Discussion

In the kinetics of the zinc incorporation reaction for the water-soluble porphyrin, the nitrogen-base-catalyzed term is of considerable interest. The catalysis is similar to that observed for magnesium ion in methanol and acetone solutions,[3] indicating that the catalysis is a general phenomenon which could be of biological importance. In understanding the mechanism of the catalysis, of significance is the fact that collidine does not catalyze the reaction whereas the closely related cyclic nitrogen compounds of comparable base strength do catalyze the reaction. If the catalysis is of the general base type there should be a Brønsted correlation between catalytic rate and base strength. There is a reasonable correlation except for collidine. The obvious difference between collidine and the other bases is the fact that it contains two methyl groups *ortho* to the ring nitrogen. Whereas these groups apparently offer but slight steric hindrance to addition of a proton so that collidine has a base strength comparable to that of pyridine, the steric hindrance for a cation such as Zn^{2+} must be quite significant. Thus the failure of collidine to catalyze the reaction implies that the nitrogen base coordinates to Zn^{2+} during the course of the reaction. Confirmatory evidence comes from studies which show that, under the conditions of the kinetic experiments, Zn^{2+} and the nitrogen bases do indeed associate.[14,15]

Finally, the fact that the empirical activation energy of the pyridine catalyzed path exceeds that for the uncatalyzed reaction is noteworthy. The situation is similar to that observed for the magnesium replacement from deuteroporphyrin ester.[16] In both cases, the observation must indicate the existence of preequilibria having favorable entropies. Use of the water-soluble porphyrin makes possible relaxation studies, now underway, which should prove useful in understanding the preequilibria.

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Thermodynamic and Infrared Studies of Tertiary Amine Oxides with Bis(2,4-pentanedionato)oxovanadium(IV)

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Abstract: The donor properties of a series of substituted pyridine N-oxide bases toward the reference acid bis(2,4-pentanedionato)oxovanadium(IV) have been studied. Heats of reaction have been determined calorimetrically and, in the case of the 4-substituted pyridine N-oxides, correlate well with σ_{PyNO}. The change of the vanadium–vanadyl oxygen stretching frequency ($\Delta\bar{\nu}_{\mathrm{V=O}}$) and the vanadium–2,4-pentanedionate stretching frequency ($\Delta\bar{\nu}_{\mathrm{V-O}}$) upon coordination were studied and were also found to correlate well with enthalpies of reaction. Substitution of alkyl groups in other than the 4 position of the pyridine N-oxide ring causes a decrease in the effective basicity toward the reference acid, $VO(acac)_2$. The usefulness of $VO(acac)_2$ as a reference acid is discussed. The system is extended to the tertiary amine oxides *p*-bromo-N,N-dimethylaniline N-oxide and trimethylamine N-oxide.

The use of the coordination compound bis(2,4-pentanedionato)oxovanadium(IV), $VO(acac)_2$, as a reference acid has been examined.[2,3] The heats of reaction of a variety of nitrogen and oxygen donors interacting with $VO(acac)_2$ were determined, and it was found that enthalpy values did not correlate well with the pK_a's of the bases.[2] Selbin, *et al.*,[3] studied the decrease of the vanadium–vanadyl oxygen stretching frequency ($\Delta\bar{\nu}_{\mathrm{V=O}}$) in the infrared upon coordination to a large variety of bases. It was concluded that there was no general correlation between $\Delta\bar{\nu}_{\mathrm{V=O}}$ and the pK_a values of the bases. Shifts in the visible absorption spectrum of $VO(acac)_2$ have been used as parameters for ordering solvent basicity.[4]

The structure of $VO(acac)_2$ has been established as being a slightly rectangular pyramid[5] with the vanadium near the center of gravity of the pyramid rather than at the base. The sixth position in the coordination sphere of $VO(acac)_2$ has been shown to be solvated in solution.[6,7] As a result of the structure of $VO(acac)_2$, the steric effects of the base can be quite important to

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coordination in the open or solvated sixth position in $VO(acac)_2$. In previous studies,[2,3] bases with constant steric effects were not employed.

