Comments on "Vapor Pressures and Thermodynamic Properties of Lanthanide Triiodides"

Suresh K. Gupta
Lamp Phenomena Research Laboratory, General Electric Co., Nela Park, Cleveland, Ohio 44112

Published comparisons of the sublimation enthalpies of lanthanide triiodides at 298K are in error due to the use of different thermodynamic functions in the treatment of data. Reevaluated enthalpies reveal significant discrepancies between the Knudsen effusion weight loss and mass spectrometric results.

In a recent publication, Hirayama, Rome, and Camp (HRC) have reported vapor pressures and thermodynamic properties of some of the lanthanide triiodides (*5*). This apparently is an extension of their earlier reported efforts in this area (*3*, *4*). The Knudsen effusion vapor pressure and mass spectrometric techniques have been used. The derivation of enthalpies and entropies of sublimation has been based on the second law method. This approach is justified since appropriate thermodynamic functions required for the third law treatment are unavailable due to lack of molecular parameters for the gaseous triiodides. Experimental thermodynamic functions for a few of the solid lanthanide triiodides are, however, available (*1*). Thus, estimated values of the thermodynamic functions C_P° (or $H_T^\circ - H_{298}^\circ$) and $S_T^\circ - S_{298}^\circ$ for the gaseous molecules are used for the conversion of the second law derived sublimation enthalpy, $\Delta H_{s,T}^\circ$ and entropy, $\Delta S_{s,T}^\circ$ to 298K, ref. *6*.

This facilitates intercomparison of results obtained from diverse experimental techniques as well as by different workers, provided that consistent sets of thermodynamic functions are used in the treatment of data. The intent of this short communication is to show that the reported comparisons among various published sublimation enthalpies, $\Delta H_{s,298}^\circ$, are in error due to the use of inconsistent thermodynamic functions, particularly the heat capacities of sublimation, $\Delta C_{p,s}^\circ$ (*5*).

Most of the published $\Delta H_{s,298}^\circ$ values are derived from the Knudsen effusion vapor-pressure data (*3*, *5*, *7*). Some are, however, based on the Knudsen effusion–mass spectrometric technique (*4*). The temperature range used in the mass spectrometric work is generally lower than that in the vapor-pressure approach. But this should not influence the ultimate results.

In their most recent article, HRC have used estimates of $H_T^\circ - H_{298}^\circ$ for LaI_3(g) reported by Krasnov and Danilova (*6*) along with data for the solid phase published by Dworkin and Bredig (*1*). However, in their earlier publications, Hirayama and coworkers (*3*, *4*) used for the heat capacity of sublimation, $\Delta C_{p,s}^\circ$, a value of −14 cal/mol deg which had been employed by Shimazaki and Niwa (*7*). The rederived $\Delta H_{s,298}^\circ$ based on the average $\Delta C_{p,s}^\circ$ presently used by HRC (*5*) are compared in Table I which clearly shows the revised discrepancies in the last column. These reevaluated $\Delta H_{s,298}^\circ$ values demonstrate lack of agreement between the enthalpies measured by the two different techniques: the vapor pressure and mass spectrometric. In fact, the mass spectrometric values are, in general, lower than those obtained from the vapor-pressure method. Only the enthalpy data of CeI_3 are in excellent agreement, whereas the discrepancies for NdI_3 and PrI_3 are very large for unknown reasons as was pointed out by the workers (*4*).

Feber's estimated quantities (*2*) are not compared in Table I since only the experimental data are considered here. Undoubtedly, further work is desired to resolve the present disagreements in the sublimation enthalpies of lanthanide triiodides. The thermodynamic functions for gaseous LaI_3 estimated by Krasnov and Danilova are the only ones available so far (*6*). However, these may be suspect since, for example, their estimate of 94.6 eu for S_{298}° of LaI_3(g) is well below the values derived by HRC for other lanthanide triiodes (*5*). On the other hand, $H_T^\circ - H_{298}^\circ$ and $S_T^\circ - S_{298}^\circ$ quantities are generally far less susceptible to changes in molecular parameters. Obviously, fundamental molecular constants of the gaseous species are needed to establish their thermodynamic properties.

Table I. Comparison of Reported Sublimation Enthalpies of Lanthanide Triiodides

	Ref *1* KE vapor pressure		Ref *2* KE mass spectrometric $\Delta H_{s,298}^\circ$, kcal/mol		Ref *6* KE vapor pressure $\Delta H_{s,298}^\circ$, kcal/mol		Discrepancies in $\Delta H_{s,298}^\circ$	
Substance	$\Delta C_{p,s}^\circ$,[a] cal/mol deg	$\Delta H_{s,298}^\circ$, kcal/mol	Reported[b]	Revised[c]	Reported[b]	Revised[c]	Reported[d]	Revised[e]
CeI_3	−11.7	75.8	79.0	77.4			3.2	1.6
PrI_3	−11.7	77.7[f]	60.8[g]	59.3[g]	75.7	74.3	16.9, 2.0	18.4, 3.4
NdI_3	−11.6	76.6[f]	62.8[g]	61.3[g]	75.8	74.2	13.8, 0.8	15.3, 2.4
GdI_3	−5.13	76.8	70.5	64.5			6.3	12.3
TbI_3	−5.74	68.0	68.0	62.6			0	5.4
DyI_3	−5.83	68.4	69.4	64.2			1.0	4.2
HoI_3	−5.85	75.4	72.5	67.5			2.9	7.9
ErI_3	−5.89	73.2	69.4	64.4			3.8	8.8

[a] Mean $\Delta C_{p,s}^\circ$ values used in ref. *5* include condensed phase transition enthalpies for some iodides. [b] Based on $\Delta C_{p,s}^\circ = -14$ cal/mol deg, refs. *4* and *7*. [c] Based on $\Delta C_{p,s}^\circ$ in col. 2 unless otherwise indicated. [d] Differences from cols. 3, 4, and 6. [e] Differences from cols. 3, 5, and 7. [f] Ref. *3*. [g] Ref. *4*. $\Delta H_{s,298}^\circ$ values considered too low for unknown reasons.

