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Reactions of MCH_3^+ (M = Fe, Co) with Nitrogen-Containing Species in the Gas Phase. Determination of Thermodynamic Properties for $FeCH_2$ and $CoCH_2$

Denley B. Jacobson,[†] James R. Gord,[‡] and Ben S. Freiser*

Herbert C. Brown Laboratory of Chemistry, Purdue University, West Lafayette, Indiana 47907

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The proton affinities of both $FeCH_2$ and $CoCH_2$ are determined to be 222 ± 5 kcal/mol by monitoring the deprotonation of the corresponding MCH_3^+ species by a series of reference bases. These results yield $\Delta H_f(FeCH_2) = 106 \pm 7$ kcal/mol and $\Delta H_f(CoCH_2) = 116 \pm 9$ kcal/mol from which $D^0(Fe–CH_2) = 87 \pm 7$ kcal/mol and $D^0(Co–CH_2) = 79 \pm 9$ kcal/mol can be derived. One source of error in these values is the uncertainty in $D^0(M^+–CH_3)$. For comparison, $D^0(Fe^+–CH_2) = 82 \pm 5$ kcal/mol and $(Co^+–CH_2) = 84 \pm 5$ kcal/mol. In addition to proton transfer, the MCH_3^+ ions also readily abstract a hydride from the amines studied. Several other interesting reactions with these bases are also observed and discussed.

Introduction

The transition metal–ligand bond has been described as being the key to linking organometallic chemistry, surface chemistry, and catalysis.[1] In particular, metal–ligand bond energies are useful in assessing whether a proposed reaction pathway is energetically feasible. To provide such quantitative data, a growing number of mass spectrometric techniques have been developed. As a result, within the last 10 years a respectable body of thermodynamic data has begun to emerge on atomic metal ion–ligand bond strengths, $D^0(M^+–L)$. These values have been obtained mainly from ionization and appearance potential measurements,[2] endothermic reaction thresholds obtained by using ion beam instruments,[3–7] photodissociation onsets measured by using Fourier transform mass spectrometry (FTMS),[8–11] and observation of exothermic reactions which yield bond energy limits.[12–14]

Of equal importance, but not as well studied, are the metal–ligand bond energies of neutral fragments, $D^0(M–L)$. Again, several mass spectrometric techniques have been developed to obtain this information, often by taking advantage of a knowledge of the heats of formation of anions and cations to complete a thermodynamic cycle. For example, Georgiadis and Armentrout[15] recently measured both the neutral and ionic Zn–methyl bond energies by monitoring the endothermic onset energies for reactions 1 and 2, respectively, using the ion-beam technique. In

$$Zn^+ + CH_3R \rightarrow ZnCH_3 + R^+ \qquad (1)$$

$$Zn^+ + CH_3R \rightarrow ZnCH_3^+ + R \qquad (2)$$

addition, observation of exothermic ion–molecule reactions can be used to bracket bond energies. These reactions have mainly involved simple proton transfer, as exemplified by reactions 3 and 4, where AH and B are reference Brønsted

$$M^- + AH \rightarrow MH + A^- \qquad (3)$$

$$VNH^+ + B \rightarrow VN + BH^+ \qquad (4)$$

acids and bases, respectively. A variety of heterolytic and homolytic M–H bond strengths were obtained by monitoring reaction 3,[16] and $D^0(V–N)$ was obtained by monitoring reaction 4 with a prior knowledge of $D^0(V^+–NH)$.[17] Photodetachment experiments have yielded electron affinities and metal–ligand bond energies for neutral metal complexes.[18] Finally, Knudsen cell mass spectrometry has also proven to be a powerful method for obtaining neutral metal–ligand bond energies.[19–21]

