103. *Rare-earth Carbides. Part I.*

By R. C. Vickery, R. Sedlacek, and Ardys Ruben.

Higher carbides of some rare earths have been prepared by reaction of rare-earth oxides and carbon at high temperatures under low pressures of argon. Formation of carbide proceeds *via* the metal, and interstitial compounds can exist of rare-earth metal held in the carbide lattice.

The higher carbides (LnC_2) adopt a tetragonal structure, but scandium differs from the lanthanons and yttrium in forming only a hexagonal monocarbide (ScC); this is attributed to the small size of the scandium ion which permits its association with only one carbon atom.

The rare-earth elements are generally accepted as forming " salt-like " carbides containing C_2^{2-} ions in their lattices.[1] This concept of an Ln(C≡C) structure is of interest because it represents the compounds as acetylide salts of bivalent elements, even for lanthanum, cerium, terbium, gadolinium, etc., which do not otherwise show indications of potential bivalency.[2] The problem is more formidable since Warf [3] and Spedding and his co-workers [4] showed that two rare-earth carbide phases exist. Warf suggests that these are LnC and LnC_3, LnC_2 being considered a mixture of these, but Spedding's group have identified both LaC_2 and La_2C_3 entities. We have confirmed the existence of two rare-earth carbide phases, LnC_2 and a lower carbide not yet completely identified.

Stackelberg [5] and Spedding *et al.*[4] attempted to explain the incongruity of the LnC_2 molecule by assuming that, of the three valency electrons in a rare-earth ion, only two are effective in carbide formation, the third (probably 5*d*) remaining " free " in a conduction band and being responsible for the metallic nature and electrical conductivity of the carbides. If this be so, then magnetic susceptibilities and *X*-ray spectra of the carbides should disclose this " free " electron; these aspects are reported in the following papers. The present paper reports synthesis of the higher carbides by reaction of rare-earth oxides and carbon, and studies on their primary reactions and crystallography.

Stackelberg's *X*-ray studies [5] indicated that the carbides (LnC_2) adopt a face-centred tetragonal structure, which Wells [1] interprets as a calcium carbide variation of the rock-salt lattice, the chloride ions being replaced by acetylide ions, thus lowering the symmetry to tetragonal with an axial ratio greater than unity. Spedding *et al.*[4] found their lower lanthanum carbide (La_2C_3) to be body-centred cubic ($a = 8{\cdot}817$) and their higher carbide (LaC_2) to be body-centred tetragonal ($a = 3{\cdot}934$, $c = 6{\cdot}572$); Warf [3] found his monocarbides to be isostructurally hexagonal, the CeC unit cell having $a = 6{\cdot}84$, $c = 12{\cdot}77$, $c/a = 1{\cdot}87$. The tricarbides were stated to be face-centred tetragonal, CeC_3 having $a = 5{\cdot}49$, $c = 6{\cdot}51$, $c/a = 1{\cdot}19$. We find the dicarbides to be tetragonal, and the powder

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[1] Sidgwick, " Chemical Elements and Their Compounds," Vol. 1, p. 440, Oxford Univ. Press, 1950; Wells, " Structural Inorganic Chemistry," p. 457, Oxford Univ., Press, 1945; Huckel, " Structural Chemistry of Inorganic Compounds," Vol. II, p. 887, Elsevier, 1951.

[2] Yost, Russell, and Garner, " Rare Earth Elements and Their Compounds," p. 4, Wiley, 1947; Vickery, " Chemistry of the Lanthanons," p. 57, Butterworths, 1953.

[3] Warf and Palineck, Status Report, July 20, 1955, U.S. Office of Ordnance Research, Project 683, Contract DA-04-495-Ord, 1955/6.

[4] Spedding and Daane, USAEC-ISC 757, 1956; Atoji, Gschneidner, Daane, Rundle, and Spedding, *J. Amer. Chem. Soc.*, 1958, **80**, 1804.

[5] von Stackelberg, *Z. phys. Chem.*, 1930, *B*, **9**, 437.

diffraction patterns indexable as either body- or face-centred structures. In the absence of single-crystal studies it is convenient to assume a structure based upon the smallest cell size possible, in this case the body-centred cell which contains two formula units per unit cell as compared with the four formula units indicated by a face-centred tetragonal habit. The values obtained in this work for crystal lattice constants, etc., are given in Table 1 wherein are indicated the lattice parameters applicable to both types of structure.