We have studied the interactions of $VO(acac)_2$ with a series of substituted pyridine N-oxides and two aliphatic tertiary amine oxides using calorimetric and infrared techniques. Compounds substituted in the 2, 3, and 4 positions of the aromatic ring were studied in order to gain further insight into the steric effect. Correlations are made with σ_{PyNO} constants developed by Ragsdale and coworkers.[8]

Experimental Section

Preparation and Purification of Amine Oxides. Pyridine N-oxide, 4-methoxypyridine N-oxide, 4-nitropyridine N-oxide, and 4-methylpyridine N-oxide were purchased from Aldrich Chemical Co. 4-Chloropyridine N-oxide was prepared from 4-nitropyridine N-oxide by the method of Ochiai.[9] Methyl isonicotinate N-oxide was prepared from methyl isonicotinate[10] (Aldrich Chemical Co.). The following amine oxides were prepared from the corresponding amines (Eastman) by oxidation with hyrogen peroxide in glacial acetic acid: 2,6-dimethylpyridine N-oxide,[11] 2,4-dimethylpyridine N-oxide,[12] 2-methylpyridine N-oxide,[13] 2,4,6-trimethylpyridine N-oxide,[11] 2,3-dimethylpyridine N-oxide,[14] 3,5-dimethylpyridine N-oxide,[9] and 3,4-dimethylpyridine N-oxide.[9] 3-Methylpyridine N-oxide and 2-ethylpyridine N-oxide were purchased from Aldrich Chemical Co. Melting and boiling points agreed with the literature. The pyridine N-oxides were purified by recrystallizing from acetone, vacuum sublimation, or distillation. *p*-Bromo-N,N-dimethylaniline N-oxide was prepared by oxidizing 20 g of *p*-bromo-N,N-dimethylaniline with 80 ml of 30% hydrogen peroxide and 93 ml of acetic acid. The mixture was stirred for 24 hr, neutralized with Na_2CO_3, and extracted with and recrystallized from chloroform yielding tan hygroscopic crystals,[15] mp 160–162°. Trimethylamine N-oxide was prepared by the method of Meisenheimer.[16]

Solvents. Spectroquality chloroform and dichloromethane obtained from Matheson Coleman and Bell were stored over molecular sieves and used without further purification.

Calorimetric Apparatus and Procedure. The basic design of the calorimeter and calibration technique is that of Arnett, *et al.*,[17] with some notable design changes. The calorimeter used in these experiments is a twin or dual calorimeter employing two identical dewar flasks, like the one described by Arnett. Both dewar flasks were immersed in a constant-temperature bath kept at 25 ± 0.5°. One of the dewar flasks replaces the base-line compensator described by Arnett. The thermistors in both dewars are arms of a Wheatstone bridge which includes a switching circuit which allows both thermistors to be used, or either thermistor to be coupled with a 5000-ohm resistor for calibration. Samples were injected into the dewar flasks simultaneously with two Hamilton No. 725-CH 250-μl syringes equipped with Chaney adapters. Both calorimeters were filled with solvent, and 1.0×10^{-2} mole of $VO(acac)_2$ was added to one of the dewar flasks. This amount of acid present is in large excess compared to base added. A solution which contained 10^{-4}–10^{-5} mole of base was injected into both calorimeters. Sample size varied from 250 μl down and depended on the enthalpy of reaction of each particular base. The advantage of the twin calorimeter is that heats of mixing and dilution as well as any heat generated by pushing the syringe plunger are cancelled and need not be separately measured. Therefore, the heat detected is due to the interaction of the acid and base. It was found that five or six repetitions were sufficient for each base. Also, several bases could be included in the same run with no detectable difference from the enthalpies obtained in individual determinations.

Treatment of Data. All lines in the figures were fit by least-squares technique. Experimental errors in ΔH values are reported as average deviations.

Preparation of the Solid Adducts. $VO(acac)_2$ was prepared as previously described[18] and recrystallized from ethanol, mp 265–268°. An ethanol solution of the approprirate pyridine N-oxide corresponding to a slight excess was added to a triethyl orthoformate[19] solution of $VO(acac)_2$. The solution was stirred for 1–2 hr at which time the product precipitated. The product was filtered, washed with ethanol and ether, and dried under reduced pressure over phosphorus pentoxide. The product was then recrystallized from chloroform.

