k_3[L] \gg k_2[P]$ and then eq 3 demands that excess P have no effect on the plot of k_{obsd} *vs.* nucleophile concentration. Figure 4 shows that this is the case within experimental error, except possibly at the lowest nucleophile concentration where the inequality is least likely to be valid. This behavior is in sharp contrast to that of the bidentate nucleophiles discussed above.

Table I shows that 1,10-phenanthroline (phen) is much less reactive than the other nucleophiles. This we attribute to the well-known inflexibility of phen relative to en and bipy.[9,10] The intercept is well below that of mnt^{2-} and i-mnt^{2-} and we attribute this to the fact that the triphenylphosphine can compete more favorably in this case.

The mechanism shown in Figure 1 involves an associative and a dissociative pathway. We have been unable to formulate any other reasonable mechanism that is consistent with the data. The nonzero intercepts for the ligands in Table I are the principal results suggesting a partial dissociative pathway. Our conclusion is that the substitution reactions proceed *via* two pathways, both of which contribute significantly to the overall reaction. As the nucleophile concentration increases, the associative pathway becomes more and more predominant. At low nucleophile concentrations the dissociative path predominates (Table I).

An attempt was made to study reaction 1 with iron as the metal. Unlike the cobalt system, it was found that a large excess of $P(C_6H_5)_3$ was needed to form $Fe(mnt)_2P(C_6H_5)_3^-$ to any detectable extent, rendering a kinetic investigation infeasible.

(9) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley and Sons, New York, N. Y., 1967, p 219.

(10) F. A. Palocsay and J. V. Rund, *Inorg. Chem.*, **8**, 524 (1969).

Contribution from the Department of Chemistry
and The James Franck Institute,
The University of Chicago, Chicago, Illinois 60637

Absorption Spectrum of Vanadium(II) Chloride from 5000 to 30,000 Cm⁻¹

By Samuel S. Kim, Stanley A. Reed, and J. W. Stout

In the preparation of VCl_2 for heat capacity measurements we obtained several pale green single crystal plates, about 0.2 mm thick and up to 1 cm in the two other dimensions, which were of suitable quality for spectroscopic measurements. Since relatively few measurements have been reported of the crystal spectra of V^{2+} $(3d^3)$ compounds, we have measured the absorption spectrum of VCl_2 in the range 5000–30,000 cm⁻¹ and report the results here.

VCl_2 crystallizes in the CdI_2-type structure[1,2] and the crystals cleave readily along planes normal to the hexagonal c axis. The small dimension of the crystallites we obtained was parallel to this axis and only the axial spectrum, unpolarized light propagated parallel to the hexagonal axis, was measured.

Experimental Section

VCl_2 was prepared by treating vanadium metal, ground to 20 mesh, with dry HCl gas at 950°. Pale green crystal plates collected in the cooler portion of the quartz reaction tube. A sample of the VCl_2 was analyzed for vanadium by titration with standard 0.1 N $KMnO_4$ solution and for chlorine gravimetrically by precipitation of AgCl. *Anal.* Calcd for VCl_2: V, 41.81; Cl, 58.19. Found: V, 41.69; Cl, 57.95. The only impurities seen in a spectrochemical analysis were, in weight per cent: Mg, 0.001; Si, 0.01; Fe, 0.05; Cu, 0.001.

