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Lewis Acidity of Bis(1,1,1,5,5,5-hexafluoropentane-2,4-dionato)oxovanadium(IV). Spin Pairing of Electrons in the 2,2,6,6-Tetramethylpiperidinyl-*N*-oxy Adduct

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Thermodynamic data for the reaction of the title Lewis acid with several Lewis bases is presented. Its Lewis acidity is interpreted in terms of its E_A and C_A parameters and is compared to that of other transition metal ion complexes. As was the case with the analogous Cu(II) complex, large donor atoms such as sulfur experience flanking-atom charge repulsion with this acid. In the adduct with the free radical base TMPO, a strong exchange interaction occurs between the odd electrons on the metal and the nitroxide. This spin pairing does not make a contribution to the measured enthalpy of adduct formation. The relevance of this conclusion to the general problem of describing antiferromagnetically coupled systems is discussed.

Introduction

Nitroxide radicals are reported to bind to paramagnetic transition-metal ions through the lone pair on the oxygen of the NO group. Upon coordination, a strong exchange interaction occurs between an odd electron on the metal and the one on the nitroxide.[1,2] For example, previous work from this laboratory[2] has shown that the nitroxide radical 2,2,6,6-tetramethylpiperidinyl-*N*-oxy (TMPO) binds strongly to copper(II) bis(hexafluoroacetylacetonate) ($Cu(hfac)_2$) forming a copper–oxygen bond. In this adduct, the two spins are strongly coupled, with $2J$ being about -725 cm^{-1}, which corresponds to 2.0 kcal/mol. It was expected that an exchange interaction this large might make a noticeable contribution to the adduct bond strength.

Several years ago, this group developed an empirical equation which correlates the enthalpies of adduct formation for a wide range of Lewis acids and bases. This equation, known as the *E* and *C* equation[3] is

$$-\Delta H = E_A E_B + C_A C_B \qquad (1)$$

where E_A and C_A are the parameters for the acid and E_B and C_B are the base parameters. The parameterization has resulted in E_A (E_B) values which parallel our qualitative notions of the tendency of the acid (base) to undergo electrostatic interaction while C_A (C_B) parallels the tendency toward a covalent interaction. In the absence of complicating effects such as steric problems, the *E* and *C* equation predicts the enthalpy of σ-bond formation between an acid and a base.

One of the significant applications of the *E* and *C* equation involves finding systems which do not obey the relationship. When a pattern for the exceptions is established, added insight about the factors influencing coordinate bond strengths results. In systems where more than σ-bond formation is involved, the stabilizing or destabilizing effects from such interactions can be probed. For example, if the strong spin pairing that exists in many TMPO transition-metal systems made a substantial contribution to the metal–ligand bond strength, one would expect the experimental enthalpy to be more negative than that predicted by eq 1. The *E* and *C* parameters for the acid and base have to be determined for systems that are devoid of spin-pairing interactions. The magnitude of the difference in the calculated and experimental enthalpies for systems in which spin pairing existed would reflect the stabilization from the spin-pairing interaction. Surprisingly, it was found in an earlier study that the measured enthalpy for the $Cu(hfac)_2 \cdot TMPO$ adduct is within experimental error of that predicted by the *E* and *C* equation.[2] This agreement may be fortuitous, as a result of an accidental cancellation of the extra enthalpy from spin pairing by a steric effect. On the other hand, there may be no real contribution to the enthalpy of adduct formation from spin pairing. This latter result would be interesting in view of the present controversy regarding the nature of metal–metal bonds.[4] In these cases, as in the above system, an antiferromagnetic interaction clearly indicates a bonding interaction.

The Lewis acid vanadyl bis(hexafluoroacetylacetonate) ($VO(hfac)_2$) was selected to further examine the above effect. Geometrical considerations lead one to expect a different steric problem in adducts of $VO(hfac)_2$ than in those of $Cu(hfac)_2$. If spin pairing occurs between $VO(hfac)_2$ and the nitroxide base, could a deviation from the predicted enthalpy of adduct formation be detected in this case? To answer this question it was necessary to obtain the E_A and C_A numbers for $VO(hfac)_2$.

The vanadium atom in $VO(hfac)_2$ has a +4 oxidation state. This feature, coupled with the nature of the attached groups, causes this acid to be the most highly charged center to be incorporated into the *E* and *C* correlation. In this context it would be quite interesting to compare the E_A and C_A numbers for $VO(hfac)_2$ with those for $Cu(hfac)_2$.

During the study of the $Cu(hfac)_2$ system, several interesting problems arose.[5] The $Cu(hfac)_2 \cdot B$ adduct can exist in either of two isomers; however, the E_A and C_A parameters seemed to be identical for the two isomers. A novel type of steric strain was uncovered in the $Cu(hfac)_2 \cdot B$ adduct whenever the base was a sulfur or phosphorus donor. This involved closer than van der Waals approach of the sulfur atom to the oxygen atoms flanking the copper center. It was of interest to look for these effects in the $VO(hfac)_2$ system as well. Thus, our initial objective of looking for spin pairing and its consequences

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in terms of bond strength for the $VO(hfac)_2 \cdot TMPO$ adduct also will provide additional information on the effects outlined above.