Stackelberg[5] and Gaume-Mahn[6] considered yttrium carbide to differ from the lanthanon carbides in adopting a hexagonal habit, but we found no evidence for it. However, from scandium carbide, by our procedure, we have been able to prepare only the monocarbide of hexagonal habit with cell parameters as indicated in Table 1, the unit cell containing ten formula units. Otherwise, the structures and parameters now found for the dicarbides confirm those of Stackelberg and Spedding's groups, but we must emphasise that our lattice data were formulated from powder-diffraction patterns. As Hunt and Rundle[7] demonstrated for thorium carbide, single-crystal studies are nesessary for full structural evaluation; we have been unable to produce the necessary carbide single crystals.

There is evidence that rare-earth carbides are produced by interaction of the oxide and carbon *via* the metal. This appears to be the first time that this reduction has been observed; whether the lower carbide forms as a secondary or intermediate product has yet to be determined. However, the rare-earth carbides can form compounds with interstitial rare-earth metal atoms. When heated *in vacuo*, this interstitial metal volatilises leaving LnC_2.

TABLE 1. *Parameters of higher rare-earth carbides.*

	Element (%)									
Element	Found	Calc.	C/Ln	D_0	D_T	Struct.	a_0	c_0	c/a	Molecules/ unit cell
Sc	78·0	78·9	1	3·60	3·59	hex.	5·46	10·24	1·88	10
Y	72·9	71·2	2	4·78	4·53	b.c.t.	3·66	6·17	1·68	2
					4·55	f.c.t.	5·17	6·17	1·19	4
La.........	84·6	85·3	2	5·29	5·36	b.c.t.	3·92	6·57	1·68	2
					5·36	f.c.t.	5·54	6·57	1·19	4
Ce	84·8	84·8	2	5·56	5·58	b.c.t.	3·88	6·49	1·67	2
					5·57	f.c.t.	5·49	6·49	1·18	4
Pr	86·7	85·5	2	5·58	5·72	b.c.t.	3·86	6·44	1·67	2
					5·73	f.c.t.	5·45	6·44	1·18	4
Nd	85·7	85·7	2	5·93	5·98	b.c.t.	3·83	6·40	1·67	2
					5·98	f.c.t.	5·41	6·39	1·18	4
Sm	86·3	86·2	2	6·42	6·48	b.c.t.	3·76	6·31	1·68	2
					6·47	f.c.t.	5·32	6·33	1·19	4
Gd	87·2	86·7	2	6·93	6·93	b.c.t.	3·72	6·27	1·69	2
					6·92	f.c.t.	5·25	6·27	1·19	4
Tb	86·6	86·9	2	7·09	7·19	b.c.t.	3·69	6·21	1·68	2
					7·20	f.c.t.	5·22	6·21	1·19	4
Dy	86·7	87·3	2	7·38	7·59	b.c.t.	3·64	6·15	1·69	2
					7·59	f.c.t.	5·15	6·15	1·19	4
Ho	87·5	87·4	2	7·76	7·83	b.c.t.	3·62	6·11	1·69	2
					7·83	f.c.t.	5·13	6·11	1·19	4
Er	86·8	87·5	2	7·70	7·96	b.c.t.	3·61	6·11	1·69	2
					7·97	f.c.t.	5·11	6·11	1·20	4
Yb	86·9	87·8	2	7·97	8·20	b.c.t.	3·62	6·09	1·68	2
					8·20	f.c.t.	5·12	6·09	1·19	4

Understanding of the Ln–C bond from present data is difficult. There is now little doubt that the highest carbide of yttrium and the lanthanons is the dicarbide. This work confirms the appropriate area of Spedding and his co-workers' phase diagram, and Chupka *et al.*[8] indicate that the dicarbide is thermodynamically the most stable compound: there is thus little support for Warf's LaC_3 structure, which was probably LaC_2 plus excess of carbon.

Although the higher electron affinity of the $(C{\equiv}C)^{2-}$ entity favours formation of the

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[6] Gaume-Mahn, *Bull. Soc. chim. France*, 1956, 1862.

[7] Hunt and Rundle, *J. Amer. Chem. Soc.*, 1951, **73**, 4777.

