Thermochemistry of the Gaseous Vanadium Chlorides VCl, VCl_2, VCl_3, and VCl_4

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Gaseous equilibria in the V−Ag−Cl system were studied at elevated temperatures by effusion-beam mass spectrometry, where the pertinent species were generated by reaction of $Cl_2(g)$ with V + Ag granules in the effusion cell source. Reaction enthalpies were derived from the equilibrium data, and the standard enthalpies of formation at 298 K of gaseous VCl, VCl_2, and VCl_3 were found to be +49.7, −34.8, and −85.6 kcal mol^{-1}, respectively. The corresponding bond dissociation energies at 298 K are D(V−Cl) = 102.9 kcal, D(ClV−Cl) = 113.5 kcal, D(Cl_2V−Cl) = 79.8 kcal, and D(Cl_3V−Cl) = 69.5 kcal. From these data, the dissociation energy $D°_0$(VCl) = 101.9 kcal mol^{-1} or 4.42 eV is obtained. An alternate value, $\Delta_f H°_{298}(VCl_3,g) = -87.0$ kcal mol^{-1} was derived from third-law analysis of literature sublimation data for VCl_3(s). In addition, literature thermochemical data on VCl_4(g) were re-evaluated, leading to $\Delta_f H°_{298} = -126.1$ kcal mol^{-1}. The results are compared with various estimates in the literature.

Introduction

In the gaseous V−Cl system, only the tetrachloride VCl_4 has been characterized in terms of thermochemical and spectroscopic properties,[1,2] although there is some uncertainty about distortion of the tetrahedral structure because of vibronic interactions. Thermochemical data have been reported[3] for gaseous VCl_2, based on effusion studies of the sublimation of VCl_2(s). However, subsequent mass spectrometric studies[4] showed that the dichloride sublimes by decomposition to VCl_3(g) and V(s), so that the earlier results,[3] interpreted in terms of congruent sublimation of VCl_2, are invalid. An approximate enthalpy of formation ($\Delta_f H°_{298}$) was reported[5] for gaseous VCl_3 from electron impact threshold measurements of fragmentation processes in $VOCl_3$, along with estimates of $\Delta_f H°_{298}$ for VCl and VCl_2. More recently, two different theoretical approaches[6,7] have yielded values of the dissociation energy of VCl_2, differing by about 12 kcal mol^{-1}.

We report here a systematic study of the thermochemistry of the gaseous V−Cl system by means of equilibrium measurements involving species in the V−Ag−Cl system, by using mass spectrometric monitoring. The thermochemistry of VCl_4(g) was also reviewed. Thermochemical information of this type is useful in a number of applications, including the chemical equilibrium modeling of vapor deposition processes in which the lower-valent metal chlorides are the principal carriers from which the metals are deposited.

Experimental Section

All measurements were made with the 60° magnetic sector, 30.5 cm radius mass spectrometer system equipped with a high-temperature effusion-beam vapor source.[8,9] The effusive source was a cylindrical effusion cell with 0.15 cm diameter orifice and gas inlet tube in the base, each section fabricated from high-density graphite.[10] Chemical species to be studied were generated by admission of $Cl_2(g)$ to the base of the heated cell containing granules of V and Ag, and the Cl_2 flow was controlled with a precision leak valve. Upper and lower sections of the cell were separated by a thin W partition with 0.03 cm diam holes around the periphery to enhance internal collisions. The Ag granules were added to provide the AgCl bond strength as an established thermochemical reference value.[11] Heating was provided by a spiral tantalum resistance element surrounding the cell, with the whole contained within a set of tungsten radiation shields. Cell temperature was measured by optical pyrometry, sighting on a blackbody cavity in the cell lid, by using a standard lamp for calibration. Species in the effusion beam were ionized by electron impact, drawn out, accelerated, mass analyzed in the magnetic field, and detected with a particle multiplier. Neutral precursors in the beam were identified from the masses, isotopic patterns, and threshold appearance energies (AE) of the observed ion signals. Threshold AEs were evaluated by the vanishing current method, by using the established ionization energy (IE) of AgCl at 10.08 ± 0.01 eV as reference.[12] Measured ion species were checked for their effusion cell origin by means of the characteristic beam profiles obtained by translation of the neutral beam-defining slit. All other aspects of the experimental procedure and data interpretation are as described in previous publications.[8−10] The V and Ag granules and the cylinder Cl_2 sample were of reagent grade quality.