The purpose of this study was to determine the metal–carbene bond energies of $FeCH_2$ and $CoCH_2$. These species are of importance due to the role that metal carbenes play as intermediates in a number of important catalytic transformations. In addition, while bond strengths have been determined for $Fe^+–CH_3$,[22] $Co^+–CH_3$,[4] $Fe–CH_3$,[23] $Co–CH_3$,[4] $Fe^+–CH_2$,[9] and $Co^+–CH_2$,[9] no experimental information on the neutral $M–CH_2$ (M = Fe, Co) bond strengths has been obtained. Here, a strategy analogous to that used to determine $D^0(V–N)$ by monitoring reaction 4 is used to obtain information on the MCH_2 species. Specifically, the proton affinity of MCH_2 (M = Fe, Co) was bracketed by monitoring reaction 5 with

$$MCH_3^+ + B \rightarrow MCH_2 + BH^+ \qquad (5)$$

a series of reference bases. Determination of the proton

[†] Current address: Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105.

[‡] National Science Foundation Predoctoral Fellow.

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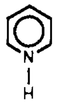
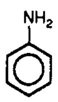
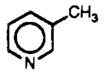
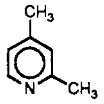
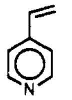
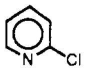
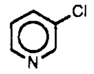
Table I. Distribution of Neutral(s) Lost for the Reactions of MCH_3^+ (M = Fe, Co) with Several Bases[a]

	$FeCH_3^+$		$CoCH_3^+$	
base	neutral(s) lost	distributn, %	neutral(s) lost	distributn, %
NH_3	NR[b]		CH_3	100
$CH_3CH_2CH_2NH_2$	$(FeCH_4)$ CH_4 $CH_4 + H_2$ $CH_4 + NH_3$	58 30 3 9	$(CoCH_4)$ CH_4 $CH_4 + H_2$ $CH_4 + NH_3$	8 4 33 55
$(CH_3CH_2)_2NH$	$(FeCH_4)$ $(FeCH_2)$	82 18	$(CoCH_4)$ $(CoCH_2)$	80 20
$(CH_3CH_2)_3N$	$(FeCH_4)$	100	$(CoCH_4)$	100
$(CH_3)_3N$	$(FeCH_4)$ $(FeCH_2)$	91 9	$(CoCH_4)$ $(CoCH_2)$ CH_4	74 16 10
$NH_2CH_2CH_2NH_2$	$(FeCH_2)$	100	CH_3 $(CoCH_2)$	59 41
	$(FeCH_4)$ $(FeCH_2)$	92 8	$(CoCH_4)$ $(CoCH_2)$ CH_4 $CH_4 + H_2$	31 33 9 27
	$(FeCH_4)$ $(FeCH_2)$	54 46	$(CoCH_4)$ $(CoCH_2)$ CH_3 CH_4 $CH_4 + H_2$ $CH_4 + C_2H_4$	14 26 10 10 31 9
	c CH_3	76 24	CH_3	100
	c CH_3 CH_4	35 53 12	CH_3 CH_4	84 16
	c CH_3 CH_4	45 20 35	CH_3 CH_4	62 38
	c CH_3 CH_4 $(FeCH_2)$	12 9 75 4	CH_3 CH_4 $(CoCH_2)$	20 77 3
	c CH_3 CH_4 $(FeCH_2)$	42 23 24 11	CH_3 CH_4 C_2H_4 $(CoCH_2)$	55 26 11 8
	CH_3 HCl $(FeCH_3Cl)$	29 55 16	CH_3 HCl $(CoCH_3Cl)$	38 46 16
	c CH_3 CH_4	79 11 10	CH_3 CH_4	42 58
	c CH_3 CH_4 (FeH_2)	62 10 4 24	CH_3 CH_4 (CoH_2)	50 42 8

[a] Product distributions are reproducible to ±15%. [b] Denotes no reaction observed. [c] Denotes a condensation of the neutral reactant and the ion with no neutrals eliminated.

affinity of MCH_2, $PA(MCH_2)$, which is the enthalpy of process 6, yields the $M-CH_2$ bond strength since the heats

$$MCH_3^+ \rightarrow MCH_2 + H^+ \qquad \Delta H_{rxn} = PA(MCH_2) \quad (6)$$

of formation of both H^+ and MCH_3^+ (M = Fe, Co) are known. This study was complicated both by the high reactivity of MCH_3^+, which leads to interesting side reactions, and by indirect formation of BH^+ by product ions.