Although $VO(hfac)_2$ has not been studied extensively, $VO(acac)_2$ has been used in several studies as a Lewis acid.[6-9] The enthalpies of adduct formation for a series of $VO(acac)_2 \cdot B$ adducts have been correlated with shifts of the V=O stretching frequency in the IR.[6] These measurements were carried out in the solvents CH_2Cl_2 and $CHCl_3$, both of which are capable of hydrogen bonding to the bases and to the vanadyl oxygen of the acids and adducts. Shifts in the visible spectrum have been correlated with changes in the EPR parameters of the VO center.[7] These measurements were carried out in the pure bases as solvents. A large solvent dependence of undetermined origin is reported for the pyridine adduct of $VO(acac)_2$ in pyridine–benzene mixtures.[8] Enthalpies for the formation of a series of base adducts of vanadyl bis(acetylacetonate) have been reported[9] in the solvent nitrobenzene.

The spectral and EPR handles on this system make it a very attractive one for the investigation of the electronic changes in the acid that accompany adduct formation. Clearly, the spectral changes cannot be understood without information on the strength of the acid–base interaction. Thus, enthalpies of adduct formation are required, and they must be measured in solvents in which differential solvation of the products and reactants is minimal. The fluorinated derivative was selected for our studies since both the enthalpies and the equilibrium constants for adduct formation are larger than those for the unfluorinated analogue.

Experimental Section

Materials. $VO(hfac)_2$ was synthesized by a published procedure[10] by using a pH meter to ensure good pH control. Subjecting the compound to vacuum leads to decomposition. After several recrystallizations from purified benzene and after air-drying of the crystals, light, drab green crystalline needles were obtained. The maximum solubility in benzene at room temperature is close to 5×10^{-3} M. Addition of most bases raises the solubility significantly and darkens the color. Anal. Calcd: C, 24.97; H, 0.42; V, 10.59; F, 47.40. Found: C, 25.11; H, 0.50; V, 10.59; F, 47.05.

Tetrahydrothiophene (THTP) and pyridine were distilled from calcium hydride at 1 atm. *N*-Methylimidazole (MeIm) was distilled from KOH at 20 torr (90 °C). Pyridine *N*-oxide and 2,2,6,6-tetramethylpiperidine-*N*-oxyl[2] (TMPO) were vacuum sublimed three times. The pyridine *N*-oxide was weighed out in a drybox since it is extremely hygroscopic. Dimethylacetamide (DMA) and dimethyl sulfoxide (Me_2SO) were stored over barium oxide and molecular sieves, respectively, for several days and then distilled from barium oxide at 35 and 15 torr. Acetonitrile was stored over calcium hydride for several days and then distilled from P_2O_5 at 1 atm. Benzene and methylene chloride were distilled from calcium hydride immediately before use.

Solid $VO(hfac)_2 \cdot B$ adducts were prepared by using Burdick and Jackson "distilled in glass" pentane as solvent. The acetonitrile and Me_2SO adducts were made by mixing $VO(hfac)_2$ and the base in pentane at room temperature. The dioxane and TMPO adducts were prepared by dissolving the acid and base mixture in pentane and cooling the solution in a refrigerator. The solid adducts were filtered and dried. The dioxane adduct was filtered under N_2 since it is quite hygroscopic. Elemental analyses were good except for the dioxane adduct which seems to be a mixture of 1:1 and 2:1 adducts. Attempts to isolate other adducts of the bases studied here have not yielded clean products, but only oils and gums.

Anal. Calcd for $VC_{10}H_2O_5F_{12} \cdot C_2H_3N$: C, 27.60; H, 0.97; V, 9.76; N, 2.68. Found: C, 27.49; H, 1.09; V, 9.96; N, 2.63. Calcd for $VC_{10}H_2O_5F_{12} \cdot C_2H_6SO$: C, 25.77; H, 1.44; V, 9.11. Found: C, 25.50; H, 1.46; V, 9.16. Calcd for $VC_{10}H_2O_5F_{12} \cdot C_9H_{18}NO$: C, 35.81; H, 3.16; V, 7.99; N, 2.20. Found: C, 35.51; H, 3.07; V, 8.21; N, 2.21.

Apparatus and Calculations. The calorimeter has been previously described.[11] It has recently been modified to eliminate the reference cell by substituting an electronic base line compensator.[12] Approximatley 1 M base solutions were injected into approximately 5×10^{-3} M acid solutions. The total volume was about 105 mL of benzene solvent. Spectrophotometric titrations were done on a Cary 14 in the visible range. EPR spectra were run on a Varian E-9 instrument by using benzene solvent. IR spectra were run on a PE 457 spectrophotometer as either CH_2Cl_2 solutions or Nujol mulls on cesium bromide plates. Magnetic susceptibility measurements were made in solution by the Evans NMR method[13] with a Varian EM-390 instrument which operates at 90 MHz and in the solid state with an Evans[14a] or Faraday[14b] balance.

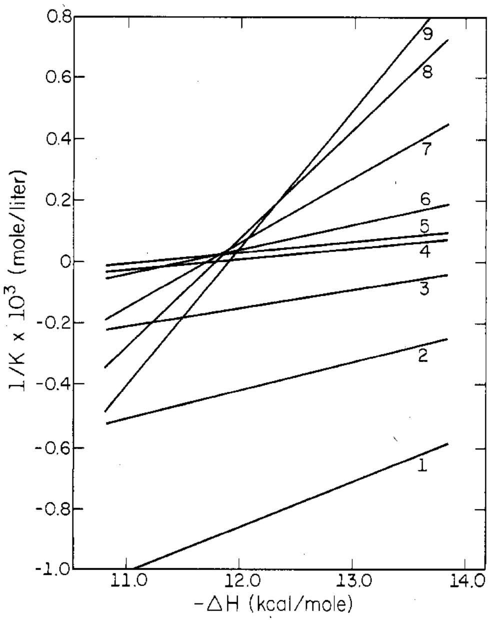


Figure 1. $1/K$ vs. ΔH plot for the formation of the $VO(hfac)_2$ adduct with $(CH_3)_2SO$. The numbers indicate the order of base injections, that is, increasing base concentration.