The spectra were measured with a Cary Model 14 spectrophotometer. The crystal of VCl_2 was mounted on a copper plate with an accurately machined aperture and assembled in the lower section of a cryostat which also carried an empty matched aperture. The lower section of the cryostat could be rotated to place either the blank aperture or the crystal in the beam of the spectrophotometer, and the difference between the measured absorbance of the crystal and the blank was determined. The temperature of the copper plate on which the VCl_2 crystal was mounted was measured with a copper–constantan thermocouple. Spectra were measured at room temperature and with liquid helium in the cryostat reservoir in thermal contact with the sample holder. The principal uncertainty in the molar extinction coefficients arises from uncertainties in the thickness of the crystals. The thickness of one sample of VCl_2 which was fairly uniform was determined by measurement of weight and area (0.88 cm²) and also with a micrometer caliper. The average thickness was 0.08 ± 0.02 mm. Thicknesses of other samples on which spectra were measured were determined by comparison of the room-temperature absorbance of the 8.98 × 10³ and 13.92 × 10³ cm⁻¹ peaks with those measured for the sample whose thickness was most accurately measured. Small corrections for surface reflection and scattering were made by drawing a base line through the measured absorbances at 17,000 and 5800 Å in the liquid helium experiments.

Results

The molar extinction coefficients of VCl_2 at 298 and 22°K are plotted *vs.* wave number in Figures 1 and 2. The errors in the extinction coefficients are ±25% because of uncertainty in thickness of the sample, but the relative error of various parts of the spectrum below 29 × 10³ cm⁻¹ is less than 10%. In Table I are listed the wave numbers of the principal peaks observed in the spectra at 22 and 298°K. The two strong near-infrared bands and the very narrow absorption at 15.940 × 10³ cm⁻¹ seen in the 22°K spectrum are well separated from other features. These curves are Gaussian in shape, and their width at half-height, $\Delta\bar{\nu}$, and the oscillator strength, f (uncorrected for refractive index), are listed in Table I. Above 19 × 10³ cm⁻¹ the spectrum is not resolvable into well-

(1) W. Klemm and L. Grimm, *Z. Anorg. Allgem. Chem.*, **249**, 198 (1942).

(2) P. Ehrlich and H. J. Seifert, *ibid.*, **301**, 282 (1958).

TABLE I

WAVE NUMBERS ($\bar{\nu}$) OF OBSERVED PEAKS IN THE AXIAL SPECTRUM
OF VCl$_2$ AT 22 AND 298°K AND OF CALCULATED ELECTRONIC
ENERGIES WITH $B = 755$ CM^{-1} AND $Dq = 800$ CM^{-1}, WIDTHS
AT HALF-HEIGHT ($\Delta\bar{\nu}$), AND OSCILLATOR STRENGTHS (f) OF
RESOLVED BANDS

Excited level	Calcd electronic $10^{-3}\bar{\nu}$, cm^{-1}	$10^{-3}\bar{\nu}$, cm^{-1}	—22°K— $10^{-3}\Delta\bar{\nu}$, cm^{-1}	f	$10^{-3}\bar{\nu}$, cm^{-1}	—298°K— $10^{-3}\Delta\bar{\nu}$, cm^{-1}	f
$^4T_{2g}$	8.00	9.30	1.34	3×10^{-5}	8.98	1.99	4×10^{-5}
Doublet	$\begin{cases} 11.83 \\ 12.3 \end{cases}$						
$^4T_{1g}(^4F)$	13.09	14.22	1.65	7×10^{-5}	13.92	2.35	12×10^{-5}
Doublet		15.940	0.089	1×10^{-7}			
		19.13					
		20.25					
		20.85					
$^4T_{1g}(^4P)$	22.24	22.244			21.84		
		22.483					
		22.724					
		22.956					
		23.36			23.14		
		23.87					
		24.88			25.02		
		25.09					
		25.28					
		28.25			27.82		
		30.95			30.89		

Figure 1.—Molar extinction coefficient, ϵ, *vs.* wave number, $\bar{\nu}$. Axial spectrum of VCl$_2$ between 6×10^3 and 19×10^3 cm^{-1} at 22 and 298°K.

separated bands and only the positions of peaks are listed in Table I. Between 32×10^3 and 50×10^3 cm^{-1} the absorbance of VCl$_2$ is very strong, and no transmittance was measurable with a 0.08-mm thick sample.