[8] Chupka, Berkowitz, Giese, and Inghram, *J. Phys. Chem.*, 1958, **62**, 611.

dicarbide, there must be a limiting radius for the cation to which such a strongly directional anion can be attached. From the formation of ScC, this limit appears to lie between 0·8 and 1·00 Å. We might expect a tendency, through the lanthanide contraction, for the formation of carbides variant from LnC_2, but this is not apparent. The fact that YC_2 parameters come before those of DyC_2 instead of after is considered to indicate the development of covalency as one proceeds towards the heavier and smaller lanthanons, and this might well suffice to compensate for the strain introduced by the decreasing atomic radii. To some extent this is substantiated by sesquicarbides' (analogous in concept to Ln_2O_3) not having been observed [4] in rare earths of ionic radius less than that of holmium. On the other hand, if the C_2^{2-} unit behaves similarly to an oxygen atom, as suggested by Chupka *et al.*, the formation of ScC as a stable entity seems to be inconsistent with the stable ScO predicted by them.

It is significant that hexagonal ScC is isostructural with Warf's monocarbides and with scandium metal, which suggests some similarity to Hägg's interstitial structure.[9] It is of interest to compare scandium carbide and nitride. The latter (ScN) is face-centred cubic and is very inert chemically; nitrides of the other rare earths are also cubic (at least as far as gadolinium) but less resistant to reagents.[6] It is generally accepted that hard, high-melting carbides of the type MX adopt a cubic NaCl type of structure, but scandium carbide is anomalous, particularly since the radius ratio of 0·48 for ScC is adequately close to the value 0·41 theoretically required for an exact fit in the NaCl structure. However, as Hume-Rothery [10] points out, the close-packed hexagonal structure contains one " octahedral interstice " per metal atom, which permits the same anion environment for the anion in MX as does the cubic structure. Our preparation of hexagonal scandium monocarbide, and considerations on the serial position of yttrium carbide, agree with Hume-Rothery's thesis that covalency is necessary in these compounds. Again, in comparison, the weaker, triply bonded nitrogen atoms clearly require a crystal structure of lower symmetry than do those with quadrivalent carbon.*

TABLE 2. *Comparison of melting points.*

	1	2	3	4		1	2	3	4
La	1600°	2000°	600°	>2000°	Sm	1700°	2000°	1100°	>2200°
Ce	1600	>2000	620	>2300	Gd	1700	>2000	1000	>2200
Pr	1650	1900	750	>2200	Y	1950	>2000	1250	>2300
Nd	1650	1900	650	>2000					

1, Temp. of carbide formation; 2, m. p. of oxide; 3, m. p. of metal; 4, m. p. of carbide (all at 10 mm. Hg).

TABLE 3. *Ratios of radii and composition of some Group III carbides.*

Element	Metal radius, Å	Radius ratio,* C/Me	Carbide	Composition ratio, C/Me
B	0·87	0·76	B_4C	0·25
Al	1·43	0·47	Al_4C_3	0·75
Sc	1·60	0·42	ScC	1·00
Y	1·80	0·37	YC_2	2·00
La	1·87	0·36	LaC_2	2·00
Yb	1·93	0·34	YbC_2	2·00

* Radius of C = 0·665 Å.

A further aspect of the radius-ratio effect and covalency in carbides can be developed by comparing the ratios and compositions for Group III carbides (Table 3). Spedding *et al.*[4] have shown that the C–C bond distance in LaC_2 is intermediate between that of a

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* No data appear to be available on scandium phosphide or silicide, but from the above it would seem logical to expect hexagonal structures for these compounds.

[9] Hägg, *Z. phys. Chem.*, 1929, *B*, **6**, 221; 1931, *B*, **12**, 33.

[10] Hume-Rothery, *Phil. Mag.*, 1953, **44**, 1154.

double and a triple bond, whilst in the sesquicarbide the distance is that of a double bond. A simple construction could therefore be presented which, whilst accounting for the LnC_2 structure, does not require the concept of a " free " electron. In a unit cell with two formula-units, the six valency electrons of the two La atoms are allocated between one triple-bonded and one double-bonded C_2 unit. Such a system would adequately account for the mixture of hydrocarbons evolved on hydrolysis, but seems invalidated by the apparent conductivity of the carbides.

In the ScC structure, with 10 units per unit cell, the construction of a hexagon from $(C{-}C)^{6-}$ bonds is simple; such a structure can well be expected to have the resistance to hydrolysis and acid shown by this monocarbide.