Results

With $Cl_2(g)$ admitted to the cell at about 1000 K, ion signals with the indicated threshold AEs in eV were observed: Ag^+(7.5), $AgCl^+$(10.0), VCl^+(11.0), VCl_2^+(9.0), VCl_3^+(9.0), and VCl_4^+(9.3), all ±0.3 eV. All signals had the characteristic neutral beam profiles of effusion cell species. For all signals except VCl^+, these AEs remained unchanged as the cell was heated into the range 1400−1600 K. At these higher temperatures, the AE of VCl^+ dropped to 7.5 eV, signifying the appearance of a new species, clearly neutral VCl, with an IE approaching that of atomic V at 6.74 eV. The ionizing orbital in VCl is expected to have a high degree of vanadium character, but as successive Cl atoms are added, the IEs will rise as the degree of Cl character increases. Thus, the VCl^+ threshold of 11.0 eV observed at 1000 K is most likely associated with fragmentation of VCl_2. Our AE for VCl_4^+ is in accord with the

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TABLE 1: Equilibrium Data and Third-Law Enthalpies for the Gaseous Reaction $VCl_2 + VCl_4 = 2VCl_3$

T (K)	$K_1 \times 10^{-3}$	Δgef_{298} (cal deg^{-1} mol^{-1})	$\Delta H°_{298}$ (kcal mol^{-1})
1027	1.39	4.66	−9.9
1027	1.44	4.66	−10.1
1027	1.47	4.66	−10.1
1027	1.58	4.66	−10.2
1027	1.58	4.66	−10.2
1056	1.23	4.65	−10.0
1133	1.07	4.64	−10.4
1133	1.09	4.64	−10.5
1133	1.29	4.64	−10.9
1133	0.924	4.64	−10.1
1133	0.998	4.64	−10.3
			−10.3[a]
			−6.9 ± 2.2[b]

[a] Average. [b] Second law.

TABLE 2: Equilibrium Data and Third-Law Enthalpies for the Gaseous Reaction $Ag + VCl_3 = AgCl + VCl_2$

T (K)	K_2	Δgef_{298} (cal deg^{-1}mol^{-1})	$\Delta H°_{298}$ (kcal mol^{-1})
1089	1.91	5.43	4.5
1089	1.80	5.43	4.6
1089	1.70	5.43	4.8
1133	1.73	5.42	4.9
1133	1.85	5.42	4.8
1133	1.69	5.42	4.9
1133	1.76	5.42	4.9
1133	1.81	5.42	4.8
1133	1.64	5.42	5.0
1501	3.67	5.30	4.1
1564	3.59	5.29	4.3
1564	3.69	5.29	4.2
1604	3.33	5.28	4.6
1604	3.34	5.28	4.6
1643	3.05	5.27	5.0
1643	3.13	5.27	4.9
			4.7[a]
			6.0 ± 0.7[b]

[a] Average. [b] Second law.

TABLE 3: Equilibrium Data and Third-Law Enthalpies for the Gaseous Reaction $Ag + VCl_2 = AgCl + VCl$

T (K)	$K_3 \times 10^4$	Δgef_{298} (cal deg^{-1}mol^{-1})	$\Delta H°_{298}$ (kcal mol^{-1})
1643	3.77	7.58	38.2
1643	3.78	7.58	38.2
1684	5.33	7.53	37.9
1740	5.74	7.46	38.8
1740	5.90	7.46	38.7
			38.4[a]
			41.9 ± 7.4[b]

[a] Average. [b] Second law.

