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ARTICLES

Low-Lying Electronic States and Dissociation Energies of the Monochlorides of Cr, Mn, Fe, Co, and Ni

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Published equilibrium data involving the gaseous monochlorides of Cr, Mn, Fe, Co, and Ni have been re-examined by thermochemical analysis, using more recent information on the low-lying electronic states, yielding $D°_0$ values in kcal mol^{-1} of CrCl (90.0), MnCl (79.8), FeCl (79.3), CoCl (81.3), and NiCl (88.1). Although this revised approach is believed to yield more reliable values of the FeCl, CoCl, and NiCl dissociation energies, results show that use of M$^+$ electronic levels in place of the adopted MCl values leads to alternate $D°_0$(MCl) values agreeing within 1.6 kcal mol^{-1}, providing a useful check on electronic-level contributions to the thermochemical calculations.

Introduction

In an earlier paper,[1] the dissociation energies of some transition metal monochlorides were derived from equilibrium studies of the reaction MCl + Ag = M + AgCl, where M = Cr, Mn, Fe, Co, and Ni, using the accurately known value[2] $D°_0$(AgCl) = 74.4 ± 0.4 kcal mol^{-1} as reference. Equilibrium constants were evaluated from species abundances monitored by molecular-beam mass spectrometry, and reaction enthalpies were derived from thermodynamic analysis. This analysis requires reasonably accurate knowledge of the MCl molecular constant parameters, particularly the energies and configurations of all low-lying electronic states. The latter can be problematical for some of the transition metal species of interest here with their unfilled 3d electron shells that may contribute significant extra energy levels and thermodynamic complexity, especially when these energy levels are uncertain or unknown.

In the earlier publication,[1] the unknown electronic levels were approximated by using those of the corresponding M$^+$ positive ions, which are known accurately from atomic spectra.[3] This approach was suggested earlier by Brewer and colleagues[4,5] and assumes that the electronic partition functions of MCl and MCl$_2$ species are close to those of the M$^+$ and M^{++} ions. Recently, new low-lying states of NiCl have been identified experimentally,[6] and high-level theoretical calculations[7] have begun to supply pertinent information about some of the low-lying states of related MCl species. It is now possible to fill some of the gaps in our knowledge and to check the accuracy of the M$^+$ level approximation. In a closely related issue, Ram, Bernath, and Davis[8] have called attention to the remarkable correspondence between the electronic states of transition metal monohydrides and monohalides and in particular to the correlation between the low-lying states of CoF, CoH and Co$^+$. A more recent study[9] shows in addition that the known states of CoCl correlate well with those of CoF and CoH. All of this information has been used here to re-evaluate the electronic levels, thermodynamic functions, and dissociation energies of the monochlorides of Cr, Mn, Fe, Co, and Ni.

Equilibrium Data

The experimental equilibrium data for the gaseous reaction

$$\mathrm{Ag + MCl = AgCl + M} \qquad (1)$$

where M = Cr, Mn, Fe, Co, and Ni are given in the 1995 publication,[1] and are fully described therein. Measurements were made by molecular-beam mass spectrometry at effusion cell temperatures of about 1300 to 1600 K, and equilibrium constants, K, were evaluated from the parent ion analogs, which are estimated to be accurate within a factor of 1.5. Reaction enthalpies were then derived from the relation $\Delta H°_{298} = T(\Delta \mathrm{gef}_{298-} - R \ln \mathrm{K})$, where gef$_{298}$ is the Gibbs energy function, the thermodynamic quantity $-(G°_T - H°_{298})/T$ that can be evaluated for each gaseous species from spectroscopic and molecular constant data, including the properties of the relevant electronic states; this is the so-called Third-law method of deriving reaction enthalpies from equilibrium data.

More accurate rotational and vibrational constants are now available for all the MCl species, and the earlier values[1] have been upgraded, although the effects on derived reaction enthalpies and dissociation energies are relatively small; Table 1 lists the adopted values of the molecular constants for the MCl species treated here in terms of the internuclear distance, r_e, the moment of inertia, I, the vibrational frequency, ω_e, the ground state, X, and the energy, T_e, and degeneracy, g, of the electronic state.

