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Thermochemical Properties of the Gaseous Bromo-iodides of Dy and of the Na−Dy Tetrahalo Complexes

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The gaseous mixed dimers $NaDyBr_4$ and $NaDyI_4$ and the bromo-iodide species DyBrI, $DyBr_2I$, $DyBrI_2$, $NaDyBr_3I$, $NaDyBr_2I_2$, and $NaDyBrI_3$ were generated in an effusion cell reactor at elevated temperatures using several different source configurations and were identified by mass spectrometry. A number of gaseous equilibria involving these species were studied, and thermochemical properties were derived with the aid of thermal functions based on estimated molecular constants. Enthalpies of formation of $NaDyBr_4$ and $NaDyI_4$ are compared with values in the literature, while results for the bromo-iodides are in close accord with values interpolated from data on the pure metal bromides and iodides.

Introduction

Salt mixtures in both the Na−Dy−Br and Na−Dy−I systems have been used in metal halide lamps because of the favorable color renditions associated with the two metal emitters under lamp operating conditions. A point of interest has been the enhancement of Na and Dy vapor concentrations due to formation of the stable gaseous mixed dimers $NaDyBr_4$ and $NaDyI_4$, and the effect on lamp performance. Chemical modeling of local equilibrium conditions is a useful tool in predicting lamp behavior, and for this reason studies of the vaporization thermodynamics of the NaBr−$DyBr_3$ [1] and NaI−DyI_3 [2,3] systems have been reported. Similar studies of the NaI−ScI_3 system have also been reported.[4,5] In addition, Hilpert[6] has reviewed much of the information on complexation of metal halide vapors.

The published thermodynamic data on the NaBr−$DyBr_3$ and NaI−DyI_3 systems[1,2] were obtained primarily from second-law analysis, i.e., from the temperature variation of reaction equilibrium constants determined by mass spectrometry. To our knowledge, however, there is no published information on the thermal functions or estimated molecular constants of $NaDyBr_4$ or $NaDyI_4$ that would be useful in third-law analysis of the results or in chemical modeling of these systems. Moreover, accounting for the extensive electron-impact fragmentation of the mixed dimers is a major factor in evaluation of the absolute reaction equilibrium constants involving these species. We have obtained additional equilibrium data on the NaBr−$DyBr_3$ and NaI−DyI_3 vapor systems, also by the mass spectrometric technique, and have estimated the molecular constants of the two mixed dimers for use in thermodynamic analysis. These results, presented here, provide a useful independent evaluation of the equilibrium constant data, using a somewhat different approach. In addition, we have studied mixtures of the Na−Dy bromides and iodides, and obtained thermodynamic values for the gaseous mixed bromo-iodide species.

Experimental Section

All mass spectrometric measurements were made with the 60° sector, magnetic instrument described previously,[7,8] equipped with heated molecular effusion-beam source and electron impact ion source. All salt samples (NaBr−$DyBr_3$, $NaDyI_4$, NaBr−$DyBr_3$−$NaDyI_4$, and $DyBr_3$−DyI_3) were contained in conventional graphite effusion cells with 1.0 mm diameter orifices. A few measurements on the Dy−Br−I system were made using a graphite gas-inlet cell containing granules of Dy(s) in the effusion chamber, reacting with a gaseous mixture of Br_2/I_2 admitted to the base of the cell. Temperatures were measured with a Pt, Pt/Rh thermocouple of known calibration. Ion appearance energies (AE) were evaluated by the vanishing current method with an accuracy of ± 0.3 eV, and species partial pressures were evaluated from the pertinent ion intensities measured at 3 eV above the respective thresholds. Species were identified from the masses, isotopic distribution, and threshold AE values of the observed ion signals; all were checked for their effusion cell origin by the response to translation of the neutral beam-defining slit. All other aspects of the measurements, analysis, and interpretation are as described previously.[7,8]

The metal halide salts used in these studies were all of reagent grade quality or better, and were obtained from the following suppliers: NaBr, $DyBr_3$ − Aldrich Chemical Co.; DyI_3 − Alfa Aesar; and $NaDyI_4$ − APL Engineered Materials. The latter sample was in the form of small spheres prepared from the melt of an equimolar mixture, while the NaBr−$DyBr_3$ sample was a mixture of the two salts. All materials were stored and manipulated in an inert atmosphere enclosure to avoid contamination by moisture.