We have also considered the possibility that, since an oxide is reduced to metal during formation of the carbides, bivalent samarium and ytterbium might also be produced. Our magnetochemical work on the carbides develops this theme and now we are concerned with the structures which might be developed around Sm^{2+} and Yb^{2+}. Such bivalent lanthanons could be assumed to associate with the $[C{\equiv}C]^{2-}$ without requiring a free-electron. The bivalent ions would, however, be larger than the tervalent form, and this should be reflected in the size of the crystal lattice. Comparison of the lattice parameters of SmC_2 with those of the neodymium compound shows, however, only the average difference between neighbours (interpolation of promethium being allowed for). The lattice parameters of ytterbium carbide are, however, identical with those of erbium carbide, which might be attributable to ytterbium's becoming bivalent, with correspondingly larger atomic radius.

EXPERIMENTAL

Previous work contains few details of synthesis of rare-earth carbides. Spedding's group [4] prepared their carbides by reaction of rare-earth metal and carbon in the electric arc but apparently did not investigate the Ln_2O_3–C systems. Moissan [11] heated rare-earth oxides and carbon in an electric arc furnace but gave no details. de Villélume [12] reduced La_2O_3 by carbon at 2000° C in nitrogen or hydrogen, carbide formation in the former instance being preceded by that of nitrides. He reported that CeC_3 was pyrophoric, and that carburisation proceeded rapidly at 1000° C. Gaume-Mahn [6] states that the carbides fuse at 1800—2000° C but gives no indications of the atmosphere or pressure employed. We avoided nitrogen or hydrogen, employing argon instead, and confirmed that CeC_2, alone of the dicarbides, is pyrophoric and that all the dicarbides have m. p.s higher than 1800° C. (In subsidiary work we found no direct carbide formation to occur between rare-earth oxides and carbon below 1600° C in nitrogen.)

The rare-earth oxides and carbon used were more than 99·8% pure, the oxides having been separated from crude sources by ion exchange, and the carbon being " Black G " grade which had been vigorously outgassed at high temperatures. We used two types of furnace—a 5 kv induction furnace for massive carbide formation, and a low-capacity high-temperature resistor furnace operating at up to 300 A to give a crucible temperature of *ca.* 2500° C. Both furnaces could be used under vacuum or with argon.

The general reactions involved in producing the lowest and the highest carbide reported appear to be:

$$2Ln_2O_3 + 7C \longrightarrow 4LnC + 3CO_2$$

$$2Ln_2O_3 + 15C \longrightarrow 4LnC_3 + 3CO_2$$

Varying ratios of Ln_2O_3 : C were employed in preliminary studies but, since the crucible used was of graphite, observation of differential effects was difficult. Molybdenum crucible liners reacted with the oxide–carbon mixture at the temperatures employed, and in some runs at low carbon ratios and low temperatures gave evidence for the formation of increased amounts of a silvery lower carbide, but generally the results were not reproducible. The most definite example of lower carbide production was obtained from a 1 : 5 mole ratio of La_2O_3 : C at 1900° C and 1·5 mm. pressure of argon. The carbide produced was visibly heterogeneous, the gold-coloured high carbide at the crucible–product interface enclosing a central body of silvery, lower carbide. Analyses showed the two phases to be LaC_2 and LaC, respectively.

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[11] Moissan, *Compt. rend.*, 1900, **131**, 595.

[12] de Villélume, *Ann. Chim.*, 1952, **7**, 265; *Compt. rend.*, 1951, **231**, 142, 1497; **232**, 235.

The appearance of the carbide slugs and their proximity to the crucible wall suggested that liquefaction occurred during reaction. Although CO and CO_2 were always evolved, attempts to obtain a material-balance were spoilt by reaction of the crucible carbon.

Through several preparations the synthetic procedure developed was: appropriate oxide–carbon mixtures were placed in a graphite crucible in a 5 kv induction furnace. The system was thrice evacuated and flushed with pure argon. Finally the temperature was raised to *ca.* 1600° c, with pressure maintained at 15 lb./sq. in. of argon. During the preliminary heating the reactants shrank from the crucible walls, but little if any reaction occurred at 15 lb./sq. in. At 1600° c, vacuum was gradually applied until reaction proceeded steadily, as shown by continuous evolution of gas. The pressure required for such reaction varied slightly with temperature, and for the formation of lanthanum carbide, the pressures at 1600°, 1700°, 1800°, and 1900° were 10, 14, 17, and 20 mm. Hg, respectively.