$[VO(acac)_2(4\text{-}CH_3C_5H_4NO)]\cdot 0.5H_2O$. *Anal.* Calcd for $C_{16}H_{22}NO_{6.5}V$: C, 50.20; H, 5.74; N, 3.66. Found: C, 50.22; H, 5.76; N, 3.89.

$[VO(acac)_2(C_5H_5NO)]$. *Anal.* Calcd for $C_{15}H_{19}NO_6V$: C, 50.00; H, 5.28; N, 3.89. Found: C, 49.12; H, 5.41; N, 4.08.

$[VO(acac)_2(4\text{-}ClC_5H_4NO)]\cdot H_2O$. *Anal.* Calcd for $C_{15}H_{20}NO_7ClV$: C, 43.69; H, 4.85; N, 3.40. Found: C, 43.28; H, 4.48; N, 3.79.

Infrared Spectra. Solution spectra were run as previously described[20] in Spectroquality dichloromethane (Matheson Coleman and Bell) in the sodium chloride region. Matched 0.1-mm sodium chloride cells were used on either a Beckman IR5-A or a Perkin-Elmer 521 infrared spectrophotometer. Solid samples were run as Nujol mulls or KBr disks on a Perkin-Elmer 521 spectrophotometer.

Results

Heats of reaction (ΔH) are reported in Table I for 14 substituted pyridine N-oxides interacting with $VO(acac)_2$ in dichloromethane. The values range from -0.87 ± 0.02 to -8.03 ± 0.09 kcal/mole. Similar data for the 4-substituted pyridine N-oxides and $VO(acac)_2$ in chloroform are also reported. The enthalpies of reaction in chloroform solvent are approximately 3 kcal lower than those of similar bases reacting in dichloromethane.

The heats of reaction of the 4-substituted pyridine N-oxides in dichloromethane and chloroform are plotted *vs.* σ_{PyNO} in Figure 1. Figure 2 is a plot of $\Delta\bar{\nu}_{V=O}$ (the vanadium–vanadyl oxygen stretching frequency) *vs.* ΔH for the 4-substituted pyridine N-oxides in dichloromethane. Figure 3 is a plot of $\Delta\bar{\nu}_{V=O}$ *vs.* ΔH for the remaining pyridine N-oxides in dichloromethane. Infrared data are reported in Table III for adducts of the pyridine N-oxide bases with $VO(acac)_2$ in KBr disks and as Nujol mulls. Enthalpy data are also reported for the tertiary amine oxides *p*-bromo-N,N-dimethylaniline N-oxide and trimethylamine N-oxide (Table I).

Discussion

Calorimetry. As has been pointed out, enthalpy measurements in the gas phase are closely approximated in hydrocarbon solvents.[21-23] However, solubilities

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Table I. Heats of Reaction with $VO(acac)_2$

Base	pK_a[a]	σ_{PyNO}	$-\Delta H_{rxn}$ (in CH_2Cl_2), kcal/mole	$-\Delta H_{rxn}$ (in $CHCl_3$), kcal/mole
4-Dimethylaminopyridine N-oxide	3.88	−1.48	10.5[b]	
4-Methoxypyridine N-oxide	2.05	−0.603	8.03 ± 0.09	4.75 ± 0.14
4-Methylpyridine N-oxide	1.29	−0.240	7.22 ± 0.08	3.50 ± 0.20
Pyridine N-oxide	0.79	0.0	6.21 ± 0.16	2.57 ± 0.10
4-Bromopyridine N-oxide			6.07[b]	
4-Chloropyridine N-oxide	0.36	0.206	5.72 ± 0.08	2.18 ± 0.14
4-Cyanopyridine N-oxide	−1.17	0.94	3.09[b]	
4-Nitropyridine N-oxide	−1.7	1.19	2.24 ± 0.08	
Methylisonicotinate N-oxide	−0.41	0.574	3.68[b]	0.85 ± 0.02
2-Methylpyridine N-oxide	1.02	−0.110[c]	4.06 ± 0.06	
2-Ethylpyridine N-oxide			3.65 ± 0.06	
3-Methylpyridine N-oxide	1.08	−0.139[c]	5.57 ± 0.17	
2,3-Dimethylpyridine N-oxide			4.55 ± 0.09	
2,4-Dimethylpyridine N-oxide			5.37 ± 0.10	
2,6-Dimethylpyridine N-oxide	1.44	−0.311[c]	0.87 ± 0.02	
3,4-Dimethylpyridine N-oxide			7.10 ± 0.15	
3,5-Dimethylpyridine N-oxide			6.72 ± 0.10	
2,4,6-Trimethylpyridine N-oxide			2.06 ± 0.03	
p-Bromo-N,N-dimethylaniline N-oxide	4[d]		33.9 ± 1.7	
Trimethylamine N-oxide	4.65		37.6 ± 2.2	