Results

Reaction equilibrium constants, *K*, were evaluated from the pertinent ion intensity analogues measured at ionizing energies of AE + 3 eV to minimize fragmentation effects. For isomolecular reactions, the ion intensity analogues of *K* were used

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TABLE 1: Intensities, Appearance Energies, and Neutral Precursors of Ions in Mass Spectrum of Vapor over NaBr−DyBr$_3$ System at 927 K

ion	intensity[a]	AE, eV		neutral
		SRI	ref 1	
Na^+	232	8.8, 10.0	10.7	NaBr, $NaDyBr_4$
$NaBr^+$	79.2	8.3	9.1	NaBr
Dy^+	8.5	19.6	19.8	$DyBr_3$
$DyBr^+$	9.1	15.0	15.0	$DyBr_3$
$DyBr_2^+$	36.9	11.1	11.6	$DyBr_3$
$DyBr_3^+$	7.3	10.1	10.6	$DyBr_3$
$NaDyBr^+$	8.5	20.0		$NaDyBr_4$
$NaDyBr_2^+$	14.8	14.5	14.1	$NaDyBr_4$
$NaDyBr_3^+$	268	10.0	10.4	$NaDyBr_4$
$NaDyBr_4^+$	8.6	9.3	8.9	$NaDyBr_4$

[a] Measured at ionizing energy of AE + 3 eV.

TABLE 2: Equilibrium Constants and Third Law Enthalpy Changes for the Gaseous Reaction $NaDyBr_4 = NaBr + DyBr_3$ (1)

T/K	K_1, atm	$\Delta H°_{298}(1)$ kcal mol^{-1}	T/K	K_1, atm	$\Delta H°_{298}(1)$ kcal mol^{-1}
834.0	2.60E−8	59.2	926.3	8.95E−7	59.0
834.2	2.71E−8	59.1	926.7	9.19E−7	59.0
860.2	9.43E−8	58.8	926.8	8.51E−7	59.1
896.5	2.86E−7	59.2	947.0	1.59E−6	59.2
897.0	3.04E−7	59.1	973.9	3.49E−6	59.3
897.5	2.89E−7	59.2	1015.5	9.20E−6	59.8
				Av.	59.2
				Second law	57.5 ± 5

$\log K_1 = 6.887 - (12029/T)$

TABLE 3: Intensities, Appearance Energies, and Neutral Precursors of Ions in Mass Spectrum of Vapor over NaI−DyI$_3$ System at 880 K

ion	intensity[a]	AE, eV		neutral
		SRI	ref 2	
Na^+	13.5	7.9		NaI, $NaDyI_4$
NaI^+	12.1	7.1	8.3	NaI
DyI_2^+	1.70	9.9	9.8	DyI_3
DyI_3^+	1.01	9.1	9.3	DyI_3
$NaDyI_2^+$	1.40	12.3		$NaDyI_4$
$NaDyI_3^+$	20.3	8.3	9.2	$NaDyI_4$
$NaDyI_4^+$	2.52	7.6	8.8	$NaDyI_4$

[a] Measured at ionizing energy of AE + 3 eV.

directly, without further correction, since the pressure calibration constants cancel. Where required, a pressure calibration constant was included, as derived from ion intensity data on laboratory vapor pressure standards such as Ag, Au, and Sn. Partial pressure, P, is related to ion intensity I^+ by the relation

$$P = (kI^+ T)/\sigma$$

where k is the pressure calibration constant, T is the sample temperature, and σ is the species cross section for electron impact ionization. Atomic cross sections were taken from the compilation of Mann,[9] and molecular values were estimated from additivity of atomic values; no correction factor was applied. Reaction enthalpies were then derived from the equilibrium data with the aid of thermal functions taken from literature sources or calculated from estimated molecular constants, as described in the Appendix.

A. NaBr−DyBr$_3$ System. Table 1 shows the major ions observed in the mass spectrum of the vapor over the NaBr(s)−DyBr$_3$(s) salt mixture at 927 K, their threshold AEs, the ion intensities corrected for isotopic distribution at AE + 3 eV, and the assigned neutral precursors. Our observed threshold AEs are in reasonable agreement with those reported by Hilpert and Miller,[1] as seen in Table 1. Ions associated with the dimeric species Na_2Br_2, Dy_2Br_6, and Na_2DyBr_5 were also observed, but are not included in the analysis, which is concerned solely with the properties of $NaDyBr_4$. The intensities indicate clearly that neutral $NaDyBr_4$ is the major species in the vapor, manifested primarily as the fragment ions $NaDyBr_3^+$ and Na^+. Separate mass spectra on NaBr vapor show that the intensities of Na^+ and $NaBr^+$ are very similar, so that Na^+ is a major fragment ion from $NaDyBr_4$, as seen also in $NaScI_4$ vapor.[4,5]

