Thermochimica Acta, 88 (1985) 407–414
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

MASS SPECTRA OF TRIS-2,2,6,6-TETRAMETHYL-3,5-HEPTANEDIONEGADOLINIUM

C. HIRAYAMA, R.G. CHARLES, R.D. STRAW and P.G. SULLIVAN

Westinghouse Research and Development Center, Pittsburgh, PA 15235 (U.S.A.)

(Received 27 December 1984)

ABSTRACT

Tris-2,2,6,6-tetramethyl-3,5-heptanedionegadolinium [Gd(thd)$_3$] is characterized by a complex mass spectrum which consists of a multitude of ions that are formed by electron impact. The spectrum appears to show the presence of metastable species at high *m/e*. The ionization and appearance potentials of the three dominant ions, Gd(thd)$_3^+$, [Gd(thd)$_3$–C$_4$H$_9$]$^+$, and Gd(thd)$_2^+$, are 7.0, 9.5 and 12.5 ± 0.2 eV, respectively.

INTRODUCTION

Sievers and coworkers [1–3] demonstrated that the lanthanides form stable and volatile complexes with 2,2,6,6-tetramethyl-3,5-heptanedione (Hthd), and they showed that these compounds, Ln(thd)$_3$, could be used for the gas chromatographic separation of the lanthanides. The vapor pressures of the solid and liquid phases were measured over a pressure range of 0.1–10 Torr [3]. The mass spectra of these compounds were determined and briefly reported by McDonald and Margrave [4]. The latter authors presented some numerical mass spectrometric data only for the chelates of lanthanum and europium, while the appearance potentials for the chelates of the other lanthanides were presented graphically. The precision of the appearance potentials was ± 0.5 eV, at best. Westmore [5], in his review on the mass spectra of metal chelates, stated that the ionization potential of Ln(thd)$_3$ should be lower than the values reported by McDonald and Margrave.

As part of an on-going study of Gd(thd)$_3$ we determined the mass spectra of this compound in more detail with higher precision than in the earlier work [4].

EXPERIMENTAL

Preparation of Gd(thd)$_3$

Gadolinium nitrate of 99.9% purity (Ventron Corp.) was dissolved in a water–methanol solution and further purified (with respect to other lanthanides) by the anion exchange method of Molnar et al. [6]. A center cut from the eluted gadolinium-containing fractions was used to precipitate gadolinium oxalate which was then ignited to the oxide.

Purified Gd_2O_3 (616 mg) was mixed with 10 ml of water and dissolved by adding 5 ml of concentrated nitric acid and heating. After diluting to 100 ml with water, aqueous NaOH (1 M) was added a little at a time to initiate precipitation. Any solid which formed was redissolved with the minimum quantity of dilute HNO_3. Eastman Hthd (1.75 g) was dissolved in 10 ml ethanol and added dropwise to the rapidly stirred gadolinium solution. Dilute NaOH solution was then added until the resulting liquid phase was slightly basic to indicator paper. The mixture was allowed to stand at room temperature for an hour after which the solid precipitate was filtered off on a sintered glass crucible.

After drying in a vacuum desiccator, the solid was dissolved in 50 ml toluene and the solution filtered into a separatory funnel. Water (200 ml) was added and the two-phase system was shaken for a few minutes to ensure equilibrium. After a suitable period of quiescence to achieve phase separation, the toluene layer was transferred to a beaker and evaporated to dryness in a vacuum desiccator. The resulting solid was transferred to a sintered glass filtering crucible with *n*-hexane and then washed on the filter with three 25-ml portions of *n*-hexane. Final drying was in a vacuum dessiccator at room temperature. Yield of crystalline solid = 0.96 g.