The raw calorimetric data were analyzed by using reported procedures[5,15] and also by assuming an infinite equilibrium constant. Fits of the thermodynamic results to obtain E_A, C_A, and W parameters were calculated by the least-squares technique.[16]

Results and Discussion

Solution Equilibrium Studies. Analysis of the spectrophotometric titration data[15] for the reaction of $VO(hfac)_2$ with TMPO in methylene chloride gave an equilibrium constant for adduct formation of about 4×10^{10} L/mol which is essentially infinite. Complete complexation is also indicated by EPR, where one can detect either the acid or the base at very low concentrations, but both species are never detected at the same time. Whenever $VO(hfac)_2$ is in excess, no TMPO is seen and vice versa. This is consistent with a very large equilibrium constant. Our inability to detect an EPR spectrum for the adduct under these conditions indicates either strong spin pairing or very fast electronic spin relaxation in the adduct.

The raw calorimetric data for the reaction of $VO(hfac)_2$ with the bases pyridine, Me_2SO, TMPO, DMA, acetonitrile, pyridine *N*-oxide, *N*-methylimidazole, and tetrahydrothiophene are given in Table M-1 (supplementary material). The calorimetric results for the reaction of $VO(hfac)_2$ with the bases studied always indicated a very high equilibrium constant because very little heat evolution was observed past the equivalence point. However, with every base studied, the $1/K$ vs. ΔH plot for solutions containing a large excess of acid deviated from a 1:1 equilibrium expression. A typical plot is illustrated in Figure 1 for the base Me_2SO. For 1:1 adduct formation all of the lines in this plot should intersect at the same point. Every adduct studied in benzene and the $VO(hfac)_2 \cdot py$ adduct in methylene chloride all showed the pattern in which the lines for the low mole ratio base to acid solutions fell below the intersection.

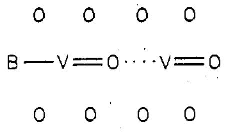
We speculate that coordination of the base enhances the basicity of the vanadyl oxygen giving rise to a weak acid–base

Table I. Summary of Calorimetry Data and Comparison with Calculated Heats

base	E_B	C_B	$-\Delta H_{\text{exptl}}$[a,b]	$-\Delta H_{\text{calcd}}$[a,c]	diff[a]
py	1.17	6.40	12.3[d]	12.6	+0.3
Me_2SO	1.34	2.85	11.5	10.9	−0.6
TMPO	0.92	6.20	10.7	10.5	−0.2
DMA	1.32	2.58	10.0	10.5	+0.5
acetonitrile	0.886	1.34	6.0	6.1	+0.1
py-*N*-O[e]	1.34	4.52	11.0	12.3	+1.3
THTP[e]	0.341	7.90	1.3	7.4	+6.1

[a] kcal/mol. [b] It is customary to report the marginal standard deviation and the ratio of marginal standard deviation to conditional standard deviation. These parameters are measures of the error limits and the goodness of fit. They are not reported here since the system did not fit a 1:1 equilibrium, and only the total heat evolved was used to find ΔH. Thus our usual statistical analysis was not possible. [c] Calculated by using $E_A = 7.7$, $C_A = 0.85$, and $W = 1.9$ kcal/mol. [d] Corrected for 0.9 kcal/mol specific interaction with benzene.[19] [e] Not used to determine E_A, C_A, and W. See text.

interaction between the vanadyl oxygen in the adduct and another $VO(hfac)_2$ molecule whenever the acid is in excess.



$$B{-}V{=}O\cdots V{=}O$$

This extra interaction would cause the failure of the $1/K$ vs. ΔH plot to fit a simple 1:1 equilibrium constant expression. However, the values of the net ΔH's would not be affected since only $VO(hfac)_2{\cdot}B$ adducts are present whenever base is in excess. Similar problems are encountered in studies of the hydrogen-bonding alcohols where the basic alcoholic oxygen becomes more basic upon hydrogen bond formation and could lead to a 2:1 phenol–base adduct in excess acid. For this reason, Lewis base hydrogen bonding studies are usually carried out in excess base. Precedence for a basic vanadyl oxygen can be obtained from both X-ray structural studies[17] on a Schiff base vanadyl complex and solution studies.[7,18] The V=O stretch of the free acid in the solid state (Nujol mull) occurs at 948 cm^{-1}, compared to the high energy solution band at 1030 cm^{-1}, suggesting a polymeric $\cdots V{=}O\cdots V{=}O\cdots V{=}O\cdots$ arrangement in the solid state.

In all calorimetry runs, base was added until no more heat was evolved, usually a threefold excess. The total heat evolved (H') and the amount of acid present (moles of VO) were used to directly calculate the molar heat of adduct formation ($-\Delta H = H'$/mol of VO). These numbers are tabulated in the fourth column of Table I.