Intensities of the principal ions $NaBr^+$, $DyBr_3^+$, and $NaDyBr_3^+$ were then measured at AE + 3 eV at a series of temperatures. From the mass spectra of NaBr, $DyBr_3$, and that of NaBr−DyBr$_3$ reported here, the fragmentation patterns of each of the gaseous neutrals NaBr, $DyBr_3$, and $NaDyBr_4$ in the mixture were sorted out so that the total ion yields of each at AE + 3 eV could be evaluated from the intensities of the principal ions noted above. The derived fragmentation factors, defined as the total ion yield from a given neutral, were as follows: $\Sigma I^+(NaBr) = 1.8\ I(NaBr^+)$; $\Sigma I^+(DyBr_3) = 8.0\ I(DyBr_3^+)$; and $\Sigma I^+(NaDyBr_4) = 1.8\ I(NaDyBr_3^+)$. Ion yields were combined with the estimated ionization cross section ratio, pressure calibration constant for AE + 3 eV, and temperature to evaluate K for the gaseous reaction

$$NaDyBr_4 = NaBr + DyBr_3 \qquad (1)$$

in the range 834 to 1015 K as shown in Table 2. Also included in the table are the derived third law enthalpy changes for reaction 1, evaluated with the molecular constants and thermal functions described in the Appendix. The average third law enthalpy, $\Delta H^\circ_{298}(1) = 59.2 \pm 2.5$ kcal mol^{-1}, is in good agreement with the second law value of 57.5 ± 3 kcal mol^{-1}. This second and third law accord indicates that the estimated molecular constants and calculated thermal functions of $NaDyBr_4$ are internally consistent with the experimental equilibrium data. All tabulated second law enthalpies, here and elsewhere, are corrected to 298 K with the aid of thermal functions. Comparison with literature values and derivation of standard enthalpies of formation will be addressed in the Discussion section.

B. NaI−DyI$_3$ System. In similar fashion, measurements on the $NaDyI_4$(s) spheres at 879.9 K yielded the mass spectrum shown Table 3, along with the observed AEs and assigned neutral precursors. Here, too, our threshold AEs are in fair agreement with those of Hilpert and Miller[2] as shown in Table 3. Again, weaker signals associated with dimeric species Na_2I^+ and $Na_2DyI_5^+$ are not included. The most intense peak is the fragment ion $NaDyI_3^+$ appearing at a threshold AE of 8.3 eV, while the parent ion $NaDyI_4^+$ has a lower AE of 7.6 eV. The neutral mixed dimer $NaDyI_4$ is clearly a major species in the vapor over the salt mixture. As with the Na−Dy−Br system, the fragmentation patterns of NaI, DyI_3, and $NaDyI_4$ in the mixture were sorted out by comparison with the mass spectra of the individual binary iodides, so that the total ion yields needed in third law calculations could be evaluated. The derived fragmentation factors were as follows: $\Sigma I^+(NaI) = 1.35\ I(NaI^+)$; $\Sigma I^+(DyI_3) = 3.8\ I(DyI_3^+)$; and $\Sigma I^+(NaDyI_4) = 1.2\ I(NaDyI_3^+)$. A relatively brief set of ion intensity measurements at AP + 3 eV was made here on the gaseous reaction equilibrium

$$NaDyI_4 = NaI + DyI_3 \qquad (2)$$

at four temperatures in the range 784 to 880 K; the equilibrium data and resulting third law enthalpy changes are shown in Table

TABLE 4: Equilibrium Constants and Third Law Enthalpy Changes for the Gaseous Reaction $NaDyI_4 = NaI + DyI_3$ (2)

T/K	K_2, atm	$\Delta H^\circ_{298}(2)$ kcal mol^{-1}
784.4	3.09E−9	57.5
795.6	5.23E−9	57.4
873.1	7.64E−8	58.2
879.9	9.53E−8	58.3
	Av.	57.9
	Second law	50 ± 10
$\log K_2 = 5.071 - (10639/T)$		

TABLE 5: Intensities, Appearance Energies, and Neutral Precursors of Major Na−Dy−Br−I Ions in Mass Spectrum of Vapor over $NaBr-DyBr_3-NaDyI_4$ System at 931 K

ion	intensity[a]	AE, eV	neutral
$NaDyBr_3^+$	523	10.0	*b*
$NaDyBr_4^+$	4.3	9.5	$NaDyBr_4$
$NaDyI_3^+$	108	8.5	*c*
$NaDyI_4^+$	14.9	8.0	$NaDyI_4$
$NaDyBrI^+$	42.0	13.0	*d*
$NaDyBr_2I^+$	808	9.0	*e*
$NaDyBrI_2^+$	409	8.5	*f*
$NaDyBr_3I^+$	15.2	9.0	$NaDyBr_3I$
$NaDyBr_2I_2^+$	45.7	8.5	$NaDyBr_2I_2$
$NaDyBrI_3^+$	42.8	8.0	$NaDyBrI_3$

[a] Measured at ionizing energy of AE + 3 eV. [b] $NaDyBr_4$, $NaDyBr_3I$. [c] $NaDyI_4$, $NaDyBrI_3$. [d] $NaDyBr_3I$, $NaDyBr_2I_2$, $NaDyBrI_3$. [e] $NaDyBr_2I_2$, $NaDyBr_3I$. [f] $NaDyBr_2I_2$, $NaDyBrI_3$.