Experimental Section

The theory, instrumentation, and methodology of ion cyclotron resonance (ICR) spectrometry[24,25] and Fourier transform mass spectrometry (FTMS)[26-30] have been discussed elsewhere. All experiments were performed by using a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail[30] and equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. The cell was constructed in our laboratory and includes a $^1/_4$-in. diameter hole in one of the transmitter plates that permits irradiation with various light sources. High-purity foils of the appropriate metals were supported on the opposite transmitter plate. Metal ions are generated by focussing the beam of a Quanta Ray Nd:YAG laser (frequency doubled to 532 nm) onto a metal foil.[31]

Chemicals were obtained commercially in high purity and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases. An uncalibrated Bayard–Alpert ionization gauge was used to monitor pressure. The MCH_3^+ ions were formed by reaction of laser desorbed Fe^+ and Co^+ with methyl iodide[32] (reaction 7). The methyl iodide reagent gas was

$$M^+ + CH_3I \rightarrow MCH_3^+ + I \qquad (7)$$

introduced into the vacuum chamber through a General Valve Corp. Series 9 pulsed solenoid valve.[33] MCD_3^+ was generated in an identical manner using CD_3I. Both the laser and pulsed valve were triggered concurrently. The methyl iodide filled the vacuum chamber to a maximum pressure of $\sim10^{-5}$ Torr and was pumped away by a high speed 6-in. diffusion pump in ~250 ms. The MCH_3^+ ions were then isolated by swept double-resonance ejection pulses[34] and allowed to react with a static pressure ($\sim10^{-7}$ Torr) of a selected base in the absence of complicating reactions with methyl iodide.[35]

The MCH_3^+ ions may be generated with excess internal energy that could lead to spurious values for the proton affinities of MCH_2. In order to minimize this problem, a high pressure ($\sim5 \times 10^{-6}$ Torr) of argon relative to the selected base was maintained throughout these experiments allowing for thermalizing collisions to occur prior to reaction.

Results and Discussion

The reactions of MCH_3^+ (M = Fe, Co) with a series of bases are summarized in Table I and include proton transfer as well as hydride abstraction reactions. In addition a variety of other interesting processes are observed as discussed below.

Proton Affinity of MCH_2. The proton affinities of $FeCH_2$ and $CoCH_2$ were bracketed by monitoring reaction 5 for $FeCH_3^+$ and $CoCH_3^+$ with a series of reference bases. Since the neutral MCH_2 species could not be generated

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Table II. Deprotonation Reaction Data

base	proton affinity,[a] kcal/mol	direct protonation of base obsd
ammonia	204	no[b]
aniline	209.5	no
3-chloropyridine	217.8	no
n-propylamine	217.9	no
pyridine	220.8	no
4-vinylpyridine	223.2	yes
3-methylpyridine	224.1	no
piperazine	224.2	yes
trimethylamine	225.1	yes
diethylamine	225.6	yes
piperidine	226.4	yes
2,4-dimethylpyridine	226.9	yes
triethylamine	232.3	no

[a] All proton affinities taken from: Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *No.* 4, 13. [b] Indicates a rate constant for proton transfer of $<1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

directly, the reverse of reaction 5 could not be monitored, precluding a more exact bracketing of PA(MCH_2). Since exothermic proton transfers are usually rapid and occur with little or no activation barrier, the break between observation of reaction 5 and failure to observe reaction 5 should define PA(MCH_2). However, a reaction that is endothermic by up to about 3 kcal/mol may be observed. As seen in Table II, no proton transfer is observed for bases with PA < 220.8 kcal/mol (pyridine). Proton transfer occurs for all bases with PA > 223.2 kcal/mol (4-vinylpyridine), except for 3-methyl-pyridine (PA = 224.1 kcal/mol) and triethylamine (PA = 232.3 kcal/mol). However, in these two cases alternative reaction pathways compete effectively with proton transfer. In fact for all of the cases in which proton transfer occurs, it accounts for only a minor fraction of the product distribution ranging from a low of 3% to a high of 46% (Table I). The proton affinity of the MCH_2 species is believed to fall between that of pyridine and 4-vinylpyridine and is assigned as 222 ± 5 kcal/mol. The error (±5 kcal/mol) is a conservative estimate assigned due to the uncertainty in the bracketing technique (vide supra).