Mass spectra

The mass spectrometric measurements were made on a Nuclide (Model HT-90) spectrometer which was interfaced with an IBM-PC computer to facilitate data acquisition. Both positive and negative ion spectra were determined. The sample was vaporized from a tantalum Knudsen cell with a thin orifice of 0.0762 cm diameter. A small-diameter thermocouple of W5%Re–W20%Re was inserted into a 0.15 cm diameter hole in the bottom of the crucible, and the temperature was read on a calibrated Omega (Model 2160A) digital thermometer. The temperature was maintained constant to within ± 2 K during measurements. The molecular beam from the Knudsen cell was chopped at a frequency of 3600 Hz, and the output signals from both the lock-in amplifier and the electrometer were recorded on a strip-chart recorder. All measurements of the relative intensities of the positive ions at a fixed electron bombardment energy were made at identical instrumental settings, such as electron emission current and multiplier voltage, so that the relative intensities for the different measurements were directly comparable. Scans for negative ions were made at electron energies varying from near zero to 50 eV.

Approximately 0.3 g of sample was used in each measurement, and the sample was loaded into the spectrometer and maintained at a vacuum of at least 1×10^{-6} Torr overnight. Then the cell was slowly heated until evaporating species were observed.

The appearance potentials of the three major peaks at *m/e* 524, 650 and 707 were determined by measuring the ion intensities at 0.5-eV intervals. The ionization efficiency curve of H_2O^+ was similarly determined to calibrate the appearance potentials. The measured ionization potential of H_2O^+ agreed to within ±0.1 eV with the published value [7]; our measurements on Ag^+ and Au^+, besides that of H_2O^+, have been consistently within ±0.1 eV of the published values [7].

RESULTS

The 50-eV spectrum of $Gd(thd)_3$ shows the formation of many ionization fragment species as a result of electron bombardment. Figure 1 shows the spectrum taken from the output of the lock-in amplifier at a sample temperature of 140°C. The spectrum taken from the electrometer output was identical to that from the lock-in, but the former spectrum, because of the higher sensitivity, showed some of the very low intensity peaks which were not discernible in that from the lock-in. The background at $m/e > 204$ was clean, so that all observed peaks are attributed to species vaporizing from the Knudsen cell. That the peaks all belong to gadolinium complex species is clear from the relative intensities in accordance with the isotopic distribution of the metal. A relatively weak peak of Hthd, centered at *m/e* 183, was present in the spectrum. Table 1 summarizes the relative intensities, from the electrometer spectrum, of all peaks present at $m/e > 280$; as shown in the table, the spectrum was determined at 15, 20 and 50 eV.

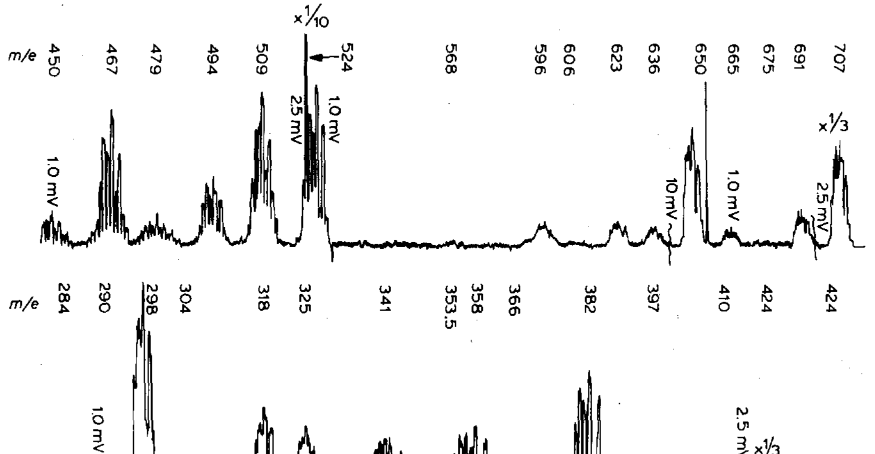

Fig. 1. Mass spectrum of $Gd(thd)_3$ at 140°C.

As the 50 eV spectrum indicates, nearly all of the peaks show the resolution of individual mass peaks. The resolution is particularly distinct for species of $m/e < 525$. The peaks at m/e 290 to 325 and 354 are less well resolved; these peaks are assigned to doubly charged ions. Table 2 summarizes the peak assignments where the m/e value refers to the most abundant isotopic species formed with ^{158}Gd. As the spectrum shows, the peaks at $m/e > 590$ are less well resolved, and the peaks at m/e 593 and 675 remained broad and diffuse over the complete electron energy range. These latter peaks are most probably attributable to metastable species.