TABLE 6: Equilibrium Constants and Third Law Enthalpy Changes for the Gaseous Reactions 3, 4, 5

T/K	K_3	$\Delta H^\circ_{298}(3)$ kcal mol^{-1}	K_4	$\Delta H^\circ_{298}(4)$ kcal mol^{-1}	K_5	$\Delta H^\circ_{298}(5)$ kcal mol^{-1}
789.1	21.4	−4.3	0.74	2.6	5.63	−0.7
826.7	23.6	−4.7	1.86	1.2	12.1	−1.9
846.0	22.0	−4.6	1.90	1.2	11.1	−1.8
896.1	32.0	−5.6	1.21	2.1	4.6	−0.4
931.3	32.6	−5.8	1.18	2.2	10.1	−1.9
	Av.	−5.0	Av.	1.9	Av.	−1.3
	Second law	4.9 ± 5		1.9 ±5		0.6 ± 5

TABLE 7: Intensities, Appearance Energies, and Neutral Precursors of Ions Observed in Mass Spectrum of Vapor Generated by Reaction of Dy(s) + Br_2(g) + I_2(g) at 1311 K

ion	intensity[a]	AE, eV	neutral
$DyBr^+$	5.3	6.0	DyBr
$DyBr_2^+$	26.1	7.5	$DyBr_2$
$DyBr_3^+$	46.6	10.0	$DyBr_3$
DyI^+	2.8	6.0	DyI
DyI_2^+	6.5	8.0	DyI_2
DyI_3^+	1.3	9.5	DyI_3
$DyBrI^+$	10.6	7.5	DyBrI
$DyBr_2I^+$	20.7	9.5	$DyBr_2I$
$DyBrI_2^+$	4.6	9.0	$DyBrI_2$

[a] Measured at ionizing energy of AE + 3 eV.

4. The average third law value $\Delta H^\circ_{298}(2) = 57.9 \pm 2.5$ kcal mol^{-1} is preferred, while the corresponding second law enthalpy change of 50 ± 10 kcal mol^{-1} is compatible, considering the small number of data points. Other derived thermochemical properties will be discussed below.

C. Na−Dy−Br−I System. To evaluate the thermochemistry of potentially important mixed bromo-iodide species in the Na−Dy−Br−I system, the mass spectrum of vapor effusing from a graphite cell containing a mixture of the salts NaBr(s), $DyBr_3$(s), and $NaDyI_4$(s) was investigated at 931 K. As noted in the previous section, the $NaDyI_4$ sample was in the form of small spheres prepared from an equimolar melt of the two binary iodides; the phase composition of the resulting solid salt is not known, and not required for interpretation of the gas phase thermochemistry. The resulting mass spectrum is shown in Table 5, along with the isotopically corrected ion intensities of the major species, their measured AEs, and the assigned neutral precursors. None of the Na−Br, Dy−Br, Dy−I or larger Na_2-DyBr−I trimer species are reported, since they are not germane to the analysis. The parent ions of the mixed species $NaDyBr_3I$, $NaDyBr_2I_2$, and $NaDyBrI_3$ were observed with AE values in the expected range, along with $NaDyBr_4$ and $NaDyI_4$, showing that all of the pure and mixed tetrahalo species were present. A series of parent ion intensity measurements at AE + 3 eV was made for the three mixed bromo-iodides and the two tetra-bromo and tetra-iodo species at five temperatures over the range 789 to 931 K. The parent ions alone were used to evaluate the equilibrium constant K for the gaseous isomolecular reactions

$$NaDyBr_4 + NaDyI_4 = 2NaDyBr_2I_2 \tag{3}$$

$$NaDyBr_4 + NaDyBr_2I_2 = 2NaDyBr_3I \tag{4}$$

$$NaDyBr_4 + NaDyI_4 = NaDyBr_3I + NaDyBrI_3 \tag{5}$$

with the assumption that the fragmentation patterns of the five dimers are sufficiently similar so that the parent ion intensity analogues of the three K values will be reasonable representations of the true equilibrium constants, and that any differences will largely cancel for these three symmetrical reactions.