TABLE 4: Third-Law Analysis of the Sublimation Process $VCl_3(s) = VCl_3(g)$

T (K)	P(VCl_3) × 10^7[a] (atm)	Δgef_{298} (cal deg^{-1}mol^{-1})	$\Delta H°_{298}(4)$ (kcal mol^{-1})
648	1.72	48.67	51.6
655	2.57	48.64	51.6
659	3.05	48.63	51.7
674	6.61	48.58	51.8
682	9.74	48.55	51.9
696	18.4	48.50	52.0
707	33.0	48.47	52.0
719	53.6	48.43	52.2
742	135.5	48.36	52.4
			51.9[b]

[a] From data of McCarley and Roddy.[3] [b] Average.

vertical IE of 9.41 ± 0.04 eV reported for VCl_4 by Cox et al.[13] from photoelectron spectroscopy. For VCl, VCl_2, and VCl_3, Flesch and Svec[5] reported approximate IEs of 8.1, 10.7, and 10.6 eV, respectively, from threshold energies of electron-impact fragmentation processes in $VOCl_3$, but these are subject to error from unknown excess energy carried away by the fragments. Although it is highly unlikely that VCl_2 and VCl_3 could have higher IEs than VCl_4, their results[5] do indicate that the di- and trichlorides do have nearly equal IEs, as observed in the work reported here.

We conclude that all of the V−Ag−Cl ion species are parent ions in their lowest threshold regions. Accordingly, we studied the gaseous isomolecular reaction equilibria in the indicated temperature ranges.

$$VCl_2 + VCl_4 = 2\,VCl_3 \qquad 1027-1133\text{ K} \qquad (1)$$

$$Ag + VCl_3 = AgCl + VCl_2 \qquad 1089-1643\text{ K} \qquad (2)$$

$$Ag + VCl_2 = AgCl + VCl \qquad 1643-1740\text{ K} \qquad (3)$$

Equilibrium constants, K, were evaluated from the ion current analogues of the species partial pressures by using ion intensities measured at ionizing energies of AE + 3 eV to avoid ion fragmentation contributions. Only corrections for isotopic distribution were applied to these K values, which are estimated to be accurate well within a factor of 2. When, at constant temperature, the VCl_2 and VCl_3 signals were varied by a factor of 10 by decreasing the Cl_2 flow, the resulting K values were unchanged, indicating that chemical equilibrium was attained in the cell. An indication of the equilibrium species distributions is given by the following uncorrected intensities, all measured at AE + 3 eV: at 1027 K, $VCl_2^+/VCl_3^+/VCl_4^+ = 2.1/113/5.1$; at 1501 K, $Ag^+/AgCl^+/VCl_2^+/VCl_3^+ = 1.53/0.45/225/11.3$; and at 1684 K, $Ag^+/AgCl^+/VCl^+/VCl_2^+ = 4.05/0.50/0.65/102$.

In Tables 1, 2, and 3 are shown the measured equilibrium data and the adopted changes in Gibbs energy function, Δgef_{298}, for the above three reactions, together with the derived third-law enthalpy changes. Gef_{298} is the thermodynamic quantity $-(G°_T - H°_{298})/T$ which can be evaluated for each gaseous species from spectroscopic and molecular constant data and with which the third-law enthalpies of reaction can be derived from the relation $\Delta H°_{298} = T(\Delta gef_{298} - R \ln K)$, where R is the gas constant. The sources of data used in evaluating gef values for the individual species are described in the Appendix. Note that the thermal functions used here are based on the ideal gas state at one atmosphere pressure. The resulting third-law enthalpies are $\Delta H°_{298}(1) = -10.3$ kcal mol^{-1}, $\Delta H°_{298}(2) = 4.7$ kcal mol^{-1}, and $\Delta H°_{298}(3) = 38.4$ kcal mol^{-1}, all with estimated uncertainties of ±2 kcal mol^{-1} due to potential errors in K and Δgef_{298}. However, the second-law values, evaluated from the temperature dependence of K and corrected to 298 K, are in good agreement with the third-law values, providing strong support for the estimated molecular constants of VCl_2 and VCl_3. The stated second-law uncertainties are twice the standard deviations of the least-squares fitting.