[a] See ref 8 and E. Ochiai, "Aromatic Amine Oxides," Elsevier Publishing Co., New York, N. Y., 1967. [b] Calculated from $\Delta\bar{\nu}_{V=O}$. [c] Calculated for this study from pK_a's. [d] Estimate based on pK_a of dimethylaniline N-oxide.

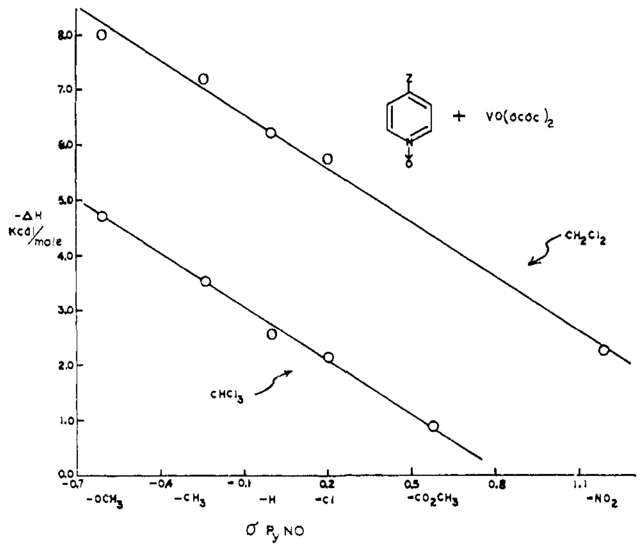

Figure 1. $-\Delta H_{rxn}$ *vs.* σ_{PyNO} for 4-substituted pyridine N-oxides and $VO(acac)_2$ in CH_2Cl_2 and $CHCl_3$.

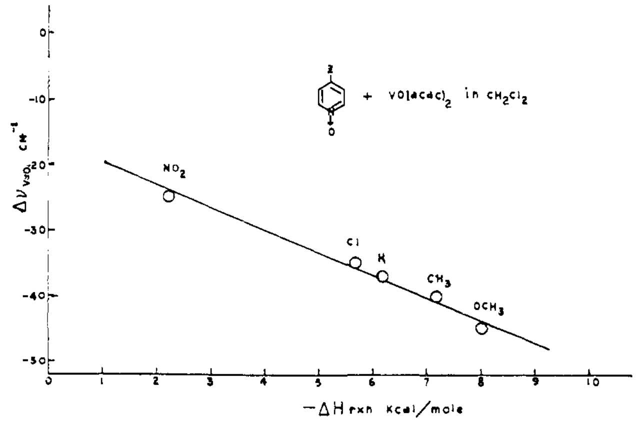

Figure 2. $\Delta\bar{\nu}_{V=O}$ *vs.* $-\Delta H_{rxn}$ for 4-substituted pyridine N-oxides and $VO(acac)_2$ in CH_2Cl_2.

are often a problem and must be considered in choosing a solvent. Dichloromethane has been chosen since it exhibits a small solvation effect coupled with a large base and acid solubility.