The MCH_3^+ ions generated in reaction 7 have been shown to exist in a metal–methyl ion structure (I) and not a hydrido–methylidene structure (II).[4,23,36] Therefore, the

$$\underset{\text{I}}{M^+{-}CH_3} \qquad \underset{\text{II}}{H{-}M^+{-}CH_2}$$

proton-transfer reaction formally involves abstraction of an alkyl proton and not a metallic proton, although rearrangement of the proton to the metal ion prior to transfer is clearly possible in the activated complex generated during the transfer process.

The above proton affinities yield $\Delta H_f(FeCH_2)$ = 106 ± 7 kcal/mol and $\Delta H_f(CoCH_2)$ = 116 ± 9 kcal/mol from which $D^0(Fe{-}CH_2)$ = 87 ± 7 kcal/mol and $D^0(Co{-}CH_2)$ = 79 ± 9 kcal/mol can be derived.[37] These values are comparable to $D^0(Fe^+{-}CH_2)$ = 82 ± 5 kcal/mol[9] and $D^0(Co^+{-}CH_2)$ = 84 ± 5 kcal/mol.[9] The above values yield IP($FeCH_2$) = 8.1 ± 0.4 eV and IP($CoCH_2$) = 7.6 ± 0.4 eV,[38] which can be compared with the reported values of IP($FeCH_3$) = 6.78 eV[23] and IP($CoCH_3$) = 7.0 ± 0.3 eV.[5] It should be noted that one source of error for the above thermodynamic quantities lies in the uncertainty of $D^0(M^+{-}CH_3)$.[37]

Process 8 has a calculated ΔH_{rxn} of 65 ± 10 kcal/mol for $FeCH_3$ and 70 ± 13 kcal/mol for $CoCH_3$.[39] These values

$$MCH_3 \rightarrow MCH_2 + H^\bullet \tag{8}$$

lie between $D^0(H_2C{-}H)$ ~ 109 kcal/mol[38] and $D^0(M{-}H)$ ~ 30–55 kcal/mol[16] and are considerably lower than $D^0(FeCH_2^+{-}H)$ = 95 ± 7 kcal/mol and $(CoCH_2^+{-}H)$ = 85 ± 9 kcal/mol. Although $D^0(MCH_2{-}H)$ is greater than typical M–H bond energies, this does not preclude the $H{-}M{-}CH_2$ structure for the neutral species.

Hydride Abstraction. Hydride abstraction (reaction 9) occurs with all of the amines studied except for aniline.

$$MCH_3^+ + (R)_3N \rightarrow (R{-}H)R_2N^+ + (MCH_4) \tag{9}$$

In a previous study, $CoCH_3^+$ was observed to undergo hydride abstraction with aliphatic alkanes larger than ethane, with the exception of 2,2-dimethylpropane.[12] In contrast, hydride abstraction was not observed for $FeCH_3^+$. Considering that it requires less energy to abstract H^- from an amine than an alkane, it is not surprising that reaction 9 is observed, especially for $CoCH_3^+$. In general hydride transfers are fast and reversible and have little or no activation energy.[40] Abstraction of an α-C–H hydride results in formation of an immonium ion which is thermodynamically the most stable product.[41] Hydride abstraction becomes more favorable as both the degree of substitution around the amine and the length of the alkyl chains increase.[42] As seen in Table I, the fraction of hydride abstraction follows this trend. In fact, for triethylamine hydride abstraction occurs exclusively even though it has the highest proton affinity of all the bases studied.