These three independent thermochemical equations, with their known $\Delta H°_{298}$ values, can be solved for the $\Delta_f H°_{298}$ values of the three unknowns, the gaseous vanadium mono-, di-, and trichlorides, yielding the results $\Delta_f H°_{298}(VCl) = +49.7 \pm 2$ kcal mol^{-1}, $\Delta_f H°_{298}(VCl_2) = -34.8 \pm 2$ kcal mol^{-1}, and $\Delta_f H°_{298}(VCl_3) = -85.6 \pm 2$ kcal mol^{-1}. Auxiliary thermochemical data for Ag and AgCl were taken from sources

TABLE 5: Comparison of New $\Delta_f H°_{298}$ Values with Literature Data

method and ref	$\Delta_f H°_{298}$ (kcal mol^{-1}) VCl(g)	VCl$_2$(g)	VCl$_3$(g)
estimate[5]	+48 ± 12		
review/compilation[18]		−44.9 ± 10	−87.3 ± 2
VCl$_2$ sublimation[3,5]		−58	
theory (DFT)[6]		−38	
theory (MRCI)[7]		−50	
VOCl$_3$ EI fragmentation[5]			−85 ± 12
third-law VCl$_3$ sub, this work			−87.0 ± 2
MS equilibrium, this work	+49.7 ± 2	−34.8 ± 2	−85.6 ± 2

TABLE 6: Comparison of Ti−Cl and V−Cl Bond Dissociation Energies at 298 K

bond	Ti−Cl (kcal mol^{-1})	ΔE^a (kcal mol^{-1})	V−Cl (kcal mol^{-1})	ΔE^a (eV)
M−Cl	97	19	102.9	6
ClM−Cl	121	0.0	113.5	7
Cl$_2$M−Cl	101	23	79.8	32
Cl$_3$M−Cl	93	(230) ?	69.5	32

[a] Approximate energy of first M atom and MCl$_n$ bonding states above ground, as taken from M positive ion energy levels.

TABLE 7: Molecular Constants of V−Cl and AgCl Species Used in Calculating Thermal Functions

species	I or $I_xI_yI_z$	σ	ω (cm^{-1})
VCl	16.9×10^{-39} g cm^2	1	410
VCl$_2$	57.1×10^{-39} g cm^2	2	310, 110(2), 480
VCl$_3$	1.19×10^{-112} g^3 cm^6	6	330, 100, 500(2), 125(2)
VCl$_4$	3.70×10^{-112} g^3 cm^6	12	487(3), 383, 129(3), 105(2)
AgCl	22.8×10^{-39}	1	341

VCl (g, ε)[a] 10, 0; 10, 517; 5, 1587; 10, 3141; 5, 4097; 3, 6169; 6, 6418; 6, 7362
VCl$_2$ (g, ε)[a] 4, 0; 8, 887; 8, 3387; 8, 3630
VCl$_3$ (g, ε)[a] 3, 0; 3, 700; 3, 1500; 3, 4000
VCl$_4$ (g, ε)[a] 4, 0

[a] ε in cm^{-1}.

TABLE 8: Second (II)- and Third (III)-Law Enthalpies of the Reaction VCl$_4$(l) = VCl$_4$(g) from Vapor Pressure Determinations[a]

ref	data points	range	$\Delta H°_{298}$(II) (kcal mol^{-1})	$\Delta H°_{298}$(III) (kcal mol^{-1})
15	equation	313−353 K	9.5	10.0
16	8	303−426 K	9.9	10.0
17	10	385−428 K	10.5	10.0
			10.0 ± 0.5[b]	10.0 ± 0.3[b]

[a] Boiling point method. Δgef$_{298}$(300 K) = 24.10 cal deg^{-1} mol^{-1};Δgef$_{298}$(400 K) = 23.64 cal deg^{-1} mol^{-1}; Δgef$_{298}$ values estimated as described in text. $\Delta_f H°_{298}$(VCl$_4$, g) = −136.1 + 10.0 = −126.1 ± 0.4 kcal mol^{-1}. [b] Average.