We observed all of the 50-eV peaks recorded by McDonald and Margrave [4] for La(thd)$_3$ and Eu(thd)$_3$, but we also found additional peaks for Gd(thd)$_3$. Similar to the La(thd)$_3$ spectrum, the most abundant ions were Gd(thd)$_2^+$ > [Gd(thd)$_3$–C$_4$H$_9$]$^+$ > Gd(thd)$_3^+$.

The appearance potentials (AP) of the three most abundant ions were determined from the semilogarithmic plot, as shown in Fig. 2; the reproducibility of the AP is better than ±0.2 eV. The APs for Gd(thd)$_3^+$, [Gd(thd$_3$)–C$_4$H$_9$]$^+$ and Gd(thd)$_2^+$ are 7.0, 9.5 and 12.5 ± 0.2 eV, respectively. The respective APs estimated from the graphical data of McDonald and Margrave are 9.8, 12.2 and 16.5 eV; these authors stated their reproducibility as ±0.5 eV and they used the AP of N$_2$ as their internal standard. As

TABLE 1

Relative intensities at 50, 20 and 15 eV and appearance potentials. Relative intensities, I^+, normalized to that of m/e 524 at 50 eV

50 eV						20 eV		15 eV	
m/e	I^+	AP (eV)	m/e	I^+	AP (eV)	m/e	I^+	m/e	I^+
284	9		509	95		424	11	424	6
290	5		524	1000	12.5±0.2	439	trace	509	trace
298	114		568	5		467	1	524	91
304	11		580	trace		479	trace	598	11
318	45		598	14	~10	494	trace	606	trace
325	32		606	trace		509	6	623	8
341	27		623	14		524	364	636	6
353.5	13		636	11		568	3	650	305
358	36		650	680	9.5±0.2	580	2	665	5
366	11		665	9		598	20	675	trace
382	72	~22	675	trace		606	2	691	9
397	14		691	13	~10	623	15	707	214
410	9		707	160	7.0±0.2	636	12		
424	32	~13				650	1000		
439	13					665	11		
450	13					675	1		
467	77					691	26		
479	13					707	350		
494	36								

TABLE 2

Ionic assignment of peaks; m/e is for species formed by ^{158}Gd

m/e	Ion	m/e	Ion
707	$Gd(thd)_3^+$	424	$[Gd(thd)_2{-}C_4H_9{-}C_3H_6]^+$
691	$[Gd(thd)_3{-}CH_3]^+$	410	$[Gd(thd)_2{-}2C_4H_9]^+$
675	metastable	397	$[Gd(thd)_2{-}2C_4H_9{-}CH]^+$ (?)
665	$[Gd(thd)_3{-}3CH_3]^+$	382	$[Gd(thd)C_2HO]^+$
650	$[Gd(thd)_3{-}C_4H_9]^+$	366	$[Gd(thd)CO]^+$
636	$[Gd(thd)_3{-}C_4H_9{-}CH_3]^+$	358	$[Gd(thd)O]^+$ or $[Gd(thd)O_2{-}CH_3]^+$
623	$[Gd(thd)_3{-}C_4H_9{-}2CH_3]^+$	353.5	$Gd(thd)_3^{2+}$
598	metastable + $[Gd(thd)_3{-}2C_4H_9]^+$	341	$Gd(thd)^+$
524	$Gd(thd)_2^+$	325	$[Gd(thd)_3{-}C_4H_9]^{2+}$
509	$[Gd(thd)_2{-}CH_3]^+$	318	$[Gd(thd)_3{-}C_4H_9{-}CH_3]^{2+}$
494	$[Gd(thd)_2{-}2CH_3]^+$	304	$[Gd(thd)_3{-}C_6H_{10}O]^{2+}$
467	$[Gd(thd)_2{-}C_4H_9]^+$	298	$[Gd(thd)_3{-}2C_4H_9]^{2+}$
450	$[Gd(thd)_2{-}C_4H_9{-}CH_3]^+$	290	$[Gd(thd)_3{-}2C_4H_9{-}CH_3]^{2+}$
439	$[Gd(thd)_2{-}C_4H_9{-}CO]^+$	284	$[Gd(thd){-}C_4H_9]^+$