Infrared Studies. Attempts were made to determine the influence of bases on the vanadyl stretching vibration and to detect the postulated 2:1 acid–base adduct by using IR methods to follow the titration. Previous work on $VO(acac)_2$ adducts has shown that the V=O stretching frequency is sensitive to the strength of adduct formation and to the isomer present.[20,21] It is possible to follow the titration of $VO(hfac)_2$ with Lewis bases in methylene chloride by observing a shift in the V=O stretching frequency. However, no evidence was obtained from the IR studies to support a 2:1 adduct. There are peaks at 991 and 1005 cm^{-1} in a methylene chloride solution of pure $VO(hfac)_2$ in addition to the 1030-cm^{-1} peak assigned to the V=O stretch. These additional bands indicate some interaction of the acid with the solvent. Upon addition of base the 1030-cm^{-1} band disappears and the band at 991 cm^{-1} increases in intensity. All of the bases affect the peaks to about the same extent; therefore, no correlation of the solution IR data with the calorimetry data is possible. For $VO(hfac)_2$ solutions in chloroform, only one band at 990 cm^{-1} is present in the V=O stretching region which does not shift or change intensity when bases are added even though the color changes of the solution indicate that adducts are being formed. The stretching frequency of the V=O group is apparently being dominated by the hydrogen bonding interaction with chloroform. Methylene chloride is a weaker hydrogen bonding solvent that also complicates the solution equilibrium.

Caira and co-workers have shown that the infrared spectra of solid $VO(acac)_2{\cdot}B$ adducts can be used to determine whether the base is bound in a basal or axial fashion.[21] Three V–O bands between 300 and 600 cm^{-1} were observed as single bands for the axial isomers, but each splits into two bands for the less symmetric basal isomers. In addition, the V=O stretching band for a series of $VO(acac)_2{\cdot}B$ complexes, where B is a substituted pyridine base, falls in two distinct regions, either 41 ± 4 cm^{-1} or 29 ± 4 cm^{-1} lower than the uncomplexed acid. With the aid of a crystal structure they concluded that the basal adducts gave rise to the 41-cm^{-1} shift and the axial isomer gave the 29-cm^{-1} shift. A similar effect might be expected for $VO(hfac)_2{\cdot}B$ adducts. Four solid adducts were isolated, and their IR spectra in Nujol were recorded. $\Delta\nu$(V=O) ranged from 22 to 45 cm^{-1}. With the limited data at hand for $VO(hfac)_2$ it is difficult to tell which adducts are axial or if the above groupings are applicable when a wider range of bases than the substituted pyridines are employed or when the acid is $VO(hfac)_2$.

***E* and *C* Analysis.** As mentioned earlier, in order to detect stabilization or destabilization in a system from effects other than normal σ-bond formation, the E and C numbers for the acid and base (in this case $VO(hfac)_2$ and TMPO) must be determined on systems where the effect is not observed. Since E_B and C_B are known for TMPO, we must evaluate E_A and C_A for $VO(hfac)_2$ in order to investigate spin-pairing stabilization in this adduct. Because of solubility considerations, benzene was used as the solvent instead of alkanes or CCl_4. Since benzene is known to be a Lewis base, it was felt that there might be significant interaction between the solvent and $VO(hfac)_2$. This interaction can be estimated by using the E, C, and W approach.[16]

Whenever there is a constant contribution to the measured enthalpy of adduct formation for a series of acid–base adducts, the E and C equation can be rewritten as eq 2, where W is

$$-\Delta H_{\text{measd}} + W = E_A E_B + C_A C_B \qquad (2)$$

the constant contribution. (See ref 16 for several examples.) For $VO(hfac)_2$, the solute–solvent ($VO(hfac)_2$–C_6H_6) interaction must be broken in order to form each adduct. This interaction is the source of the constant contribution, W. The calorimetric data are analyzed by finding E_A, C_A, and W by the least-squares technique.[16] The criteria for a good E, C, and W fit have never been fully stated. Besides the requirement that the data be accurate, it is necessary that the experiment be done so that the correlation of the three variables be kept as low as possible. The previous requirement that the bases employed have a wide range of C_B/E_B ratios ensures that the C_A and E_A variables are not highly correlated. However, this requirement is not sufficient to ensure that neither E_A nor C_A is highly correlated with W. For example, it is easy to pick several bases whose E_B numbers are all quite close to 1.2. For such a set of bases the $E_A E_B$ term in eq 2

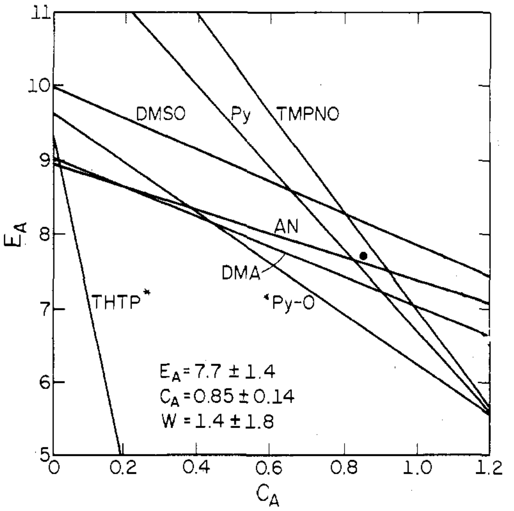


Figure 2. E_A vs. C_A plot for various Lewis base adducts of $VO(hfac)_2$ at a value of $W = 1.9$ kcal mol^{-1}. The best solution of the data is indicated by the solid circle. Those bases marked with an asterisk were not used in the least-squares fit to determine the best solution.

would be constant, and it would be impossible to separate the effects of the W and E_AE_B terms. To ensure against this, it is necessary to study a set of bases with the largest E_B range possible. Similarly, it is necessary to use a set of bases with the largest C_B range possible to ensure a low correlation of C_A and W. Usually the latter requirement is readily met. It is recommended that, when E, C, and W are computed, the analyses include the calculation of the marginal and conditional standard deviations and the correlation coefficients. Both the absolute errors and the correlation coefficients should be small to ensure a meaningful fit of the data.