TABLE 9: Ideal Gas Thermodynamic Functions of VCl, $\Delta_f H°_{298}$= +49.7 kcal mol^{-1}

T (K)	$-(G° - H°_{298})/T$ (cal deg^{-1}mol^{-1})	$S°_T$ (cal deg^{-1}mol^{-1})	$H°_T - H°_{298}$ (kcal mol^1)	C_p (cal deg^{-1}mol^{-1})
298	61.48	61.48	0.00	9.30
300	61.48	61.54	0.02	9.31
400	61.85	64.25	0.96	9.51
500	62.55	66.38	1.91	9.55
600	63.34	68.12	2.87	9.57
700	64.13	69.60	3.83	9.59
800	64.89	70.88	4.79	9.62
900	65.62	72.02	5.75	9.66
1000	66.32	73.04	6.72	9.70
1100	66.97	73.96	7.69	9.74
1200	67.59	74.81	8.67	9.79
1300	68.17	75.60	9.83	9.65
1400	68.73	76.33	10.63	9.87
1500	69.26	77.01	11.62	9.91
1600	69.76	77.65	12.62	9.95
1700	70.25	78.26	13.61	9.99
1800	70.71	78.83	14.62	10.03
1900	71.15	79.37	15.62	10.07
2000	71.57	79.89	16.63	10.11

TABLE 10: Ideal Gas Thermodynamic Functions of VCl$_2$, $\Delta_f H°_{298}$= −34.8 kcal mol^{-1}

T (K)	$-(G° - H°_{298})/T$ (cal deg^{-1}mol^{-1})	$S°_T$ (cal deg^{-1}mol^{-1})	$H°_T - H°_{298}$ (kcal mol^1)	C_p (cal deg^{-1}mol^{-1})
298	69.15	69.15	0.00	14.74
300	69.15	69.24	0.03	14.76
400	69.74	73.63	1.55	15.66
500	70.89	77.17	3.14	15.99
600	72.18	80.09	4.74	16.08
700	73.50	82.57	6.35	16.09
800	74.77	84.72	7.96	16.11
900	75.98	86.62	9.57	16.14
1000	77.13	88.32	11.19	16.19
1100	78.22	89.87	12.81	16.24
1200	79.25	91.28	14.44	16.28
1300	80.23	92.59	16.07	16.30
1400	81.15	93.79	17.70	16.32
1500	82.03	94.92	19.33	16.32
1600	82.87	95.97	20.96	16.30
1700	83.67	96.96	22.59	16.28
1800	84.44	97.89	24.22	16.25
1900	85.17	98.77	25.84	16.21
2000	85.87	99.60	27.46	16.16

described in the Appendix, and the data for VCl$_4$ are described below. From the established[11] dissociation energy $D°_{298}$(AgCl) = 75.1 ± 0.4 kcal mol^{-1}, the atomization energy of VCl$_4$ (365.7 kcal mol^{-1}, see below), and the three derived reaction enthalpies above, one can readily evaluate the individual bond dissociation energies (BDE) at 298 K in kcal mol^{-1}, D(V−Cl) =102.9, D(ClV−Cl) = 113.5, D(Cl$_2$V−Cl) = 79.8, and D(Cl$_3$V−Cl) = 69.5. For VCl, the derived $\Delta_f H°_{298}$ of +49.7 kcal mol^{-1} is equivalent to the dissociation energy $D°_0$(VCl) = 101.9 kcal mol^{-1} = 4.42 eV.

In addition to the work on VCl$_2$(s), McCarley and Roddy[3] also studied the vaporization/sublimation of VCl$_3$(s), where they found decomposition to VCl$_2$(s) + VCl$_4$(g) occurring along with congruent sublimation to VCl$_3$(g). They[3] monitored the two processes separately and reported VCl$_3$ sublimation pressures over the range 648−42 K. By using the gef$_{298}$ values for VCl$_3$ solid and gas, as described in the Appendix, we did a third-law analysis of the sublimation process

$$\mathrm{VCl_3(s) = VCl_3(g)} \tag{4}$$

with the results shown in Table 4. The small drift in third-law enthalpies with temperature indicates a likely temperature-dependent error in the sublimation pressure measurements, a not-uncommon situation, something that has a large effect on the second-law slope enthalpy but not on the third-law value. The agreement between second- and third-law enthalpies for reactions 1 and 2 provides strong support for the VCl$_3$ thermal functions, leading us to adopt the third-law sublimation enthalpy $\Delta H°_{298}(4)$ = 51.9 ± 2 kcal mol^{-1}. When combined with $\Delta_f H°_{298}$(VCl$_3$, s) = −138.9 kcal mol^{-1} from the analysis of Pancratz,[14] these results yield $\Delta_f H°_{298}$(VCl$_3$,g) = −87.0 ± 2 kcal mol^{-1}, in good accord with our new value of −85.6 kcal