The equilibrium data and derived third law enthalpies are summarized in Table 6. Note that the reaction enthalpies are all quite small, $\Delta H^\circ_{298}(3) = -5.0$ kcal mol^{-1}, $\Delta H^\circ_{298}(4) = 1.9$ kcal mol^{-1}, and $\Delta H^\circ_{298}(5) = -1.3$ kcal mol^{-1}, with estimated uncertainties of ± 2.5 kcal mol^{-1}. This is an interesting point and will be discussed below. Although there are only five data points, second law enthalpies are in reasonable accord. The third law values are preferred. Because the reaction enthalpies are so small, K is essentially temperature independent, and the experimental second law enthalpies require no correction to 298 K.

D. Dy−Br−I System. To evaluate the properties of the Dy bromo-iodides, a stream of gaseous $Br_2 + I_2$ was admitted to a graphite effusion cell reactor containing Dy granules. A summary of the observed ion species, their threshold AEs, and assigned neutral precursors at a cell temperature of 1311 K is shown in Table 7. In addition to the expected Dy−Br and Dy−I species, the mixed Dy−Br−I species DyBrI, $DyBr_2I$, and $DyBrI_2$ were also observed, with AE values consistent with those of the pure Dy bromides and iodides. A set of intensity measurements was made at AE + 3 eV over the range 1311 to 1491 K with this cell arrangement; derived equilibrium data and enthalpy changes for the gaseous reactions

$$DyBr_2 + DyI_2 = 2DyBrI \tag{6}$$

$$DyBr_3 + DyBrI_2 = 2DyBr_2I \tag{7}$$

$$DyI_3 + DyBr_2I = 2DyBrI_2 \tag{8}$$

are shown in Table 8.

As a check on potential barriers to halogen atom transfer when the trivalent salts are used as starting materials under neutral conditions, a second series of equilibrium measurements on reactions 7 and 8 was made on a $DyBr_3$(s)−DyI_3(s) mixture in the range 870 to 1023 K, with the results also shown in Table 8. As can be seen, the two different sample sources yielded

TABLE 8: Equilibrium Constants and Third Law Enthalpy Changes for the Gaseous Reactions 6−8

T/K	K_6	$\Delta H^\circ_{298}(6)$ kcal mol^{-1}	K_7	$\Delta H^\circ_{298}(7)$ kcal mol^{-1}	K_8	$\Delta H^\circ_{298}(8)$ kcal mol^{-1}
		Sublimation of $DyBr_3(s) + DyI_3(s)$				
870.6			1.24	1.6	3.57	−0.37
872.7			1.38	1.4	3.42	−0.30
879.6			1.55	1.3	3.16	−0.16
927.6			1.27	1.7	3.28	−0.24
933.6			1.41	1.5	3.62	−0.33
933.9					3.62	−0.43
1021.8			1.36	1.8	3.11	−0.17
1022.6			1.31	1.8	3.37	−0.33
		Reaction of $Dy(s) + Br_2(g) + I_2(g)$				
1311.0	0.659	4.6	1.48	2.1	0.99	2.7
1311.0	0.831	4.0	1.66	1.8	1.05	2.6
1389.0	0.630	5.0				
1389.0	0.686	4.8				
1409.0	0.825	4.4	0.93	3.5	1.18	2.4
1409.0	0.846	4.3	1.44	2.3	1.51	1.7
1429.0	0.698	4.9	1.87	1.6	0.80	3.5
1429.0	0.777	4.6	1.92	1.5	1.03	2.8
1491.0	0.751	4.9	1.45	2.4	1.30	2.3
1491.0	0.890	4.4	1.61	2.1	1.38	2.1
	Av.	4.6	Av.	1.9	Av.	1.1
	Second law			−0.3 ± 5		−0.5 ± 5
		2.4 ± 5		0.3 ± 5		4.4 ± 5

TABLE 9: Summary of Derived Thermochemical Results

gaseous reaction	ΔH°_{298} kcal mol^{-1}	Δgef$_{298}$(1000 K) cal mol^{-1} deg^{-1}	gas species	$\Delta_f H^\circ_{298}$ kcal mol^{-1}
(1)	59.2	35.9	$NaDyBr_4$	−225.3 ± 2
(2)	56.6	33.9	$NaDyI_4$	−157.7 ± 2.5
(3)	−5.0	0.6	$NaDyBr_2I_2$	−194.0 ± 3.5
(4)	1.9	2.7	$NaDyBr_3I$	−208.7 ± 4
(5)	−1.3	2.6	$NaDyBrI_3$	−175.6 ± 5
(6)	4.6	2.7	DyBrI	−38.1 ± 3.2
(7)	1.9	2.3	$DyBr_2I$	−112.4 ± 3.5
(8)	1.1	2.1	$DyBrI_2$	−95.4 ± 3.5