Discussion

In VCl$_2$ each V^{2+} ion is surrounded by a nearly regular octahedron of Cl$^-$ ions. The ^4F and ^4P terms of the free V^{2+}(3d^3) ion are split[3] in a ligand field of octahedral symmetry into $^4A_{2g}$, $^4T_{2g}$, $^4T_{1g}(^4F)$, and $^4T_{1g}(^4P)$. The $^4A_{2g}$ level lies lowest and the electronic energies of the other quartet states above the $^4A_{2g}$ are

$$E(^4T_{2g}) = 10Dq$$

$$E(^4T_{1g}, {}^4P, {}^4F) = 7.5B + 15Dq \pm$$
$$\tfrac{1}{2}[225B^2 - 180BDq + 100(Dq)^2]^{1/2}$$

Here Dq is the octahedral field parameter and B is a Racah parameter. The observed separation[4] of the ^4F and ^4P terms in gaseous V^{2+} ion, 11.332×10^3 cm^{-1}, is $15B$, or $B = 755$ cm^{-1}.

The bands with peaks at 9.30×10^3 and 14.22×10^3 cm^{-1} at 22°K are identified as transitions from the ground $^4A_{2g}$ level to the $^4T_{2g}$ and $^4T_{1g}(^4F)$ electronic levels. The strong variation of oscillator strength of these bands with temperature is evidence that their transition moment arises from interactions with vibrations of odd parity, and the observed peak positions will include energy of vibrational excitation. The energy of the electronic excitation will lie near the low-energy side of the vibronic bands, or near 8.0×10^3 and 13.0×10^3 cm^{-1}, respectively. We therefore

Figure 2.—Molar extinction coefficient, ϵ, *vs.* wave number, $\bar{\nu}$. Axial spectrum of VCl$_2$ between 19×10^3 and 32×10^3 cm^{-1} at 22 and 298°K.

choose $Dq = 800 \pm 50$ cm^{-1} and assign the difference between the observed peaks of the bands and the calculated electronic energies, shown in Table I, to vibrational excitation.

The weak structure at 11.83×10^3 and 12.3×10^3 cm^{-1} and the narrow peak at 15.940×10^3 cm^{-1}, seen in the 22°K spectrum, are presumably transitions from the ground state to doublet levels in the crystal. The energy matrices of the doublet levels of a d^3 system were calculated by Finkelstein and Van Vleck[5] and by Tanabe and Sugano.[6] In the case of the free V^{2+} ion, however, the position of the d^3 ^2P level assigned by White[7] is some 4500 cm^{-1} lower than

(3) J. S. Griffith, "The Theory of Transition Metal Ions," Cambridge University Press, Cambridge, England, 1961.

(4) C. E. Moore, "Atomic Energy Levels," National Bureau of Standards Circular No. 467, Vol. II, U. S. Government Printing Office, Washington, D. C., 1952.
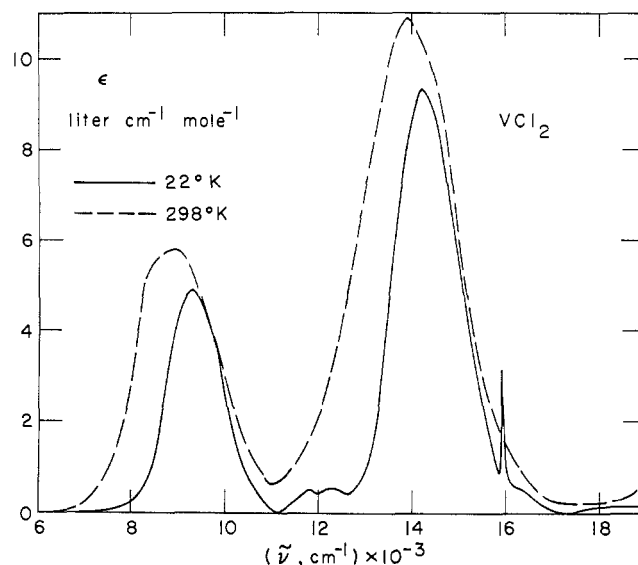
(5) R. Finkelstein and J. H. Van Vleck, *J. Chem. Phys.*, **8**, 790 (1940).