There are only a handful of immonium ions whose heats of formation are known. Thermodynamic calculations for both $(CH_3)_3N$ and $CH_3CH_2CH_2NH_2$ indicate that formation of M and CH_4 as the neutral products in reaction 9 is exothermic.[43] However, formation of stable $CoCH_4$[12] and FeH_2[44] species has recently been proposed; therefore, MCH_4 formation in reaction 9 is possible. Failure to observe hydride abstraction with aniline is due to the absence of an α-C–H bond. Hydride abstraction from a series of amines (except for *tert*-butylamine) by Co^+ has also been observed in the gas phase.[45]

Miscellaneous Reactions. Ammonia is completely unreactive with $FeCH_3^+$, whereas it readily displaces CH_3 from $CoCH_3^+$. These results imply $D^0(Fe^+{-}NH_3) < D^0(Fe^+{-}CH_3)$ = 65 ± 5 kcal/mol[11] and $D^0(Co^+{-}NH_3) > D^0(Co^+{-}CH_3)$ = 57 ± 7 kcal/mol.[11] The completely inert behavior of $FeCH_3^+$ with ammonia is also consistent with PA($FeCH_2$) ≫ PA(NH_3).

Reactions with aniline are simple and involve CH_3 displacement as well as condensation. This is in contrast to

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[36] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 3900.

[37] These calculations used $D^0(Fe^+{-}CH_3)$ = 65 ± 5 kcal/mol and $D^0(Co^+{-}CH_3)$ = 57 ± 7 kcal/mol from ref 11 and heats of formation from ref 38. These values are in reasonable agreement with recent ion-beam results of $D^0(Fe^+{-}CH_3)$ = 58 ± 2 kcal/mol and $D^0(Co^+{-}CH_3)$ = 49 ± 4 kcal/mol from: Armentrout, P. B.; Georgiadis, R. *Polyhedron* **1988**, *7*, 1573.

[38] Auxiliary thermochemistry taken from: Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data Suppl. 1* **1977**, *6*.

[39] These calculations used $\Delta H_f(FeCH_3)$ = 93 ± 7 kcal/mol derived from IP($FeCH_3$) = 6.78 eV (from ref 23) and $D^0(Fe^+{-}CH_3)$ = 65 ± 5 kcal/mol (from ref 11) and $\Delta H_f(CoCH_3)$ = 98 ± 10 derived from IP($CoCH_3$) = 7.0 ± 0.3 eV (from ref 5) and $D^0(Co^+{-}CH_3)$ = 57 ± 7 kcal/mol (from ref 11). See also ref 37.

[40] Meot-Ner, M.; Field, F. H. *J. Chem. Phys.* **1976**, *64*, 277.

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[43] These calculations used $\Delta H_f((CH_3)_2N^+CH_2)$ = 158 ± 2 kcal/mol and $\Delta H_f(CH_3CH_2CH{=}N^+H_2)$ = 152 ± 2 kcal/mol from ref 42.

[44] Halle, L. F.; Klein, F. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2543.

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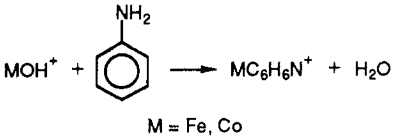
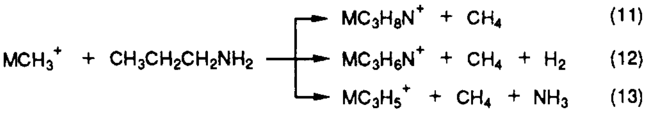
MOH^+ (M = Fe, Co) where dehydration (reaction 10) is dominant.[46]



(10)

Reaction of both piperidine and piperazine with $FeCH_3^+$ involves only proton transfer and hydride abstraction. In addition to these processes, $CoCH_3^+$ also generates dehydrogenation products reminiscent of the reactions of cyclohexane with $CoCH_3^+$.[36] Reaction with piperazine also yields some displacement of CH_3 as well as some cleavage of the piperazine ring with $CoCH_3^+$.