concordant third law enthalpies for reaction 7, while the same values for reaction 8 differ by 2.8 kcal mol^{-1} on average. The latter is not a significant difference, since the overall uncertainties in the third law values are on the order of ± 2.5 kcal mol^{-1}, stemming largely from an estimated uncertainty of a factor of 2 in the K values evaluated from ion intensities. In each instance, the second law reaction enthalpies for each of the five reaction studies are all within 2 kcal mol^{-1} of the third law values. The accepted values are $\Delta H^\circ_{298}(6) = 4.6$ kcal mol^{-1}, $\Delta H^\circ_{298}(7) = 1.9$ kcal mol^{-1}, and $\Delta H^\circ_{298}(8) = 1.1$ kcal mol^{-1}, all ± 2 kcal mol^{-1}; the latter are taken from the average of the two sets of determinations. Again, note that the reaction enthalpies are all relatively small, only a few kcal.

Discussion

Hilpert and Miller[1] made a detailed study of reaction 1, involving dissociation of the mixed dimer $NaDyBr_4$, by Knudsen effusion mass spectrometry and derived the second law enthalpy change $\Delta H^\circ_{298}(1) = 58.0 \pm 1.3$ kcal mol^{-1}; this result is in good agreement with our corresponding value of 57.5 ± 3 kcal mol^{-1}. Similarly, Hilpert and Miller[1] evaluated the absolute equilibrium constant, K, of reaction 1, leading to the value $K_1 = 2.0 \times 10^{-7}$ atm at 900 K, compared to the corresponding value 3.3×10^{-7} atm from our results in Table 2. The agreement between these two independent determinations is quite good, considering that Hilpert and Miller[1] evaluated the partial pressures of species from mass spectra obtained at ionizing energies of 15 to 17 eV, while our spectra were obtained at 11 to 12 eV, the latter yielding a much smaller degree of fragmentation. Since the detailed approaches to evaluating partial pressures from ion intensities were somewhat different, one can have some degree of confidence in the overall integrity of the results. Our third law value $\Delta H^\circ_{298}(1) = 59.2 \pm 2.5$ kcal mol^{-1} agrees well with the two second law values noted above. We select the rounded value $\Delta H^\circ_{298}(1) = 59.0 \pm 2$ kcal mol^{-1} for this quantity, which leads to the enthalpy of formation $\Delta_f H^\circ_{298}(NaDyBr_4,g) = -225.3 \pm 2$ kcal mol^{-1}.

For reaction 2 involving $NaDyI_4$ dissociation, Hilpert and Miller[2] derived the second law enthalpy change $\Delta H^\circ_{298}(2) = 51.9 \pm 1.4$ kcal mol^{-1} and the equilibrium constant $K_2 = 1.3 \times 10^{-7}$ atm at 840 K, using the same approach described in the preceding paragraph. Our study of reaction 2 was much less detailed than our corresponding study of reaction 1, involving only five data points over the range 784 to 880 K, but the results are sufficient to yield the third law enthalpy change $\Delta H^\circ_{298}(2) = 57.9 \pm 3$ kcal mol^{-1}and $K_2 = 2.5 \times 10^{-8}$ atm at 840 K. This latter result is a factor of 5 smaller than the corresponding value reported by Hilpert and Miller[2], which is not an unreasonable difference considering the careful sorting out of neutral precursors and the fragmentation corrections required. The difference would seem to arise from the fact that Hilpert and Miller[2] observed NaI signals about a factor of 10 larger than those arising from $NaDyI_4$, while these signals were of the same order of magnitude in the present work. For reaction 1, both the present studies and those of Hilpert and Miller[1] observed roughly comparable NaBr and $NaDyBr_4$ signals that led to K values in good agreement. As a compromise for the Na−Dy−I system, we suggest that the average of the log K_2 values from the two different studies be adopted, leading to the selected value $K_2 = 5.7 \times 10^{-8}$ atm at 840 K, and $\Delta H^\circ_{298}(2) = 56.6 \pm 2.5$ kcal mol^{-1}. On the other hand, Kaposi et al.[3] reported $K_2 = 4.6 \times 10^{-6}$ atm at 880 K, a factor of 48 higher than our value at that temperature, in substantial disagreement with both our results and those of Hilpert and Miller[2], and those results[3] were not considered further. Hilpert and Miller[2] attribute this large difference to excessive fragmentation effects caused by the use of 50 eV ionizing electrons in the work of Kaposi et al.[3] On the whole, our derived thermochemical results for $NaDyBr_4$ and $NaDyI_4$ are in relatively good agreement with those of Hilpert and Miller,[1,2] thereby validating the somewhat different approaches taken in interpreting the complex mass spectrometric measurements.