discussed by Westmore [5], the ionization potentials reported by McDonald and Margrave for the $Ln(thd)_3$ are too high. Our APs are summarized in Table 1; also included here are estimates of the APs of some of the other ions as determined from a rapid decrease in the recorded intensity at a rapid, constant rate of decrease in the electron energy for the specific m/e peak. The reproducibility of these APs is no better than ±1 eV. As shown in Table 1, all of the ions with $m/e < 424$ were absent at 20 eV; however, twelve of the ions still persisted at 15 eV, with most of these being in the high mass range where the ion was formed by the elimination of a *t*-butyl or methyl group.

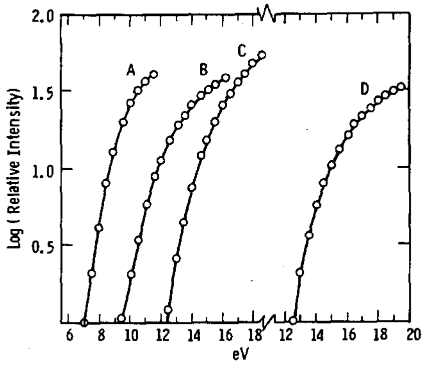

Fig. 2. Semilogarithmic plot of relative ion intensity as a function of electron energy for: (A) $Gd(thd)_3^+$; (B) $[Gd(thd)_3{-}C_4H_9]^+$; (C) $Gd(thd)_2^+$; (D) H_2O^+.

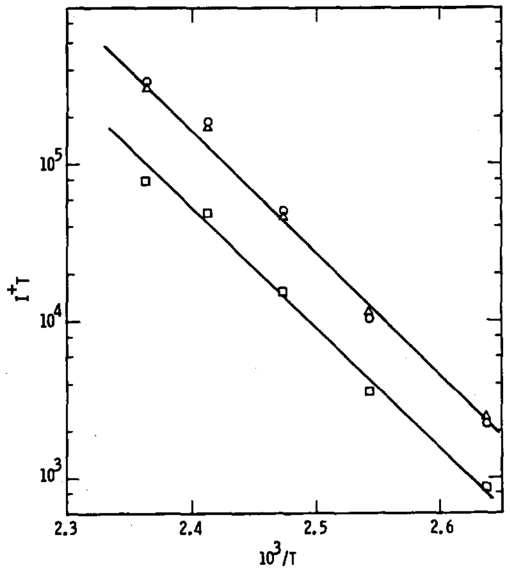

Fig. 3. Log I^+T vs. $1/T$ for ions of m/e 524 (○), 650 (△), 707 (□).

The temperature dependence of the relative intensities of the three most abundant ions, plotted as log I^+T against reciprocal absolute temperature, is shown in Fig. 3. I^+ is the relative ion intensity. A least-squares fit was made for each ion, and the enthalpies of vaporization were 35.2, 36.9 and 39.1 kcal mol^{-1}, respectively, for $Gd(thd)_3^+$, $[Gd(thd)_3–C_4H_9]^+$, and $Gd(thd)_2^+$; the average enthalpy of sublimation was 37.1 kcal mol^{-1} at the intermediate temperature of 410 K. Because of the scatter in the data points and the narrow temperature range of 50°C, the estimated precision in our measurement is no better than ± 3 kcal mol^{-1}. Our ΔH_s value is in satisfactory agreement with 38.55 kcal mol^{-1}, at 438 K, as determined by Sicre et al. [3] from vapor pressure measurements.