The only aliphatic amine studied that yields unique reactivity with MCH_3^+ is *n*-propylamine. In addition to hydride abstraction, reactions 11–13 are observed. These

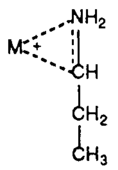


$$MCH_3^+ + CH_3CH_2CH_2NH_2 \rightarrow MC_3H_8N^+ + CH_4 \quad (11)$$

$$\rightarrow MC_3H_6N^+ + CH_4 + H_2 \quad (12)$$

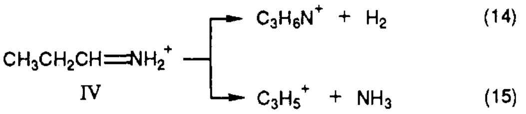
$$\rightarrow MC_3H_5^+ + CH_4 + NH_3 \quad (13)$$

reactions may proceed by initial hydride abstraction followed by elimination of CH_4 forming the immonium ion-metal complex (III). Intermediate III can then decompose



III

by either dehydrogenation or by NH_3 elimination. Further evidence for these processes is that the immonium ion (IV) decomposes predominantly by dehydrogenation and NH_3 elimination (reactions 14 and 15).[41,47]

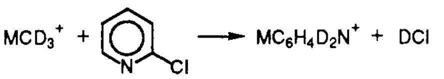


$$CH_3CH_2CH{=}NH_2^+ \rightarrow C_3H_6N^+ + H_2 \quad (14)$$

$$\rightarrow C_3H_5^+ + NH_3 \quad (15)$$

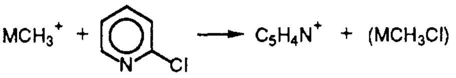
Pyridine and methylpyridines react similarly with the MCH_3^+ ions. These pyridines yield displacement of CH_3 as well as CH_4 elimination. In addition, condensation products are observed with $FeCH_3^+$. 2,4-Dimethylpyridine is the only pyridine studied to undergo proton abstraction (reaction 5).

The three chloropyridines all show varied reactivity toward the MCH_3^+ ions. Elimination of DCl (reaction 16)



(16)

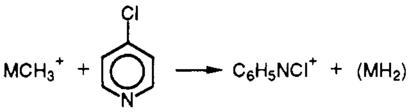
is dominant for 2-chloropyridine. However, this process is completely absent for both 3-chloro- and 4-chloropyridine. This significant geometric effect suggests strong precoordination of the metal ion center to nitrogen. Loss of DCl and not a ring hydrogen precludes the formation of a benzyne-type complex.[48-50] In addition, chloride abstraction also occurs (reaction 17). Formation of M and



(17)

CH_3Cl is calculated to be endothermic by 69 and 61 kcal/mol for $FeCH_3^+$ and $CoCH_3^+$, respectively.[50] This implies formation of a $Cl–M–CH_3$ species in reaction 17.

3-Chloropyridine behaves very similarly to pyridine with MCH_3^+ (Table I). 4-Chloropyridine yields similar products to 3-chloropyridine; however, an additional reaction, (18), is observed. This complex reaction formally involves carbyne abstraction from MCH_3^+.



(18)

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(48) Stable benzyne complexes have been reported for nickel, tantalum, and niobium. See for example: (a) Gowling, E. W.; Kettle, S. F. A.; Sharples, G. M. *Chem. Commun.* **1968**, 21. (b) McLain, S. J.; Schrock, R. R.; Scharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263.

(49) Y^+ dehydrogenates benzene forming $YC_6H_4^+$ in the gas phase, presumably a benzyne complex. Wise, M. B. Ph.D. Thesis, Purdue University, 1984. (In addition, it has recently been demonstrated that Sc^+ dehydrogenates benzene to form the corresponding benzyne complex.)

(50) Dietz, T. G.; Chatellier, D. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1978**, *100*, 4905.

(51) These calculations used $\Delta H_f(2\text{-}C_5H_4N^+)$ = 260 kcal/mol from: ABD El-Kader, F. H.; Allam, S. H.; Shehap, A. H. *Int. J. Mass Spectrom. Ion Processes* **1986**, *69*, 127. ΔH_f(2-chloropyridine) = 25 kcal/mol calculated using group additively values from: Franklin, J. L.; Dillard, J. G.; Rosenstock, H. M.; Herron, J. T.; Draxl, K. *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.* **1969**, *26*.