The linearity exhibited in Figure 1 is evidence that $VO(acac)_2$ can function as a reference acid if a series of bases having a constant steric interaction is chosen. Since σ_{PyNO} constants are derived from pK_a values where the interaction is with a proton, it is not surprising that steric considerations would be more important with $VO(acac)_2$ which is a large, bulky acid. The plot in Figure 1 shows a good correlation of $-\Delta H$ of reaction and σ_{PyNO} for the 4-substituted pyridine N-oxides. In Figure 2, a linear relationship of $\Delta\bar{\nu}_{V=O}$ and ΔH is found. A trend exists in Figure 3 for ΔH and $\Delta\bar{\nu}_{V=O}$. However, there is no longer a relationship between ΔH or $\Delta\bar{\nu}_{V=O}$ and σ_{PyNO} due to steric interaction of substituents in the 2 and 3 positions of pyridine N-oxide. As can be seen by comparing Figures 2 and 3, correlations are limited to the 4-substituted pyridine N-oxide system. Substitution of a methyl group in the 2 position in pyridine N-oxide causes a large decrease in ΔH. Using a value for σ_{PyNO} of −0.11 calculated from the pK_a of 2-methylpyridine N-oxide and the correlation in Figure 1, a ΔH of −6.6 kcal/mole would be expected. The actual value found was −4.06 ± 0.06 kcal/mole and the difference of 2.5 kcal can be assigned to the steric interaction. A more striking steric effect is seen with 2,6-dimethylpyridine N-oxide whose σ_{PyNO} constant of −0.31 would be expected to give a heat of reaction of −6.3 kcal/mole with $VO(acac)_2$. The experimental value is −0.87 ± 0.02 kcal/mole, which means that 2,6-dimethylpyridine N-oxide is a weaker base, by more than a factor of 8, toward $VO(acac)_2$ than would be expected. Substitution of the first methyl group in an *ortho* position apparently still allows the base to adjust its position enough to allow considerable interaction. When a methyl group is also added to the remaining *ortho* position in 2,6-dimethylpyridine N-oxide, the steric effect is greatly increased. Now the methyl groups impose a

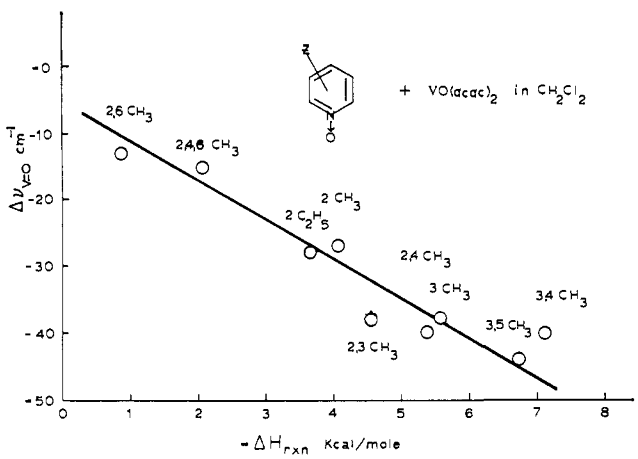

Figure 3. $\Delta\bar{\nu}_{V=O}$ *vs.* $-\Delta H_{rxn}$ for alkyl-substituted pyridine N-oxides and VO(acac)$_2$ in CH$_2$Cl$_2$.

severe steric condition and will not allow a large interaction. The pK_a values are not yet known for any of the other 2-substituted pyridine N-oxides, so comparisons of actual and expected values for ΔH are not possible.

An effect that might not be expected is that 3-substitution in the pyridine N-oxides causes a significant difference in calculated and experimental ΔH values in the interaction with VO(acac)$_2$. Based on the σ_{PyNO} constant for 3-methylpyridine N-oxide and the correlation in Figure 1, ΔH is expected to be about -6.8 kcal/mole. The value found is -5.57 ± 0.17 kcal/mole. The deviation from the expected value is 1.2 kcal which is less than the 2.5-kcal difference found for 2-methylpyridine N-oxide.