The observed temperature of reaction at 10 mm. Hg appeared to increase through the series from La to Tb, being highest with yttrium at 1950° c. The rate was controlled by adjusting both temperature and pressure until the reaction had passed through the degassing stage (*a*), followed by a molten stage (*b*), to a reconsolidation stage (*c*). The whole sequence for a charge containing *ca.* 15 g. of Ln_2O_3 was complete in about 3 hr. As soon as stage (*b*) was reached, the temperature was generally increased to *ca.* 2100° to accelerate passage of (*b*) and (*c*) stages.

When cool, the product was a crystalline, yellow button containing excess of carbon, most of which, derived from the crucible, was separated, after crushing, by levigation with anhydrous kerosene or benzene. (Complete absence of water is necessary to avoid hydrolysis.) After removal of gross free carbon, the carbide was washed twice with anhydrous acetone, twice with ether, and then stored in evacuated tubes. Rate of hydrolysis with water, either directly or derived from the atmosphere, increases with decreasing size of the carbide granules, and it was undesirable to reduce this below about 100 mesh.

The carbides were analysed (Table 1) by dissolution in dilute acid, removal of remaining free carbon by filtration, and precipitation of the rare-earth content as oxalate followed by ignition to oxide. Scandium carbide is somewhat refractory to this treatment; it hydrolyses and dissolves in acid much less readily than do the other rare-earth carbides; also, it is greyish-black whereas, for example, LaC_2, GdC_2, and YC_2 are brassy yellow.

X-Ray diffraction patterns were taken on a G.E. XRD powder camera with a radius of 14·32 cm. in Cu-K_α radiation, with a nickel filter, at 50 kv and 16 mA. The exposure time was 5 hr. which gave generally satisfactory results for most carbides. Adequate patterns for samarium and gadolinium carbides were obtained only with Mo-K_α radiation, since the absorption spectra and edges of the carbides differ markedly from those of the corresponding metals or oxides. Data for *X*-ray absorption spectra suggest gross perturbation of the *K* and *L* levels of the rare-earth ions on carbide formation (see Part III).

In general, *X*-ray studies showed the lanthanon and yttrium carbides to be tetragonal; cell constants and derived densities are listed in Table 1, together with densities determined pyknometrically against anhydrous *p*-xylene.

The liquefaction and reconsolidation observed during reaction, coupled with the appearance of carbide ingots, suggested formation of an intermediate of lower m. p. than the final carbide. This could be postulated as due to (*a*) melting of the oxide, (*b*) intermediate formation of a lower carbide of low m. p., or (*c*) intermediate production of metal. Supplementary direct observations in the resistor furnace showed that the final carbide was formed at temperatures below the m. p. of the oxide and that of the higher carbide but above that of the metal (Table 2).

Spedding *et al.*[4] have reported a eutectic in the La–C system, *viz.*, La_4C, melting at *ca.* 840° c; they employed metal as one reactant, however, and we could not obtain this quadricarbide in oxide–carbon systems. Instead, experiments in which Ln_2O_3–C mixtures were quenched just at the liquefaction point showed the presence of reguli, identifiable by *X*-ray and chemical examination as rare-earth metal.

Mixtures of rare-earth metals, and oxides with the carbon required for higher carbide stoicheiometry, yielded, when heated under the conditions given above, a metallic-looking carbide which, on levigation from the mass, was reheated *in vacuo*. A vapour was produced, and the carbide granules crumbled to a fine powder. The vapours condensed in thin films shown by *X*-ray and chemically to be rare-earth metal, on cool molybdenum surfaces. The residual powders were shown similarly to be LnC_2 carbides, whereas chemical examination of the primary product gave Ln contents higher than required for, *e.g.*, LnC, although *X*-ray patterns showed little difference from the LnC_2 pattern. The rare-earth carbides thus appear somewhat analogous to those of uranium, in which similar interstitial behaviour is observed.

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HORIZONS INCORPORATED, CLEVELAND 4, OHIO, U.S.A.
[Present address (R. C. V.): STANFORD RESEARCH INSTITUTE,
SOUTHERN CALIFORNIA LABORATORIES,
S. PASADENA, CALIFORNIA.]

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