Selection of Data on Low-Lying Electronic States

CrCl and MnCl have multiplet ground states, but no other electronic states below 8000 cm^{-1}. Likewise the ions Cr$^+$ and Mn$^+$ have no states below 9500 cm^{-1}, so there are no unknown levels to consider in the thermochemical analysis of the

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TABLE 1: Selected Molecular Constants of MCl Species[a]

	CrCl	MnCl	FeCl	CoCl	NiCl
r_e	2.197	2.236	2.175	2.065	2.045
$I \times 10^{39}$	16.8	17.8	16.9	15.5	15.1
ω_e	390	386	402	400	426
X	$^6\Sigma$	$^7\Sigma$	$^6\Delta$	$^3\Phi$	$^2\Pi$
ref	21, 22	23	24	25	26
low-lying electronic states			6, 1211	3, 1129	4,158
(g, T_e)			12, 2515	6, 1452	4, 386
				6, 3710	4, 1646
			8, 664[b]	10, 4597	2, 1768
			12, 2270	5, 5323	
			12, 3460		

[a] r_e in angstroms, I in g cm^2, ω_e, T_e in cm^{-1}. [b]Alternate levels from FeH.

TABLE 2: Summary of Thermochemical Data and Dissociation Energies

	CrCl	MnCl	FeCl	CoCl	NiCl
Electronic state contribution to gef at 1500 K, cal/mol·K					
MCl states	3.6	3.9	5.8	4.3	5.0
M^+ states	3.6	3.9	6.5	5.2	3.8
Third Law $\Delta H^\circ_{298}(1)$, kcal mol^{-1}					
MCl states	15.6	5.4	5.1, 4.5[a]	6.9	13.6
M^+ states	15.6	5.4	3.5	5.6	15.2
D°_0, kcal mol^{-1}					
MCl states	90.0	79.8	79.3, 78.7*	81.3	88.1
M^+ states	90.0	79.8	77.7	80.0	89.7
M^+,1995, ±1.6	89.7	80.2	78.1	80.0	89.2
Bach et.al (1996)			81.6		
Bauschlicher (1996)			86.0		89.2
IVTAN2005	86.0	93.2	81.6	83.6	88.9

[a] From Δgef calculated with FeH low-lying states.

equilibrium data for these two species. At experimental temperatures up to 1600 K, electronic states above 5000 cm^{-1} have a negligible effect on the thermochemical analysis.

Ram et al.[9] have recently identified the $C^3\Delta$ state of CoCl lying at about 2500 cm^{-1} above ground, noting again the correlation of CoCl states with those of CoF and CoH; this supplements earlier work[8] showing the strong correspondence between the low-lying states of CoF, CoH, and Co^+. In the absence of other reported results on CoCl low-lying states, it seems reasonable to adopt as a substitute the calculated results of Freindorf et al.[10] on CoH which yielded five states, at 1129, 1452, 3710, 4597, and 5323 cm^{-1}.

For FeCl, the theoretical calculations of Delaval and Schamps[11] indicate two states at 1211 and 2236 cm^{-1}. These states have not been observed experimentally, but are adopted here. As a cross-check, one is tempted to assume that the low-lying states of FeCl correlate closely with those of FeH, just as in the foregoing, although there is no supporting evidence one way or the other. Nevertheless, the ab initio calculations of Sodupe et al.[12] show three low-lying states for FeH at 664, 2270, and 3460 cm^{-1} above ground, and these are adopted as an alternate set of levels for verification purposes.

In contrast to the foregoing, Rice et al.[6] summarize the rather complete spectroscopic observations on NiCl leading to the identification of four states at 158, 386, 1646, and 1768 cm^{-1}; these are based largely on the spectroscopic studies of Pinchemel, Bernath and co-workers[13,14] plus their own work.[6] In addition, Zou and Liu[7] report the results of theoretical studies that are in good accord.

The electronic energy levels listed here have been adopted for use in the thermochemical analysis; these values (T_e) and their degeneracies (g) are summarized in Table 1. Note that the desired D°_0 values are related to the ΔH°_{298} values by the relation $D^\circ_{298}(\mathrm{MCl}) = D^\circ_{298}(\mathrm{AgCl}) + \Delta H^\circ_{298}(\mathrm{MCl})$, and $D^\circ_0(\mathrm{MCl}) = D^\circ_{298}(\mathrm{MCl}) - (D^\circ_{298} - D^\circ_0)_{\mathrm{MCl},}$ where the latter quantity can be readily evaluated from the thermodynamic functions of MCl.