The best fit using the data for TMPO, pyridine, DMA, acetonitrile, and Me_2SO (five bases) gives $E_A = 7.7 \pm 1.4$, $C_A = 0.85 \pm 0.14$, and $W = 1.9 \pm 1.8$ kcal/mol, where the reported errors are one standard deviation. The large error limit for W reflects the fact that the error curve has only a shallow minimum for variation of W even though E_B ranges from 0.89 to 1.34. This range encompasses nearly all of the oxygen and nitrogen donors in the E and C correlation. The values for E_A and W are highly correlated, so E_A also has a large error limit. In order to ascertain the accuracy of the enthalpy prediction for this acid, we held W fixed at 1.9 kcal mol^{-1}, and the error limits were determined. Standard deviations of 0.39 in E_A and 0.10 in C_A were obtained. The value of W obtained is quite reasonable since one can calculate an enthalpy of adduct formation of 2.0 kcal/mol for the $VO(hfac)_2 \cdot C_6H_6$ adduct by using the E and C numbers for $VO(hfac)_2$ and those for benzene[22] ($E_B = 0.11$, $C_B = 1.4$). The E_A vs. C_A plot for $W = 1.9$ kcal/mol is given in Figure 2. The observed and calculated enthalpies are compared in Table I.

The experimental enthalpy of formation for the *N*-methylimidazole adduct could not be determined. From the raw calorimetry data (Table M-1) it is obvious that something in addition to simple adduct formation is occurring. After addition of even a fivefold excess of base, heat is still evolved at an increasing rate! *N*-Methylimidazole is probably displacing the hfac ligand. *N*-Methylimidazole is the strongest base used in this study and would thus be the most likely to suffer from this complication.

Several of the enthalpies for bases in Table I miss the best E_A, C_A, and W fit by a considerable amount. The pyridine *N*-oxide heat is lower than predicted. Pyridine is reported[19] to undergo specific adduct formation with benzene which is broken upon formation of a pyridine acid–base adduct. This interaction requires about a 0.9-kcal/mol correction to measured heats in this solvent. If pyridine *N*-oxide undergoes a similar interaction with the solvent benzene, the correction would bring the pyridine *N*-oxide adduct enthalpy into very good agreement with the calculated heat. We are reluctant to propose that pyridine *N*-oxide data in benzene be corrected on the basis of one measurement but want to note the possibility. A steric effect involving ring protons of pyridine *N*-oxide and the hfac groups may also exist. The measured enthalpy of formation of the Me_2SO adduct is about 0.6 kcal/mol high for some unknown reason. As can be seen in Figure 2, the data for all five bases would have fit within 0.2 kal/mol if this enthalpy were lower.

The THTP heat is much lower than the E and C predicted enthalpy, as was expected. Previous work with $Cu(hfac)_2$ always gave low enthalpies of adduct formation with sulfur donors.[5] This was attributed to steric interaction between the electron density on the sulfur atom of the base and the electron density on the oxygen atoms of the hfac ligands. In order for the sulfur atom to come to optimum bonding distance from the metal center, it must also come within closer than van der Waals distance to the flanking oxygen atoms. The interaction of the diffuse electron cloud of the sulfur with the electron density on the electronegative oxygens results in a repulsion that weakens the adduct bond strength. It was expected that this repulsion would be even larger in the vanadyl case than in that of $Cu(hfac)_2$ because the vanadium atom is formally in the +4 oxidation state and should be smaller than copper(II). Furthermore, the X-ray structure of the $VO(acac)_2 \cdot {}^1/_2$dioxane adduct[23] shows that the vanadium atom is displaced out of the plane of the ligands toward the vanadyl oxygen and away from the dioxane molecule. In $Cu(hfac)_2 \cdot$base adducts,[24] the copper is displaced toward the base. This difference should cause shorter contacts between the sulfur donor atom and the ligand oxygen atoms in the vanadyl adduct and increase the steric interaction relative to the copper case. For $Cu(hfac)_2 \cdot$THTP the difference between calculated and experimental heats is 4.0 kcal/mol,[5] while $VO(hfac)_2 \cdot$THTP misses the predicted enthalpy of 7.4 kcal/mol by 6.1 kcal/mol.

It is interesting to compare the E_A and C_A parameters found here ($E_A = 7.7$, $C_A = 0.85$) to those reported[5] for $Cu(hfac)_2$ ($E_A = 3.46 \pm 0.06$, $C_A = 1.36 \pm 0.02$). The E_A number for $VO(hfac)_2$ is much larger while the C_A number is significantly smaller. Several effects contribute to the difference in the behavior of these two systems. There are differences in the d-electron configuration, in the formal charge of the metal center, in the steric availability of the metal center, and in the amount of structural reorganization that occurs upon adduct formation. In going from d^1 to d^{10} configuration, i.e., moving from left to right across the first transition period, the metals in a given oxidation state become smaller, and the charge to size ratio increases. However, the different d-electron configurations for various geometries can be considered polarization mechanisms which cause reversals in metal–ligand bond strengths. For example, d^7–d^9 metals often prefer nitrogen and sulfur donors over oxygen donors while d^1–d^3 metals prefer oxygen donors to sulfur and nitrogen. These observations suggest increased covalent character as one moves from d^1 to d^{10}. In comparing vanadyl to copper(II), one expects that the higher formal charge on the vanadium atom in $VO(hfac)_2$ should give rise to a larger E_A number. But a smaller C_A number is expected because the vanadium is not polarizable, and the orbital extent should be smaller resulting in diminished overlap with the base lone-pair orbital. The differences in the E_A and C_A values for $VO(hfac)_2$ and $Cu(hfac)_2$ thus parallel the trends in the qualitative observations of reactivity for the first transition series.