In deriving the thermochemical properties of gaseous $NaDyI_4$, we prefer to use the third law value $\Delta H^\circ_{298}(2) = 56.6 \pm 2.5$ kcal mol^{-1} based on the selected value $K_2 = 5.7 \times 10^{-8}$ atm at 840 K as noted above. The second law value of Hilpert and Miller[2] $\Delta H^\circ_{298}(2) = 51.9 \pm 1.4$ kcal mol^{-1} appears somewhat low, since their corresponding entropy change $\Delta S^\circ_{298}(2) = 31.2$ cal mol^{-1} K^{-1} is well below both the value[1] $\Delta S^\circ_{298}(1) = 35.0$ cal mol^{-1} K^{-1} found for reaction 1 and the value $\Delta S^\circ_{298} = 36.0$ cal mol^{-1} K^{-1} recommended by Shafer[10] from a survey of alkali metal $AlkMX_4$ dissociation reactions. From the preferred third law value $\Delta H^\circ_{298}(2) = 56.6 \pm 2.5$ kcal mol^{-1}, we derive $\Delta_f H^\circ_{298}(NaDyI_4,g) = -157.7 \pm 2.5$ kcal mol^{-1}.

Table 9 gives a summary of the gaseous reaction equilibria studied in this work, together with derived third law enthalpy changes and standard enthalpies of formation, $\Delta_f H^\circ_{298}$, of the Na−Dy−Br−I species evaluated from these results. The six independent thermochemical relations (3−8) were solved to obtain the six unknown $\Delta_f H^\circ_{298}$ values for the species $NaDyBr_3I$, $NaDyBr_2I_2$, $NaDyBrI_3$, DyBrI, $DyBr_2I$, and $DyBrI_2$, after evaluation of $\Delta_f H^\circ_{298}$ for $NaDyBr_4$ and $NaDyI_4$ from the thermochemistry of reactions 1 and 2. Auxiliary thermodynamic

TABLE 10: Comparison of Estimated and Experimental Enthalpies of Formation for Na−Dy−Br−I and Dy−Br−I Mixed Halide Species

	$\Delta_f H^\circ_{298}$, kcal mol^{-1}	
species	estimated[a]	experimental
$NaDyBr_3I$	−208.4	−208.7
$NaDyBr_2I_2$	−191.5	−194.0
$NaDyBrI_3$	−174.6	−175.6
DyBrI	−40.4	−38.1
$DyBr_2I$	−114.1	−112.4
$DyBrI_2$	−96.7	−95.4

[a] Estimated from $\Delta_f H^\circ_{298}$ of pure bromides and iodides, based on their fractional content in the mixed halides.

data used in evaluating the $\Delta_f H^\circ_{298}$ values were taken from sources described in the Appendix. Also shown in Table 9 are values of the change in Gibbs energy function Δgef_{298} at 1000 K for the reactions studied, where $gef = -(G^\circ - H^\circ_{298})/T$. The estimated spectroscopic and molecular constants used in calculating Δgef_{298} and other thermal functions are discussed in the Appendix.

Table 9 shows that the enthalpy changes for the ligand exchange reactions 3−8 are all relatively small, only a few kcal mol^{-1}, compared to the Na−X and Dy−X, where X = Br or I, bond strengths ranging from 65 to 100 kcal mol^{-1}. The nearly thermoneutral behavior of these isomolecular exchange reactions illustrates that the individual Na−X and Dy−X bond strengths are not noticeably affected by changes in the type of metal−halogen bonds in their various molecular environments. In reaction 7 for example, the $Br_2Dy{-}Br$ and $BrIDy{-}I$ bonds broken are, in a thermochemical sense, essentially equivalent to the $BrIDy{-}Br$ and $Br_2Dy{-}I$ bonds formed. This seems a reasonable result, and can be used with confidence in making reliable estimates of the critical $\Delta_f H^\circ_{298}$ values for other mixed halogenides of the metals that have not been investigated. Such estimates should be exceptionally reliable, and may obviate the need for experimental thermochemical studies in all but the most critical cases. This is a welcome concept, since $\Delta_f H^\circ_{298}$ is the most difficult database value to estimate when reliable experimental data are lacking.

Hilpert and Niemann[11] summarized the thermochemistry of several isomolecular ligand exchange reactions involving $SnBr_2$, SnI_2, SnBrI, $HoBr_3$, HoI_3, $HoBr_2I$, and $HoBrI_2$, similar to reactions 7 and 8, and also found the reaction enthalpies to be close to zero. They[11] did not comment specifically on this point, but noted that the equilibria describing formation of SnBrI, $HoBr_2I$, and $HoBrI_2$ "are practically entropy determined"; these results are fully in accord with those found here for such reactions.

