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Stability of Complex Dilanthanum Carbide Molecules

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Experimental investigations of the equilibrium vapor above metal–graphite systems by Knudsen-cell mass spectrometry over the last two decades have resulted in the thermodynamic characterization of a large number of stable gaseous carbides of the principle formula type MC_n with $n = 1–4$ [1, 2]. Information concerning the bond energies and molecular structure of gaseous metal carbides is of importance to organometallic chemistry and to an understanding of metal catalysis for petrochemical industrial processes.

Since our first report of complex gaseous metal carbides of the type MC_n with more than four carbon atoms [3] for the cerium carbides, we have confirmed the occurance of such molecules for uranium [4], yttrium [5], thorium [6], titanium [7] and scandium [8]. Very little is known about dimetal carbides. The molecules M_2C_2 have been reported for aluminum and gallium [9, 10] and molecules Ce_2C_n ($n = 1–6$) have been observed and their approximate atomization energies presented [3]. Here we report the experimental observation of the dilanthanum carbides, La_2C_n ($n = 2–6$) and the determination of their atomization energies.

The mass spectrometer and experimental approach used for this investigation have been described elsewhere [11]. The dimetal lanthanum carbides were observed over a lanthanum–iridium–graphite system, following the investigation of gaseous LaIr [12] and the lanthanum carbides LaC_n ($n = 1–6$) [13]. The La–Ir-sample used was intimately mixed with excess graphite to insure unit activity of carbon and contained in a graphite Knudsen cell that was enveloped by a tantalum Knudsen cell. A small amount of gold was added for calibration purposes. The dilanthanum carbides were identified by their mass-to-charge ratio and where possible, their appearance potentials.

The third law enthalpies of the reactions

$$2La(g) + nC(graph.) = La_2C_n(g) \qquad (1)$$

involving the molecules La_2C_2, La_2C_3, La_2C_4, La_2C_5 and La_2C_6 are summarized in Table I. Also given are the derived atomization energies. The data correspond to measurements in the temperature range 2540–2800 K. At the highest temperatures of investigation the molecules La_2C and La_2C_8 were also observed. The estimation of the necessary Gibbs energy functions and heat content functions according to standard statistical thermodynamic procedures was based on assumed linear $La–C_n–La$ geometries and the same electronic contribution as given for La^{2+} [14]. The experimental reaction enthalpies were combined with the known heat of sublimation of graphite [15] to yield the atomization energies given. Also listed in Table I are the average $La–C_n$ bond energies as obtained by taking half of the difference between the atomization energies for La_2C_n in Table I and that of the corresponding carbon molecules, C_n [16].

There appears to be an increase in the average $La–C_n$ bond energy in La_2C_n with n. This may be attributed to an enhanced π electron resonance energy of the carbon chain [17] by the presence of the La atoms of the end of the carbon chain. The observed alternation in the average $La–C_n$ bond ener-

TABLE I. Third-law Reaction Enthalpies, ΔH°_0, Measured between 2573 and 2800 K and Derived Atomization Energies, $D^\circ_{a,o}$ of Gaseous Dilanthanum Carbides.

Reaction	No. of Dat Sets	ΔH°_0 ^a 3 rd law (kJ)	$D^\circ_{a,o}$ (M)^b (kJ mol^{-1})	M	D(La-C_n) (kJ mol^{-1})
(1) $2La(g) + 2C(graph.) = La_2C_2(g)$	6	−245 ± 5	1667 ± 45	La_2C_2	535
(2) $2La(g) + 3C(graph.) = La_2C_3(g)$	9	−203 ± 3	2337 ± 45	La_2C_3	519
(3) $2La(g) + 4C(graph.) = La_2C_4(g)$	9	−219 ± 2	3064 ± 45	La_2C_4	615
(4) $2La(g) + 5C(graph.) = La_2C_5(g)$	6	−147 ± 2	3702 ± 50	La_2C_5	587
(5) $2La(g) + 6C(graph.) = La_2C_6(g)$	6	−128 ± 3	4395 ± 50	La_2C_6	692

[a] Error term corresponds to standard deviation. [b] Using $\Delta H^\circ_{v,o}$ [C(graph)] = 711.3 ± 2.0 kJ mol^{-1} (Ref. 15). The error terms correspond to estimated overall errors. [c] Using the atomization for C_n from Leider *et al.* (Ref. 16).

gies can be attributed to an enhanced ionic contribution to this bond in the molecules with an even number of carbon atoms.

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References

1 G. De Maria and G. Balducci, *Int. Rev. Sci. Ser. One, 10,* 209 (1972).
2 K. A. Gingerich, *Curr. Topics Mat. Sci., 6,* 345 (1980).
3 K. A. Gingerich, D. L. Cocke and J. E. Kingcade, Jr., *Inorg. Chim. Acta, 17,* L1 (1976).
4 S. K. Gupta and K. A. Gingerich, *J. Chem. Phys., 71,* 3072 (1979).
5 K. A. Gingerich and R. Haque, *J. Chem. Soc. Faraday Trans. II, 76,* 101 (1980).
6 S. K. Gupta and K. A. Gingerich, *J. Chem. Phys., 72,* 2795 (1980).
7 S. K. Gupta and K. A. Gingerich, *High Temp.-High Pressures, 12,* 273 (1980).
8 R. Haque and K. A. Gingerich, *J. Chem. Phys., 74,* (1981).
9 W. A. Chupka, J. Berkowitz. C. F. Giese and M. G. Inghram, *J. Phys. Chem., 62,* 611 (1958).
10 C. A. Sterns and F. J. Kohl, *J. Phys. Chem., 77,* 137 (1973).
11 K. A. Gingerich, *NBS Special Publ.,* 561 (1979), pp. 289–300.
12 R. Haque, M. Pelino and K. A. Gingerich, *J. Chem. Phys., 71,* 2929 (1979).
13 K. A. Gingerich, M. Pelino and R. Haque, submitted to High Temperature Science.
14 C. E. Moore, *Natl. Bur. Stand. Circ.* 467, Vol. III (1958).
15 R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser and K. K. Kelly, 'Selected Values of the Thermodynamic Properties of the Elements', *Am. Soc. Metals,* Metals Park, Ohio (1973).
16 H. R. Leider, O. H. Krikorian and D. A. Young, *Carbon, 11,* 555 (1973).
17 S. J. Strickler and K. S. Pitzer, in 'Molecular Orbitals in Chemistry, Physics and Biology', B. Pullman and P.-O. Löwdin, Eds., Academic Press, New York (1964), pp. 281–291.