Magnetic Susceptibility Studies. To measure the amount of spin pairing, we made a determination of the magnetic susceptibility of the $VO(hfac)_2 \cdot TMPO$ adduct in solution and in the solid state. In solution, TMPO gave a magnetic moment of 1.7 μ_B, while the measured moment of the solution for the 1:1 adduct was 1.0 μ_B. The uncorrected susceptibility of the solid adduct was quite small and varied for different preparations in the range from -125×10^{-6} to 75×10^{-6} cm^3/mol. Assumption of a diamagnetic correction of -290×10^{-6} cm^3/mol gives a magnetic moment of 0.6–0.9 μ_B. A variable-temperature susceptibility study showed that the magnetic moment declined from 0.91 μ_B at room temperature to 0.74 μ_B at 82 K. It is apparent that there is a large antiferromagnetic interaction in the $VO(hfac)_2 \cdot TMPO$ adduct since a magnetic moment of 2.7 μ_B would be expected in the absence of an interaction, while the measured moment is about 1.0 μ_B. The observed moment is attributed to a 5–10% paramagnetic impurity which dominates the measured susceptibility. A spin equilibrium possibility is eliminated because the variable-temperature moment does not drop fast enough as the temperature is lowered. The variability in the room-temperature susceptibility with sample preparation and for a given sample with time also indicates some impurity. Since the nitroxide is quite volatile, it is probable that some TMPO is lost from the solid on standing, leaving uncomplexed, paramagnetic $VO(hfac)_2$ behind. The magnetic data indicate that $-2J$ is at least 700 cm^{-1}, and as is the case for the related copper complex,[2] the odd electrons in the $VO(hfac)_2 \cdot TMPO$ adduct are almost completely spin paired at room temperature. ($2J$ is the energy separation of the singlet and triplet states.)

Very recently, Richardson and Kreilick[25] reported the EPR spectrum of the vanadyl bis(trifluoroacetylacetonate)–*p*-pyridyl iminonitroxide adduct. They report that $2J$ is -386 cm^{-1} for this complex. The fact that no EPR signal is observable for the $VO(hfac)_2 \cdot TMPO$ complex supports a value of $-2J$ considerably in excess of 400 cm^{-1} and is consistent with a value of over 700 cm^{-1} estimated from the magnetic study.

Consequences of the Spin-Pairing Interaction. Although an accurate value of $2J$ has not been obtained for $VO(hfac)_2 \cdot TMPO$, the magnetic data conclusively show that there is a large exchange interaction between the odd electrons on the vanadium and the nitroxide. However, since the enthalpy of adduct formation is correctly predicted by the E and C equation, the spin pairing does not make an additional contribution to the enthalpy of adduct formation. Thus, in both the $Cu(hfac)_2 \cdot TMPO$ and $VO(hfac)_2 \cdot TMPO$ cases there is no extra enthalpy of stabilization due to spin pairing. It has been suggested in the case of the $Cu(hfac)_2 \cdot TMPO$ adduct that the extra heat associated with J might be cancelled by compensating steric interaction between the methyl groups of the nitroxide and the ligands on the acid. A significantly greater steric interaction is expected and is demonstrated toward sulfur donors in $VO(hfac)_2$ than in $Cu(hfac)_2$. Thus, nearly exact cancellation of the spin-pairing and steric effects in both the vanadyl and copper TMPO systems would be quite fortuitous. Thus, it appears that spin pairing does not contribute to the enthalpy of adduct formation.

With no net stabilization of the ground singlet state of the adduct from spin pairing, that is, no stabilization over and above the stabilization that occurs when the systems with unpaired electrons interact with diamagnetic acids and bases, the large J value must result from destabilization of the excited triplet state. This proposal can be made more clear with the aid of Figure 3 which depicts a molecular orbital description of the interaction of a Lewis acid, A, and a Lewis base, B (each of which contains odd electrons), to form C. The electron spins are labeled α and β. The acids are $VO(hfac)_2$ or $Cu(hfac)_2$, for example, and the base is TMPO. The essential acid–base interaction involves orbitals 3 and 8 while the spin pairing involves orbitals 2 and 9. Molecular orbital 6 represents a very weak interaction between 2 and 9 providing relatively little stabilization of the ground singlet state from spin pairing. This effect is not included in the E and C parameters and would lead to an underestimate of the adduct bond strength if it existed (~0.3 kcal mol^{-1} of stabilization would not be detected in our experiment). Next we must account for the fact that the value of $2J$ is much larger than the energy difference of orbitals 6 and 7. The quantity $2J$ is not directly related to the energy difference of the ground-state levels 6 and 7 but is related to the difference in the energy of the ground and triplet *states*. In the conversion to a triplet state, an electron with β spin is placed in a higher energy molecular orbital with a spin change. In an SCF analysis, many of the integrals involved in this triplet state and in the ground state differ. Those anticipated to make the most significant difference in increasing the energy of the triplet state involve certain core and exchange integrals. The core integrals involving the promoted electron in the triplet state are less negative than the corresponding ground-state integrals involving this electron. The exchange integrals in the ground state involving the β-spin electron in level 6 with all other β-spin orbitals are lost and replaced by smaller $\kappa_m(\alpha)_n(\alpha)$ exchange integrals with triplet state; that is $\kappa_6(\beta)_5(\beta) > \kappa_7(\alpha)_6(\alpha)$ where

$$\kappa_{mn} = \int\int [\psi_m^*(i)][\psi_n(i)](e^2/r_{ij})[\psi_m(j)][\psi_n^*(j)](dv)_i\,(dv)_j$$

With m and n denoting orbitals and i and j electrons, exchange integral $\kappa_7(\alpha)_6(\alpha)$ in the triplet state normally tends to stabilize the triplet state when 9 and 2 have significant differential overlap. However, in this system, the geometry of the adduct results in poor overlap of 9 and 2. This leads not only to a minor decrease in the energy of 6 relative to 9 and 2 but also to a very small differential overlap between 7 and 6 destabilizing the triplet state. This poor differential overlap is in part due to the difference in energy of the vanadium and nitroxide centers, resulting in bonding and antibonding orbitals that are mainly on opposite centers. A significant value for J results because the triplet state is destabilized.