It is of interest to examine the results obtained with the tertiary amine oxides *p*-bromo-N,N-dimethylaniline N-oxide and trimethylamine N-oxide. The N-methyl groups interact strongly enough with each other to prevent maximum coordination through the ligands themselves.[24-28] It would seem that these same N-methyl groups might cause steric interaction with VO(acac)$_2$. The experimental ΔH values are -37.6 ± 2.2 kcal/mole for trimethylamine N-oxide and -33.9 ± 1.7 kcal/mole for *p*-bromo-N,N-dimethylaniline N-oxide. The pK_a for trimethylamine N-oxide is 4.65 and that for pyridine N-oxide is 0.79. The ratio of pK_a values is about 5.9 and the ratio for the ΔH values is about 6.1. This agreement of ratios means that trimethylamine N-oxide fits the correlation for the 4-substituted pyridine N-oxides. The pK_a value for *p*-bromo-N,N-dimethylaniline N-oxide is not known, but it should not differ greatly from that of N,N-dimethylaniline N-oxide which has been reported as 3.88, 4.04, and 4.21.[29] Assuming a pK_a value of 4 for *p*-bromo-N,N-dimethylaniline N-oxide and taking the ratio with the pK_a value of pyridine N-oxide, a value of 5.0 is obtained. The ratio of corresponding ΔH values is about 5.5 which is in good agreement with the pK_a ratio. The relationship of basicity and ΔH holds for these tertiary amine oxides with the reference acid VO(acac)$_2$. Apparently the N-methyl groups are able to bend back out of the way, thereby causing little steric interaction.

The two lines in Figure 1 representing the heats of reaction of 4-substituted pyridine N-oxides in chloroform and dichloromethane are seen to be essentially parallel. This parallel behavior indicates that the relative basicity effects in this system are independent of the solvent. However, the 3-kcal difference in the magnitude of the ΔH values shows that there are large solvent effects. The solvent acts in two ways to decrease the heats of reaction. First, the solvent is occupying the sixth coordination site in VO(acac)$_2$ and must be displaced.[3,4] Second, since the bases are dissolved in solvent, the solvation sphere of the base must be disrupted to allow the base to coordinate. The heats of the solution of several of the liquid pyridine N-oxides injected into the solvents neat were measured. The values in Table II show that enthalpy of solution of these bases in dichloromethane is about -1.5 kcal/mole and, within experimental error, the same for the four bases used. In chloroform, the ΔH values vary from -3.6 to -4.5 kcal/mole and follow the trend of increasing basicity. The difference between the two solvents is about 2 kcal which accounts for most of the difference in the two lines in Figure 1. This can easily be explained by the difference in hydrogen-bonding ability of chloroform and dichloromethane. The remaining difference between the two lines can then be attributed to the difference in solvation of VO(acac)$_2$ and VO(acac)$_2$·base.

Table II. Heats of Solution of Selected Pyridine N-Oxides at 25°

Base	$-\Delta H$, kcal/mole In CH$_2$Cl$_2$	In CHCl$_3$
2-Ethylpyridine N-oxide	1.46 ± 0.11	3.63 ± 0.15
2-Methylpyridine N-oxide	1.57 ± 0.04	3.70 ± 0.06
2,4-Dimethylpyridine N-oxide	1.64 ± 0.02	4.01 ± 0.02
2,4,6-Trimethylpyridine N-oxide	1.50 ± 0.04	4.47 ± 0.01

Infrared Studies. The vanadium–2,4-pentanedionate oxygen stretching frequency $\bar{\nu}_{V-O}$ has been shown to decrease in energy upon *trans*-axial coordination.[30] However, no attempts have been made to correlate $\Delta\bar{\nu}_{V-O}$ with basicity. For the 4-substituted pyridine N-oxides, a reasonable correlation of $\Delta\bar{\nu}_{V-O}$ with the ligand basicities is obtained in the the solid state (Table III). It is interesting that $\Delta\bar{\nu}_{V-O}$ correlates better in the solid state than does $\Delta\bar{\nu}_{V=O}$ as can be seen by comparing the data listed in Table III. Evidently, $\bar{\nu}_{V-O}$ is not as sensitive to crystal-packing effects and related phenomena as is $\bar{\nu}_{V=O}$.