TABLE 11: Ideal Gas Thermodynamic Functions of VCl_3, $\Delta_fH^\circ_{298}$= −85.6 kcal mol^{-1}

T (K)	$-(G^\circ - H^\circ_{298})/T$ (cal deg^{-1}mol^{-1})	S°_T (cal deg^{-1}mol^{-1})	$H^\circ_T - H^\circ_{298}$ (kcal mol^1)	C_p (cal deg^{-1}mol^{-1})
298	80.90	80.90	0.00	18.66
300	80.90	81.01	0.03	18.69
400	81.65	86.55	1.96	19.74
500	83.09	91.02	3.97	20.26
600	84.73	94.74	6.01	20.51
700	86.39	97.91	8.06	20.62
800	88.01	100.67	10.13	20.65
900	89.55	103.10	12.19	20.66
1000	91.02	105.27	14.26	20.65
1100	92.40	107.24	16.32	20.63
1200	93.72	109.04	18.38	20.62
1300	94.96	110.68	20.44	20.60
1400	96.14	112.21	22.50	20.58
1500	97.26	113.63	24.56	20.57
1600	98.32	114.96	26.62	20.55
1700	99.34	116.20	28.67	20.53
1800	100.31	117.38	30.72	20.52
1900	101.24	118.48	32.77	20.50
2000	102.12	119.54	34.82	20.48

TABLE 12: Ideal Gas Thermodynamic Functions of VCl_4 −126.1 kcal mol^{-1}

T (K)	$-(G^\circ - H^\circ_{298})/T$ (cal deg^{-1}mol^{-1})	S°_T (cal deg^{-1}mol^{-1})	$H^\circ_T - H^\circ_{298}$ (kcal mol^1)	C_p (cal deg^{-1}mol^{-1})
298	87.88	87.88	0.00	22.95
300	87.88	88.02	0.04	22.98
400	88.80	94.80	2.40	24.08
500	90.56	100.24	4.84	24.66
600	92.56	104.77	7.33	25.00
700	94.59	108.64	9.84	25.21
800	96.56	112.02	12.37	25.35
900	98.45	115.01	14.91	25.45
1000	100.24	117.70	17.45	25.52
1100	101.94	120.13	20.01	25.57
1200	103.55	122.36	22.57	25.61
1300	105.08	124.41	25.13	25.65
1400	106.53	126.31	27.70	25.67
1500	107.90	128.08	30.27	25.69
1600	109.22	129.74	32.84	25.71
1700	110.47	131.30	35.41	25.72
1800	111.67	132.77	37.98	25.74
1900	112.82	134.16	40.55	25.75
2000	113.92	135.48	43.13	25.75

mol^{-1} from the mass spectrometric equilibrium studies reported here.

Although there are no reported experimental data on the entropy and heat capacity of VCl_4(l), we have done a second- and third-law analysis of the process

$$VCl_4(l) = VCl_4(g) \qquad (5)$$

by using three independent sets of vapor pressure data,[15−17] on the assumption that values of Δgef$_{298}$ for reaction 5 will be essentially the same as those for the neighboring Ti−Cl system which has very similar properties and where there are accurate experimental data.[14,18] The results summarized in Table 8 in the Appendix show that both second- and third-law values of $\Delta H^\circ_{298}(5)$ are in close agreement on an enthalpy of vaporization of 10.0 ± 0.4 kcal mol^{-1}. Second-law values were corrected to 298 K with the aid of heat capacity data. It is important to note that the current JANAF Table[19] values of S_T and gef for $TiCl_4$(l) unexpectedly contain significant errors, whereas the Pankratz[14] and IVTANTHERMO[18] values are correct. The earlier calorimetric value[20] $\Delta_fH^\circ_{298}(VCl_4$, l), amended slightly[21] to −136.1 ± 0.4 kcal mol^{-1}, is combined with $\Delta H^\circ_{298}(5)$ to yield $\Delta_fH^\circ_{298}(VCl_4$, g) = −126.1 ± 0.6 kcal mol^{-1}; this value is equivalent to a VCl_4 enthalpy of atomization of 365.7 kcal mol^{-1} at 298 K.