These findings have some interesting consequences relative to the area of metal–metal bonding in transition-metal dimers[4] and in other systems where the adduct has a lower spin multiplicity than the reactants. The thermodynamic consequences of these interactions and their significance in terms of chemical reactivity constitute the nontrivial aspects of this area of chemistry. These effects are not readily inferred from an observation of spin pairing or a determination of $2J$.

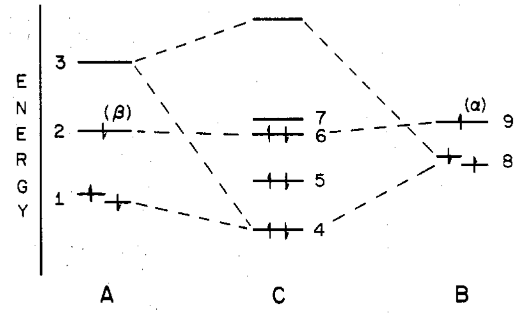


Figure 3. Simplified molecular orbital diagram illustrating the energy changes and interactions of the highest energy orbitals of an acid, A ($Cu(hfac)_2$ or $VO(hfac)_2$), and a free radical Lewis base, B (TMPO), to form a spin-paired adduct, C.

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Registry No. $VO(hfac)_2$, 15819-88-2; $VO(hfac)_2 \cdot$acetonitrile, 70528-11-9; $VO(hfac)_2 \cdot Me_2SO$, 70528-12-0; $VO(hfac)_2 \cdot TMPO$, 70528-13-1; $VO(hfac)_2 \cdot py$, 67202-77-1; $VO(hfac)_2 \cdot DMA$, 70528-14-2;

$VO(hfac)_2$·THTP, 70528-15-3; $VO(hfac)_2$·py-*N*-O, 70528-16-4; $VO(hfac)_2$·MeIm, 70528-17-5.

Supplementary Material Available: Table M-1, raw calorimetry data for $VO(hfac)_2$ (3 pages). Ordering information is given on any current masthead page.

References and Notes

(1) R. A. Zelonka and M. C. Baird, *J. Am. Chem. Soc.*, **93**, 6066 (1971); D. G. Brown, T. Maier, and R. S. Drago, *Inorg. Chem.*, **10**, 2804 (1971); A. A. Medzhidov et al., *Teor. Eksp. Khim.*, **6**, 133 (1973); N. M. Karayannis et al., *Inorg. Chim. Acta*, **7**, 74 (1973).
(2) Y. Y. Lim and R. S. Drago, *Inorg. Chem.*, **11**, 1334 (1972).
(3) R. S. Drago, G. C. Vogel, and T. E. Needham, *J. Am. Chem. Soc.*, **93**, 6014 (1971); R. S. Drago, *Struct. Bonding* (*Berlin*), **15**, 73 (1973).
(4) C. D. Garner, I. H. Hillier, M. F. Guest, J. C. Green, and A. W. Coleman, *Chem. Phys. Lett.*, **41**, 91 (1976); F. A. Cotton, C. E. Rice, and G. W. Rice, *J. Am. Chem. Soc.*, **99**, 4704 (1977); F. A. Cotton and G. G. Stanley, *Inorg. Chem.*, **16**, 2668 (1977).
(5) D. R. McMillin, R. S. Drago, and J. A. Nusz, *J. Am. Chem. Soc.*, **98**, 3120 (1976).
(6) C. J. Popp, J. H. Nelson, and R. O. Ragsdale, *J. Am. Chem. Soc.*, **91**, 610 (1969).
(7) C. M. Guzy, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc. A*, 2791 (1969).
(8) F. A. Walker, R. L. Carlin, and P. H. Rieger, *J. Chem. Phys.*, **45**, 4181 (1966).
(9) R. L. Carlin and F. A. Walker, *J. Am. Chem. Soc.*, **87**, 2128 (1965).
(10) C. Su, J. W. Reed, and E. S. Gould, *Inorg. Chem.*, **12**, 337 (1973).
(11) M. S. Nozari and R. S. Drago, *J. Am. Chem. Soc.*, **92**, 7086 (1970).
(12) R. Meyer, University of Illinois, personal communication.
(13) D. F. Evans, *J. Chem. Soc.*, 2003 (1959).
(14) (a) D. F. Evans, *J. Phys. E*, **7**, 247 (1974). (b) Temperature-dependent measurements of the susceptibility were kindly provided by Professor L. Wilson of Rice University.
(15) T. F. Bolles and R. S. Drago, *J. Am. Chem. Soc.*, **87**, (1965); R. L. Courtright, R. S. Drago, J. A. Nusz, and H. S. Nozari, *Inorg. Chem.*, **12**, 2809 (1973).
(16) R. M. Guidry and R. S. Drago, *J. Am. Chem. Soc.*, **95**, 759 (1973).
(17) M. Mathew, A. J. Carty, and G. J. Palenik, *J. Am. Chem. Soc.*, **92**, 3197 (1970).
(18) H. Taguchi et al., *Chem. Lett.*, 757 (1975).
(19) M. S. Nozari and R. S. Drago, *J. Am. Chem. Soc.*, **94**, 6877 (1972).
(20) S. Ikeda et al., *Inorg. Chem.*, **5**, 611 (1966).
(21) M. R. Caira, J. M. Haigh, and L. R. Nassimbeni, *J. Inorg. Nucl. Chem.*, **34**, 3171 (1972).
(22) R. S. Drago, L. B. Parr, and C. S. Chamberlain, *J. Am. Chem. Soc.*, **99**, 3203 (1977).
(23) K. Dichmann et al., *Chem. Commun.*, 1295 (1970).
(24) G. W. Bushnell, *Can. J. Chem.*, **49**, 555 (1971); P. Jose, S. Ooui, and O. Fernando, *J. Inorg. Nucl. Chem.*, **31**, 1971 (1969).
(25) P. F. Richardson and R. W. Kreilick, *Chem. Phys. Lett.*, **50**, 333 (1977).