DISCUSSION

The electron impact mass spectra of the $Ln(thd)_3$ should be similar to those of other β-diketonates, such as those of acetylacetone. The normally trivalent lanthanides form closed-shell compounds LnX_3, where X is the ligand, and the electron impact fragmentation results in the predominance of the LnX_2^+ ion in the spectrum [8,9]. In the case of $Ln(thd)_3$, ionization to $Ln(thd)_2^+$ results in the formation of a stable ion where the lanthanide retains its trivalency with extensive delocalization of the electrons. In spite of the unfilled f-shell of the normally trivalent lanthanides from cerium to thulium, LnX_3 behave as closed-shell compounds because of the strong coulombic interaction of the f-electrons with the metal ion. In the case of

Gd^{3+}, the half-filled *f*-shell imparts stability nearly comparable to those of the empty and filled *f*-shells of lanthanum and lutetium, respectively. As shown in Table 1 for the 50-eV spectrum, the abundance of the $Gd(thd)_2^+$ ion is approximately five times that of the parent ion.

The appearance potential of 9.5 eV for the formation of the $[Gd(thd)_3–C_4H_9]^+$ ion is appreciably lower than that for the formation of the $Gd(thd)_2^+$ ion. As suggested by Westmore [5], the dissociation of the *t*-butyl group, as well as CH_3 from the acetylacetonate complex, is best described in terms of the chelate ring opening where the metal ion retains its stable trivalency. Both the low energy for the ionization and the stabilization of the ion by ring opening probably accounts for the high abundance of this ion in the mass spectrum.

The low ionization potential of $Gd(thd)_3$ is consistent with the removal of an electron from a π-orbital of the conjugated β-diketonate. In the case of the lanthanide halides, the ionization potential is attributed to the removal of an electron from the halogen so that the ionization potential decreases with increasing atomic number of the halogen. Because the electron affinity of the halogens, such as F and C1, is appreciably higher than that of the conjugated β-diketonate ligand, the ionization potential of the lanthanide halides are appreciably higher. In the case of the iodides, where the metal iodide bond is largely covalent, the ionization potentials of GdI_3 is 9.2 eV [9].

The broad, diffuse peaks at *m/e* 596 and 680 are probably the metastables for $[Gd(thd)_3–C_4H_9]^+$ and $[Gd(thd)_3–CH_3]^+$, respectively. The latter ions and the proposed metastables appeared at similar appearance potentials of $15 > AP > 12.5$ eV. More detailed measurements are needed to confirm the existence of the metastables.

The ions of $m/e < 424$ all had $AP > 20$ eV. The formation of doubly charged ions is consistent with this highly energetic process. The large AP for the singly charged ions of low *m/e*, however, reflects the large energy requirement for the large number of bonds that must be broken to form these ionized species.

CONCLUSION

The mass spectrum of $Gd(thd)_3$ is characterized by the presence of numerous peaks with *m/e* ranging from 284 to the parent ion at 707. The complete, unequivocal assignment of each peak requires further detailed measurements; the spectrum appears to indicate the presence of at least two metastable species. The ionization potential of 7.0 ± 0.2 eV for $Gd(thd)_3$ is consistent with the electron removal from π-orbitals of the conjugated complex.

REFERENCES

1 K.J. Eisentraut and R.E. Sievers, J. Am. Chem. Soc., 87 (1965) 5254.
2 C.S. Springer, Jr., D.W. Meek and R.E. Sievers, Inorg. Chem., 6 (1967) 1105.
3 J.E. Sicre, J.T. Dubois, K.J. Eisenstraut and R.E. Sievers, J. Am. Chem. Soc., 91 (1969) 3476.
4 J.D. McDonald and J.L . Margrave, J. Less-Common Met., 14 (1968) 236.
5 J.B. Westmore, Chem. Rev., 76 (1976) 695.
6 F. Molnar, A. Horvath and V.A. Khalkin, J. Chromatogr., 26 (1967) 225.
7 J.L. Franklin, J.G. Dillard, H.M. Rosenstock, J.X. Herron, K. Draxl and F.H. Field, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., 26 (1969).
8 J.W. Hastie and J.L. Margrave, High Temp. Sci., 1 (1969) 481.
9 C. Hirayama and P.M. Castle, J. Phys. Chem., 77 (1973) 3110.