Discussion

A comparison of our new thermochemical results with various literature values is shown in Table 5. Surprisingly, there is no literature information on D°_0(VCl) other than the estimate of Flesch and Svec[5] based on a comparison with bond energy data in the V−F system; the agreement with our new result is probably fortuitous. For VCl_2, only the DFT theoretical value[5] is in reasonable accord with our new result, whereas the other experiment-related values[3,5,18] are significantly in error because of misinterpretation[3] of the nature of the VCl_2(s) sublimation process. However, for VCl_3, all values are in accord with a Δ_fH_{298} value of −85 ± 2 kcal mol^{-1}. The value[5] based on electron impact fragmentation of $VOCl_3$ is in remarkably good agreement with our results described here, whereas the compilation[18] value is apparently also based on the sublimation of VCl_3(s) and provides confirmation. In any event, we now have firm, new Δ_fH_{298} values for VCl and VCl_2 that fill these gaps in our knowledge.

The BDEs in the V−Cl system show an interesting pattern, in which the first two are similar at about 108 ± 5 kcal mol^{-1}, whereas the third and fourth are lower by 28−38 kcal mol^{-1}. However, in the neighboring Ti−Cl system, which has also been studied by the same experimental method,[22] the BDE pattern shows a quite different behavior, as seen in Table 6. For Ti−Cl, three of the BDEs average about 97 ± 5 kcal mol^{-1} whereas the fourth is some 25 kcal mol^{-1} larger. It seems likely that not all of the M or M−Cl species (where M = Ti or V) would have suitable bonding orbitals in their ground states for forming the required M−Cl bond and that some excitation or promotional energy will be needed to reach an appropriate bonding state. The energies of the electronic states of Ti and V are known, of course, but those of MCl, MCl_2, and MCl_3 are not known. As an approximation, we have taken the energy levels[23] of the positive ions M II, M III, and M IV to represent those of the three M−Cl species, so that we are mimicking the formation of M−Cl bonds by sequentially removing an electron from the Ti and V atoms and using those known positive ion energy levels to estimate the required promotion energies.

In Table 6, we list these approximate promotion energies, ΔE, which are the first excited levels above ground, except for Ti II (TiCl), where the ground-state has a 4s orbital suitable for bonding to Cl. With no excitation energy required for bonding, the ClTi−Cl bond has no energy penalty to pay and is the strongest of the four in the Ti−Cl system. Except for the Cl_3Ti−Cl bond, the other ΔE values are in approximate agreement with the differences in the sequential M−Cl BDE values and in accord with the observation that the third and fourth V−Cl BDEs are lower than the first two by more than 30 kcal mol^{-1}. The ΔE value for Cl_3Ti−Cl is clearly far out of line and makes no sense. Perhaps. there is a missing, unreported level in the Ti IV system; we have no other explanation. But the use of the positive ion levels is, in any event, an approximation at best, although it does give a fairly satisfactory correlation with the observed BDE values.