Literature Cited

(1) Dworkin, A. S., Bredig, M. A., *High Temp. Sci.*, **3**, 81 (1971).
(2) Feber, R. C., "Heats of Dissociation of Gaseous Halides", L.A. 3164, TID-4500, 40th ed., Los Alamos Scientific Laboratory, 1965.
(3) Hirayama, C., Camp, F. E., *J. Chem. Eng. Data*, **17**, 415 (1972).
(4) Hirayama, C., Castle, P. M., *J. Phys. Chem.*, **77**, 3110 (1973).
(5) Hirayama, C., Rome, J. F., Camp, F. E., *J. Chem. Eng. Data*, **20**, 1 (1975).
(6) Krasnov, K. S., Danilova, T. G., *High Temp.* (Russ.), **7**, 1131 (1958).
(7) Shimazaki, E., Niwa, K., *Z. Anorg. Allg. Chem.*, **314**, 21 (1962).

Received for review April 4, 1975. Accepted August 4, 1975.

NEW COMPOUND SECTION

Synthesis and Spectral Data of Substituted Acetylenic β-Keto-cyanides

Mowafak Y. Shandala, H. N. Al-Jallo,[1] Nazar H. Al-Jobour, and F. H. Al-Hajjar
Department of Chemistry, College of Science, University of Mosul, Mosul, Iraq

Different substituted ethyl phenylpropiolates reacted with substituted benzyl cyanides in the presence of sodium ethoxide to give substituted acetylenic β-keto-cyanides. The *o*-methyl and *o*-benzoyl derivatives of the latter were prepared. IR, NMR, and UV spectral data of the above compounds were tabulated and discussed.

In the course of our study on the reactivity of acetylenic esters toward compounds having active methylene groups, we have reported that α-(phenylpropiolyl)benzyl cyanide and 4-methoxy-α-(phenylpropiolyl)benzyl cyanide are the main products obtained from the condensation of ethyl phenylpropiolate with benzyl cyanide and *p*-methoxybenzyl cyanide, respectively (*1*). We now report similar condensation reactions by use of various substitutions in both reactants. These reactions seem to be of general application since various substituted acetylenic β-keto-cyanides (IIa–k) were obtained following a general modified procedure.

The reaction products were identified and were present in their enol forms (IIIa–k) on the basis of spectroscopic evidence (IR, NMR, and UV spectra) (Tables I and II). The NMR values for compounds IIa–k showed complex spin-spin splitting near 2.33–2.82 τ. No signals were observed at lower field which indicated that resonances due to enolic hydrogen overlapped with those due to the aromatic protons. This was concluded from the exchange of one of the protons in this region (as indicated from integration) after shaking the sample with D_2O and the appearance of the HOD signal near 5.3 τ. The presence of the enolic form in the above compounds (IIa–k) was further supported by conversion to their *o*-methyl and *o*-benzoyl derivatives. Methylation of compounds IIa–d with diazomethane gave enol ethers (IVa–d) (Table III); singlets at 5.90–5.92 τ were assigned to the methyl protons of the ether. In the same manner, compounds were benzoylated with benzoyl chloride to give the derivatives Va–k; these showed absorption in their IR spectra at 1740–1752 cm^{-1} (C=O stretching of the vinyl aromatic ester) (*2*) (Table IV).

Generally, the UV spectra of substituted acetylenic β-keto-cyanides and their *o*-methyl and *o*-benzoyl derivatives (Tables II–IV) showed three absorption bands in the range: I, 210–220; II, 230–260 (accompanied by shoulders); and III, 342–354 nm. The relative intensities of bands I and II (which are not well separated in certain cases) depend to a certain extent on the type and position of the aromatic substitution. As

Table I. IR and NMR Spectral Data of Substituted Acetylenic β-Keto-cyanides

Compound	IR stretching bands in $CHCl_3$			NMR values (τ) in $CDCl_3$	
	OH	C≡C	C=C		
IIa	2400–3200	2220	1608[a]	2.67 (m)[b]	All protons
IIb	2400–3400	2215	1608	2.5 (m)	All protons
IIc	2400–3600	2200	1612	2.59 (m) 7.62 (s)	ArH $\mathrm{Ar\underline{Me}}$
IId	2400–3570	2200	1613	2.57 (m) 7.31 (q) 8.75 (t)	ArH $\mathrm{Ar\underline{CH_2}}$ $\mathrm{CH_2{-}\underline{Me}}$
IIe	2450–3500	2260 (sh)	1600	2.33–2.78 7.72 (s)	ArH $\mathrm{Ar\underline{(CH_3)_2}}$
IIf	2400–3400	2265	1595	2.5 (m)	All protons
IIg	2400–3500	2250	1600	2.43 (m)	All protons
IIh	2300–3400	2240	1608	2.37 (m)	All protons
IIi	2400–3300	2235	1605	2.82 (m)	All protons
IIj	2400–3600	2220	1612	2.33 (m)	All protons
IIk	2500–3600	2200	1610	2.51 (m) 6.21 (s)	ArH $\mathrm{Ar\underline{OMe}}$

[a] IR in nujol. [b] s = singlet; m = multiplet; q = quartet; t = triplet.

---

[1] Present address, Chemistry Department, NRI, Atomic Energy Commission, Tuwaitha, Baghdad, Iraq. To whom correspondence should be addressed.