Results and Discussion

Table 2 gives the $\Delta H^\circ_{298}(1)$ values derived from the reaction equilibrium constants and Δgef functions of each MCl species, together with the resulting D°_0(MCl) value for each species, for both the adopted molecular electronic states and the M^+ electronic states for comparison. All calculations are based on a standard state of one atmosphere pressure. Also compared in the table are the two different electronic state contributions to gef for FeCl, CoCl, and NiCl. The estimated uncertainty in the derived ΔH°_{298} and D°_0 is ±1.3 kcal mol^{-1} and based primarily on the uncertainty of 1.5 in K. As seen in Table 2, the two different electronic state assignments for FeCl, CoCl, and NiCl lead to D°_0 values agreeing approximately within the uncertainty in D°_0. Clearly, the M^+ electronic states are seen to be satisfactory substitutes for the MCl states, within the stated limits of error. For other transition metal monohalides, it seems reasonable to conclude that the calculated states of the metal monohydrides, which should be more straightforward than the halides and may be more readily available, will be satisfactory substitutes in thermochemical calculations of the type described here. In any event, we conclude that the thermochemical dissociation energies, derived from the adopted MCl electronic state data, $D^\circ_0(\mathrm{CrCl}) = 90.0$, $D^\circ_0(\mathrm{MnCl}) = 79.8$, $D^\circ_0(\mathrm{FeCl}) = 79.3$, $D^\circ_0(\mathrm{CoCl}) = 81.3$, and $D^\circ_0(\mathrm{NiCl}) = 88.1$ kcal mol^{-1}, all ±1.3 kcal mol^{-1} are the presently most reliable values. It can also be seen that the original thermochemical values of D°_0 from the 1995 paper[1] are in accord with the new values reported here, within the stated error limits.

In Table 2, the new D°_0 values derived from this work are compared with the more recent theoretical values of Bach. et al.[15] on FeCl, and Bauschlicher[16] on FeCl and NiCl, and with values from the IVTANTHERMO 2005 Database.[17] Earlier, less-accurate values obtained by flame photometry and transport techniques are excluded but are listed in the 1995 paper.[1] Our present value for FeCl is 2.3 kcal mol^{-1} lower than the MP2 value of Bach et al.[15] (no uncertainty given), which is considered to be satisfactory agreement. However, this same value for FeCl is 6.7 kcal mol^{-1} lower than the CCSD(T) value reported by Bauschlicher,[16] (stated accuracy of 3.2 kcal mol^{-1}), while his value for NiCl is within 1.1 kcal mol^{-1} of our value. Because few accurate theoretical values for third row transition metal halides have been reported, we feel that the CCSD(T) $D°_0$(FeCl) value[16] may be less accurate than stated, and further study is needed. As it stands, we see no reason to doubt our value $D°_0$(FeCl) $= 79.3 \pm 1.3$ kcal mol^{-1}. Regarding the IVTANTHERMO 2005 Database[17] values, with the exception of MnCl they more or less agree with the $D°_0$ values reported here, but the IVTANTHERMO data sources are not reported, making it difficult to reconcile differences.

It is interesting to note that our $D°_0$ values, in going from CrCl to NiCl, first decrease then rise more or less symmetrically. We have also measured $D°_0$ values of the first row transition metal monochlorides TiCl,[18] VCl,[19] CuCl,[2] and ZnCl[20] by the same mass spectrometric technique, and these values lead to the progression TiCl (95.9), VCl (103.0), CrCl (90.0), MnCl (79.8), FeCl (79.3), CoCl (81.3), NiCl(88.1), CuCl (89.6), and ZnCl (54.7) across the series, all in kcal mol^{-1}. These variations in $D°_0$, which accompany the filling of the metal 3d shell, result from variable promotion energies required to bring the metal atom species to suitable states for bonding with the Cl ligand. On reaching the Zn atom, where the 3d shell is complete, the M−Cl bond strength drops by 40 ± 10 kcal mol^{-1} because of the extra promotion energy required to reach the Zn 4p and 5s bonding states.

It is worth noting that, among the five monochlorides studied here, only for NiCl do the energies, T_e, and the degeneracies, g, of the low-lying electronic states have a significant effect on the derived thermochemical values of $D°_0$. Neglecting the upper state data at experimental temperatures near 1500 K leads to errors of 0.6, 1.2, and 3.3 kcal mol^{-1} in the derived $D°_0$ values of FeCl, CoCl, and NiCl, respectively. At 1500 K and below, electronic levels at 1000 cm^{-1} and higher will make only minor contributions to the thermodynamic functions and calculated third-law enthalpies. By far, the major effect of the electronic term in the thermochemical calculations reported here comes from the ground state configurations, all of which are significant but are well established. In addition, it is encouraging that substitution of the accurately known M^+ energy levels for the desired MCl molecular energy levels yields thermochemical $D°_0$ values of acceptable accuracy. The latter is in line with the strong correlation observed by Ram et al.[4] for the electronic states of CoF, CoH, and Co^+, thereby providing a useful check on electronic-level contributions to the thermochemical calculations. And finally, the substitution of transition metal monohydride level data, which are more susceptible to accurate theoretical calculations, for missing metal monohalide values provides a valuable tool for deriving accurate third law dissociation energies from equilibrium data.

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