Because of the relatively weak third and fourth BDEs in the V−Cl system, the heat of atomization of VCl_4 at 298 K, 365.7 kcal mol^{-1}, is considerably lower than that of $TiCl_4$[21] at 411.9 kcal mol^{-1}. This difference likely accounts for the fact that although $TiCl_4$(l) is a thermodynamically stable liquid phase,

VCl_4(l) is only metastable[15] at 298 K, with thermodynamic calculations showing it to be unstable with respect to decomposition to VCl_3(s) and Cl_2(g). VCl_4(l) is apparently stabilized at lower temperatures by a significant kinetic barrier, because several sets[15−17] of concordant vapor pressure measurements on the liquid have been reported in the region below the normal boiling point and an accurate enthalpy of formation of the liquid has been determined[18] by burning V metal in Cl_2(g) at 298 K. However, Sytnik et al.[16] indicate that VCl_4(l) decomposes "very appreciably" at temperatures above 375 K, with formation of solid VCl_3. Clearly, the instability of the liquid is directly related to the weakness of the Cl_2V-Cl and Cl_3V-Cl bonds, which is due, in turn, to the relatively large excitation energies of the bonding orbitals in VCl_2 and VCl_3.

As noted earlier, there has been considerable discussion regarding possible distortion of the VCl_4 T_d symmetry as a result of vibronic interactions associated with the Jahn−Teller effect.[24−26] However, there have been no firm conclusions about structural details in the distorted molecule and how this might affect VCl_4 thermodynamic properties calculated from spectroscopic and molecular constants. The most recent work[26] suggests a weak Jahn−Teller energy, "comparable with the zero-point vibrational energy." Results of the work presented here indicate that the calculated thermodynamic functions of tetrahedral VCl_4 are fully compatible with the measured equilibrium data, as shown by the second- and third-law agreement for reactions 1 and 5. This is in accord with the photoelectron spectrum,[13] which yields "no evidence for a static Jahn−Teller distortion."

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Appendix

Auxiliary thermochemical data used in analysis of the experimental results were taken from sources described here. A summary of the molecular constants used in calculating thermal functions of the gaseous V−Cl and AgCl species is given in Table 7, in terms of the moments of inertia, I, the rotational symmetry number, σ, the fundamental vibrational frequency, ω, the degeneracy of the electronic state, g, and the energy of the electronic state, ε. Table 8 shows the second- and third-law enthalpies from vapor pressure determinations for the reaction $VCl_4(l) = VCl_4(g)$. Values of the V−Cl thermal functions $-(G°_T - H°_{298})/T$, $S°_T$, $H°_T - H°_{298}$, and C_p at 298−2000 K and the adopted enthalpies of formation, $\Delta_f H°_{298}$, from this work are listed in Tables 9−12. As noted earlier, these thermal functions are based on the ideal gas state at one atmosphere pressure.

Ag(g) and AgCl(g)

All data for Ag were taken from the IVTANTHERMO 2005 database.[18] For AgCl, all data are from Hildenbrand and Lau.[11] The adopted values of $\Delta_f H°_{298}$ for gaseous Ag and AgCl are +68.1 and +22.0 kcal mol^{-1}, respectively.

VCl(g)

Spectroscopic constants for the ground and excited states are from the measurements and ab initio calculations of Ram et al.[27]

VCl_2(g), VCl_3(s), VCl_3(g)

V−Cl bond lengths of 220 pm were estimated, close to that of VCl and to VCl_2 values of 218 and 225 pm from molecular theory.[6,7] A linear structure was adopted for VCl_2, in accord with experimental[28] and theoretical[6,7] indications, whereas the vibrational frequencies were estimated from those in $TiCl_2$[22,28] and from theoretical calculations.[7] Data for the low-lying electronic states of VCl_2 were taken from the MRCI calculations of adiabatic excitation energies by Vogel and Wenzel.[7] The D_{3h} symmetry and assigned frequencies[22,28] of $TiCl_3$ were used in estimating the corresponding quantities for VCl_3, whereas the low-lying electronic states of the trichloride were estimated from the modified values[19] for $TiCl_3$, based on the levels of Ti^{3+}. Values of the Gibbs energy function, gef$_{298}$, for VCl_3(s) were taken from Pankratz[14] and are based on accurate calorimetric measurements.

VCl_4(g)

The complete T_d vibrational assignment derived from far IR and Raman spectra[1,2] was adopted, together with the V−Cl internuclear distance of 213.8 pm from gas electron diffraction measurements.[25] Calculated thermal functions in Table 12 differ only slightly from those published earlier.[1] $\Delta_f H°_{298}$ was derived as described in the Results section.

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