(6) Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753, 766 (1954); **11**, 864 (1956).

(7) H. E. White, *Phys. Rev.*, **33**, 674 (1929).

that calculated by Many.[8] It appears prudent, therefore, not to attempt definite assignment of the transitions to doublet states until more information is available.

With $Dq = 800$ cm^{-1} and $B = 755$ cm^{-1} the electronic energy of the $^4T_{1g}(^4P)$ level is 22.24×10^3 cm^{-1}. The observed highly structured spectrum in this region becomes more intense at higher temperatures and is probably mainly vibronically allowed transitions to the $^4T_{1g}(^4P)$ level. The absorption observed above 24×10^3 cm^{-1} is very strong for transitions from the ground state to excited doublet states and does not become weaker at low temperatures. It is probable that this strong intensity derives from admixture of the doublet states with the nearby charge-transfer states of the crystal responsible for the very strong absorbance above 32×10^3 cm^{-1}.

Addendum.—Axial spectra of VCl$_2$ at room temperature, liquid nitrogen temperature, and liquid helium temperature have recently been reported by Smith,[9] who gave a graph of optical density *vs.* wave number but did not report quantitative intensities of absorption. There is qualitative agreement between our spectra and those reported by Smith.

(8) A. Many, *Phys. Rev.*, **70**, 511 (1946).
(9) W. E. Smith, *J. Chem. Soc., A*, 2677 (1969).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA 50010

Kinetic Studies of the Reactions of Cyclopentadienylvanadium Tetracarbonyl with Lewis Base Ligands

BY GARY C. FABER AND ROBERT J. ANGELICI

It has been reported that the carbonyl substitution reaction of C$_5$H$_5$V(CO)$_4$ with triphenylphosphine, C$_5$H$_5$V(CO)$_4$ + P(C$_6$H$_5$)$_3$ → C$_5$H$_5$V(CO)$_3$P(C$_6$H$_5$)$_3$ + CO, proceeds according to a second-order rate law, first order in C$_5$H$_5$V(CO)$_4$ and first order in P(C$_6$H$_5$)$_3$.[1] The absence of a term first order in C$_5$H$_5$V(CO)$_4$ only suggested that this complex did not react according to a mechanism in which unimolecular dissociation of a carbonyl group was rate determining. This was unusual in view of the fact that essentially all carbonyl substitution reactions of octahedral metal carbonyl complexes have been found to proceed, at least in part, according to a path governed by the unimolecular

(1) W. Strohmeier and H. Blumental, *Z. Naturforsch.*, **22b**, 1351 (1967).

dissociation of CO.[2] The pseudo-seven-coordinated nature of C$_5$H$_5$V(CO)$_4$ would suggest that it would be even less likely to react by an associative (SN2) mechanism for steric reasons. Thus, it was believed a reinvestigation of the reaction of C$_5$H$_5$V(CO)$_4$ with Lewis base ligands was warranted. Herein are reported the results of the investigation.

Experimental Section

Preparation and Purification of Materials.—C$_5$H$_5$V(CO)$_4$ was prepared according to a standard procedure.[3] The complex was sublimed twice and stored under nitrogen at $-80°$ in a foil-wrapped vial. Triphenylphosphine, P(C$_6$H$_5$)$_3$ (Aldrich Chemical Co.), was recrystallized from ethanol, washed with pentane, and dried at 85°, as the melt, under high vacuum for 1 hr. Tri-*n*-butylphosphine, P(C$_4$H$_9$)$_3$ (Aldrich Chemical Co.), was fractionally distilled under high vacuum and was stored under nitrogen. Tri-*n*-butyl phosphite, P(OC$_4$H$_9$)$_3$ (Matheson Coleman and Bell Chemical Co.), was used as obtained. Pure samples of the bicyclic phosphite, 4-*n*-propyl-3,6,7-trioxa-1-phosphabicyclo[2.2.2]octane, P(OCH$_2$)$_3$C(CH$_2$)$_2$CH$_3$, were kindly supplied by G. K. McEwen. The solvent, decalin (Baker Chemical Co.), was stirred over sodium for 6 hr at 130° and was carefully distilled under reduced pressure. Chlorobenzene (Mallinckrodt Analytical reagent) was used as obtained.