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The Partial Aminolysis of $(NPF_2)_{3,4}$[1]

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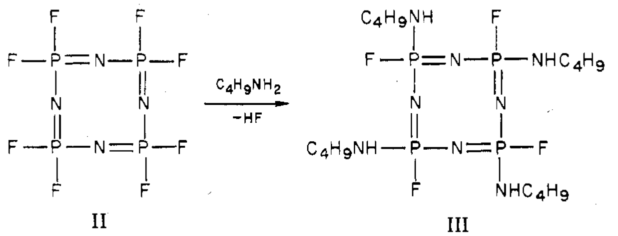
Unlike the reactions of $(NPCl_2)_{3,4}$ with simple amines, the fluorocyclophosphazenes, $(NPF_2)_{3,4}$, react with methylamine, *n*-butylamine, or dimethylamine with replacement of only one fluorine atom per phosphorus to yield products such as $N_4P_4F_5(NHMe)_3$, $N_4P_4F_4(NHMe)_4$, $N_4P_4F_5(NHC_4H_9)_3$, $N_4P_4F_5(NMe_2)_3$, $N_4P_4F_4(NMe_2)_4$, $N_3P_3F_4(NHMe)_2$, $N_3P_3F_4(NHC_4H_9)_2$, or $N_3P_3F_4(NMe_2)_2$. This behavior cannot be ascribed to steric effects because nucleophiles such as CF_3CH_2ONa, C_6H_5ONa, and $(CH_3)_2NLi$ readily replace all the fluorine atoms. The results are more compatible with an explanation based on the poor leaving-group ability of fluoride combined with the low nucleophilicity of the free amines, compared with the higher leaving-group ability of chloride and the high nucleophilicity of alkoxides, aryl oxides, or metal amides.

The reactions of cyclic or high polymeric chlorophosphazenes such as $(NPCl_2)_{3,4,n}$ with primary or secondary amines or with alkoxides or aryl oxides have been studied in detail.[2] Under suitable reaction conditions all the chlorine atoms can normally be replaced by amino, alkoxy, or aryloxy residues to yield cyclic or high polymeric phosphazenes of formula $[NP(NHR)_2]_{3,4,n}$, $[NP(NR_2)_2]_{3,4,n}$, or $[NP(OR)_2]_{3,4,n}$. The only exceptions are reactions that involve highly hindered nucleophiles such as diethylamine, diphenylamine, or amino-azo dyes, especially in reactions with the high polymer $(NPCl_2)_n$.[3,4]

Fluorocyclophosphazenes such as $(NPF_2)_{3,4}$ closely resemble chlorophosphazenes in their behavior toward alkoxides or aryl oxides. For example, $(NPF_2)_4$ reacts readily with CF_3CH_2ONa or C_6H_5ONa to yield $[NP(OCH_2CF_3)_2]_4$ or $[NP(OC_6H_5)_2]_4$ (see Experimental Section). However, a survey of the literature revealed a curious absence of reports of fully aminolyzed phosphazene trimers or tetramers derived from $(NPF_2)_{3,4}$. Compounds such as $N_3P_3F_5NHMe$, $N_3P_3F_3(NMe_2)_3$, $N_4P_4F_7NH_2$, or $N_4P_4F_4(NMe_2)_4$ had been reported,[5-7] but no species containing more than three or four amino residues were described. This was of particular interest to us because of our intention to utilize high molecular weight poly(difluorophosphazene) as a substrate for the synthesis of mixed-substituent poly(aminophosphazenes).

We wish to report here the significant difference that apparently exists between the aminolysis reactions of $(NPF_2)_3$ (I) or $(NPF_2)_4$ (II) and those of the corresponding chlorophosphazenes when these compounds are allowed to interact with an excess of primary or secondary amine. Specifically, I and II react with methylamine, *n*-butylamine, or dimethylamine with replacement of only one fluorine atom per phosphorus under conditions that lead to total replacement of chlorine in $(NPCl_2)_{3,4}$. In fact, so far we have been unable to find reaction conditions that lead to the complete aminolysis of fluorocyclophosphazenes.

The reaction conditions and the results of the present work are summarized in Table I and in the Experimental Section. A typical example is given by the conversion of II to III in the presence of butylamine. The reaction products were identified by a combination of VPC–mass spectrometric and ^{31}P NMR data as three different isomers of the nongeminal species III and two nongeminal isomers of $N_4P_4F_5(NHC_4H_9)_3$. Only trace amounts, if any, of $N_4P_4F_3(NHC_4H_9)_5$ were de-



II III