A simple model for estimating $\Delta_f H^\circ_{298}$ values in mixed halide species such as the bromo-iodides can be illustrated by considering the Na−Dy−Br−I species, where data for the Na−Dy-tetrahalo species $NaDyBr_4$ and $NaDyI_4$ are known from experiment. On the assumption that $\Delta H^\circ_{298} = 0$ for halide atom exchange reactions, as essentially borne out by the experimental results, one can estimate $\Delta_f H^\circ_{298}$ for the bromo-iodide species based on their fractional character of pure tetrabromo and tetraiodo species. For example,

$$\Delta_f H^\circ{}_{298}(NaDyBr_3I) = 3/4\ \Delta_f H^\circ{}_{298}(NaDyBr_4) + 1/4\ \Delta_f H^\circ{}_{298}(NaDyI_4) \quad (9)$$

and similarly for all the other mixed halide species. Table 10 shows such estimates for the species $NaDyBr_3I$, $NaDyBr_2I_2$, $NaDyBrI_3$, $DyBr_2I$, $DyBrI_2$, and DyBrI as compared to the direct experimental values. In all instances, the estimates agree with the directly measured values within the estimated uncertainties in the latter, thus validating the model. For the modeling of lamp phenomena under local thermodynamic equilibrium conditions, these estimated enthalpies of formation should serve admirably, eliminating the need for experimental verification.

Appendix

The 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 for the Na−Dy−Br−I and Dy−Br−I gaseous species is given in Table 11, 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.

$DyBr_3$, $DyBr_2$, DyI_3, DyI_2, NaBr, NaI. All thermochemical data for the Dy−Br and Dy−I species were taken from Hildenbrand et al.,[12] while data for NaBr and NaI were taken from the IVTANTHERMO database.[13] For $DyBr_3$ and DyI_3, the $\Delta_f H^\circ_{298}$ values derived from enthalpies of sublimation and values for the solid phases were utilized, namely −131.4, and −79.4 kcal mol^{-1}, respectively. Note that the recent sublimation enthalpy of DyI_3 monomer reported by Hilpert et al.,[14] 65.7 ± 2 kcal mol^{-1} at 298 K, is essentially identical to the value used in deriving $\Delta_f H^\circ_{298}$ of DyI_3(g) as reported above.[12] Even though Hilpert et al.[14] used somewhat different thermal functions for DyI_3 solid and gas phases compared those used by Hildenbrand et al.[12] in deriving the sublimation data, a fortuitous cancellation led to identical ΔH°_{298}(sub) values from the two different sets of experimental data.

TABLE 11: Molecular Constants of Na−Dy−Br−I Species Used in Calculating Thermal Functions[a]

	$NaDyBr_4$	$NaDyBr_3I$	$NaDyBr_2I_2$	$NaDyBrI_3$	$NaDyI_4$
$(I_AI_BI_C)$E110 g^{3}cm^6	2.0	4.4	6.8	9.2	11.7
σ	2	1	2	1	2
ω_i, cm^{-1}	280, 260, 200, 180, 160, 140(2), 100, 180(2), 50, 150	260, 240, 190, 170, 145, 130(2), 90, 75(2), 45, 140	240, 220, 175, 155, 130, 115(2), 85, 70(2), 45, 125	220, 200, 160, 140, 115, 110(2), 80, 65(2), 45, 110	200, 180, 150, 130, 100, 90(2), 70, 60(2), 40, 100

	DyBrI	$DyBr_2I$	$DyBrI_2$
$(I_AI_BI_C)$E111 g^{3}cm^6	1. 3	9.9	18.7
σ	1	2	2
ω_i, cm^{-1}	260, 180, 48	270, 260, 180, 45, 67, 47	270, 190, 180, 32, 67, 47

[a] For each species: $g_0 = 16$; $g_1 = 14$, $\epsilon_1 = 3460$ cm^{-1}.

Dy−Br−I and Na−Dy−Br−I Species. The molecular constants used in calculating the thermal functions of DyBrI, $DyBr_2I$, and $DyBrI_2$ were estimated from the corresponding constants of the Dy−Br and Dy−I species.[11] For $NaDyBr_4$ and $NaDyI_4$, the molecular constants were estimated in fashion similar to those of $NaScI_4$,[5] which in turn were based on the structure and scaling of the molecular parameters adopted for $NaAlF_4$.[15] Small adjustments in the low bending frequencies were made so as to be consistent with the entropy change ΔS°_{298} ∼36 cal mol^{-1} deg^{-1} suggested by Schafer[10] for dissociation reactions of $AlkMX_4$ dimers such as reactions 1 and 2, where Alk is an alkali metal, M is a trivalent metal, and X a halogen. The molecular parameters of $NaDyBr_3I$, $NaDyBr_2I_2$, and $NaDyBrI_3$ were interpolated between those of the tetrabromide and tetraiodide.

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