Identification of Products.—The products of the reactions, C$_5$H$_5$V(CO)$_3$L (where L = P(C$_6$H$_5$)$_3$, P(C$_4$H$_9$)$_3$, P(OC$_4$H$_9$)$_3$, and P(OCH$_2$)$_3$C(CH$_2$)$_2$CH$_3$), were not isolated. However, the products were identified by comparison of their infrared carbonyl stretching spectra with those of the already reported C$_5$H$_5$V(CO)$_3$P(C$_6$H$_5$)$_3$[4] and C$_5$H$_5$V(CO)$_3$P[N(CH$_3$)$_2$]$_3$.[5] The infrared spectra of the products were recorded with a Beckman IR-12 infrared spectrophotometer, and the carbonyl stretching frequencies are given in Table I. The infrared spectra of the reac-

TABLE I
CARBONYL STRETCHING FREQUENCIES FOR
C$_5$H$_5$V(CO)$_3$L PRODUCTS

L	Medium	Carbonyl str freq, cm^{-1}
P(C$_4$H$_9$)$_3$	*n*-Heptane	1957, 1878, 1855
P[N(CH$_3$)$_2$]$_3$[5]	Mull	1953, 1853, 1839
P(C$_6$H$_5$)$_3$[5]	Mull	1950, 1855, 1840
P(OC$_4$H$_9$)$_3$	Decalin	1970, 1893, 1868
P(OCH$_2$)$_3$C(CH$_2$)$_2$CH$_3$	Decalin	1983, 1907, 1892

tion solutions after 3 or 4 half-lives indicated the presence of another product of the type C$_5$H$_5$V(CO)$_2$L$_2$ (only when L = P(C$_4$H$_9$)$_3$ and P(OC$_4$H$_9$)$_3$). The lowest carbonyl stretching frequencies of the phosphine and phosphite products occurred at 1766 and 1817 cm^{-1}, respectively. These frequencies correspond to the lowest CO stretching frequency (1787 cm^{-1})[6] of C$_5$H$_5$V(CO)$_2$diphos.[7] Since the other CO absorption of C$_5$H$_5$V(CO)$_2$diphos occurs at 1864 cm^{-1}, it is probable that this absorption of the phosphine and phosphite product, C$_5$H$_5$V(CO)$_2$L$_2$, is masked by the bands of the predominant product, C$_5$H$_5$V(CO)$_3$L.

In reactions where the ligand concentrations were less than 0.1 *M*, decomposition was observed. When triphenylphosphine was employed, decomposition was even observed at higher concentrations. Hence, ligand concentrations employed were, for the most part, greater than 0.1 *M* and reactions with triphenylphosphine were not studied in detail.

Determination of Rates.—Reaction rates were determined by monitoring the decrease of the high-frequency infrared carbonyl stretching absorption of C$_5$H$_5$V(CO)$_4$ at 2019 cm^{-1}. In a typical

(2) R. J. Angelici, *Organometal. Chem. Rev.*, **3**, 173 (1968).
(3) R. B. King, *Organometal. Syn.*, **1**, 107 (1965).
(4) R. Tsumra and N. Hagihara, *Bull. Soc. Chem. Japan*, **38**, 1901 (1965).
(5) R. B. King, *Inorg. Chem.*, **2**, 936 (1963).
(6) H. Behrens and H. Brandle, *Z. Naturforsch.*, **22b**, 1353 (1967).
(7) diphos = 1,2-bis(diphenylphosphino)ethane.