The values of $\Delta\bar{\nu}_{V=O}$ for some 4-substituted pyridine N-oxides have previously been shown to correlate with σ_{PyNO}.[20] In this work the 4-substituted pyridine N-oxide series has been restudied and extended to include 4-cyano- and 4-nitropyridine N-oxide. For all the pyridine N-oxides studied, a trend is observed which relates ΔH with $\Delta\bar{\nu}_{V=O}$. Correlations are obtained be-

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Table III. Infrared Data of Substituted Pyridine N-Oxide Adducts of VO(acac)$_2$

Substituent	$\Delta\bar{\nu}_{V=O}$	$\Delta\bar{\nu}_{V-O}$	State
4-CH$_3$O	−48	−41	KBr
	−47	−30	Nujol
	−45	...	CH$_2$Cl$_2$
4-CH$_3$	−34	−39	KBr
	−32	−24	Nujol
	−40	...	CH$_2$Cl$_2$
H	−40	−39	KBr
	−34	−21	Nujol
	−37	...	CH$_2$Cl$_2$
4-Cl	−39	−31	KBr
	−37	−25	Nujol
	−35	...	CH$_2$Cl$_2$
4-Br	−51	−38	KBr
	−43	−26	Nujol
	−38	...	CH$_2$Cl$_2$
4-CO$_2$CH$_3$	−33	...	CH$_2$Cl$_2$
4-CN	−1	−26	KBr
	−1	−21	Nujol
	−27	...	CH$_2$Cl$_2$
4-NO$_2$	−8	−18	KBr
	−7	−5	Nujol
	−25	...	CH$_2$Cl$_2$
2,4,6-(CH$_3$)$_3$	−15	...	CH$_2$Cl$_2$
3-CH$_3$	−38	...	CH$_2$Cl$_2$
2-CH$_3$	−27	...	CH$_2$Cl$_2$
2-C$_2$H$_5$	−28	...	CH$_2$Cl$_2$
2,4-(CH$_3$)$_2$	−40	...	CH$_2$Cl$_2$
2,3-(CH$_3$)$_2$	−38	...	CH$_2$Cl$_2$
3,4-(CH$_3$)$_2$	−40	...	CH$_2$Cl$_2$
3,5-(CH$_3$)$_2$	−44	...	CH$_2$Cl$_2$
2,6-(CH$_3$)$_2$	−13	...	CH$_2$Cl$_2$
4-(CH$_3$)$_2$N	−52	...	CH$_2$Cl$_2$

tween ΔH and $\Delta\bar{\nu}_{V=O}$ for systems possessing similar steric effects, *e.g.*, the 4-substituted pyridine N-oxides (see Figure 2). Also, as shown in Figure 3, ΔH correlates with $\Delta\bar{\nu}_{V=O}$ for systems possessing varying steric effects. Neither $\Delta\bar{\nu}_{V=O}$ nor ΔH correlates with pK_a or σ_{PyNO} when the steric effects vary. For a correlation of $\Delta\bar{\nu}_{V=O}$ and ΔH, an intercept of zero might be expected, *i.e.*, $\Delta\bar{\nu}_{V=O}$ is zero when ΔH is zero. If we use the calculated value of the simple mass effect on $\bar{\nu}_{V=O}$ for a similar system,[6] which is ≈ -6 cm^{-1}, and this value from $\Delta\bar{\nu}_{V=O}$, we obtain essentially this type of correlation.

Conclusions

We have show that the vanadium–vanadyl oxygen and vanadium–2,4-pentanedionate stretching frequencies of VO(acac)$_2$ are sensitive parameters to correlate base strengths when systems possessing constant steric effects are compared. Also, the enthalpies of interaction of the 4-substituted pyridine N-oxides can be used to obtain relative base strengths. From the ΔH values, the steric effects of methyl substitution in the 2 and 3 positions in pyridine N-oxide can be estimated. ΔH values were calculated from $\Delta\bar{\nu}_{V=O}$ values for the 4-substituted pyridine N-oxides which could not be measured calorimetrically. Neither ΔH nor $\Delta\bar{\nu}_{V=O}$ correlates with basicity for all the amine oxides studied as a result of varying steric effects.

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