345. *Chemical and Magnetic Properties of Lanthanum Dicarbide and Sesquicarbide.*

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Lanthanum dicarbide and sesquicarbide have been prepared by heating lanthanum dihydride with the stoicheiometric amounts of graphite. The dicarbide is diamagnetic and the sesquicarbide very slightly paramagnetic, indicating almost complete delocalization of the extra valency electrons in a conduction band. Reactions of the carbides with a variety of reagents have been studied and compared with the corresponding reactions of calcium carbide, the gaseous products being identified and quantitatively determined by infrared spectroscopy and gas–liquid chromatography.

LANTHANUM DICARBIDE is isostructural with calcium carbide [1] and has been formulated as an ionic acetylide. As lanthanum ($5d^1 6s^2$) is normally tervalent, interest in the compound centres on the position of the third valency electron and on the influence of this electron on the chemistry of the compound. Three possibilities have been considered for the ground-state configuration of the compound: (*a*) the electron is localized on the lanthanum ion, giving rise to a bivalent acetylide $La^{2+}C_2^{2-}$; (*b*) the electron is localized in an antibonding orbital of the acetylide ion, giving $La^{3+}C_2^{3-}$; (*c*) the electron, e, is delocalized in a conduction band of the crystal, $La^{3+}C_2^{2-} + e$. Model (*a*) would explain the similarity in structure to calcium carbide, $Ca^{2+}C_2^{2-}$, and the fact that a variety of hydrocarbons rather than pure acetylene is evolved on hydrolysis.[2] Model (*b*) would explain the C–C distance, which is intermediate between those characteristic of a double and a triple bond.[3] However, both are inconsistent with the observed metallic conductivity of the dicarbide which approaches that of lanthanum itself.[4] It is clear that model (*c*) is an important component of the electronic state of the crystal, but the conductivity, by itself, does not rule out some admixture of the states (*a*) and (*b*). The crucial test is the

[1] Von Stackelberg, *Z. phys. Chem.*, 1930, *B*, **9**, 437.
[2] Wells, " Structural Inorganic Chemistry," Oxford University Press, 2nd edn., 1950.
[3] Atoji, Gschneidner, Daane, Rundle, and Spedding, *J. Amer. Chem. Soc.*, 1958, **80**, 1804.
[4] Spedding, Gschneidner, and Daane, *Trans. Met. Soc., A.I.M.E.*, 1959, **215**, 192; *J. Amer. Chem. Soc.*, 1958, **80**, 4499.

magnetic susceptibility since (*a*) and (*b*), which involve localized unpaired electrons, must confer some paramagnetism on the crystal whereas model (*c*) is essentially diamagnetic.

Lanthanum sesquicarbide, La_2C_3, also contains C_2 units in its structure [3] and has a conductivity approximately two-fifths that of metallic lanthanum.[4] Similar possibilities can be envisaged for its electronic structure and again it is clear that any tendency towards localization of electrons on either the lanthanum or the acetylide ion would lead to paramagnetism. The magnetic measurements reported in this paper were undertaken to determine whether such localization occurs.

Lanthanum dicarbide was first prepared [5] by heating lanthanum sesquioxide with carbon in an electric furnace, and most subsequent investigators have used this procedure or modifications of it,[1,6-9] although the product is invariably contaminated with oxide or carbon. The dicarbide has also been prepared by direct reaction of metallic lanthanum and carbon in an arc furnace under helium or argon.[4] The sesquicarbide has only recently been reported; [3] it was made from the elements at temperatures below its incongruent m. p., 1415°. The hydride method used in the present work, though a standard procedure for preparing carbides, has not previously been used for the carbides of lanthanum.

The chemistry of the two carbides has previously been little studied. The products of hydrolysis by water or dilute acid have been investigated, with varying results, by conventional gas analysis and by mass spectroscopy (see Discussion). In addition, reactions of the dicarbide with several non-metallic elements and their derivatives have been studied at high temperatures, though the products were not always identified.[6,10]

We have used infrared spectroscopy and gas–liquid chromatography to analyse the products of hydrolysis of calcium carbide and the carbides of lanthanum by $4N$-sulphuric acid and $2N$-nitric acid. Other protonic reagents studied were anhydrous sulphuric acid, chlorosulphonic acid, and liquid ammonia. The reaction of the three carbides with molten iodine was also investigated.

RESULTS

Lanthanum dicarbide formed greyish-yellow metallic-looking crystals, and *X*-ray powder photographs showed the symmetry to be body-centred tetragonal. Lattice constants were $a_0 = 3.935 \pm 0.005$, $c_0 = 6.750 \pm 0.005$ Å, in good agreement with the most accurate published data.[3] Lanthanum sesquicarbide formed brassy-yellow crystals which were indexed as body-centred cubic with $a_0 = 8.810 \pm 0.005$ Å (lit.,[3] 8.817 ± 0.003 Å). When heated above its incongruent m. p., the sesquicarbide disproportionated and, in an experiment at 2200°, metallic lanthanum volatilized continuously from the specimen leaving, eventually, the pure dicarbide: $2La_2C_3 = La + 3LaC_2$.

The magnetic susceptibilities (in units of 10^{-6} e.m.u. per mole) as measured by the Gouy method at room temperature were: $LaC_2 - 7.17$, $LaC_{1.5} + 25.1$, $LaH_{2.16} + 49.4$. These can be compared with published values for the paramagnetic susceptibility of metallic lanthanum, *viz.*, $+96$ [11] and $+101$.[12] Absence of ferromagnetic impurities was confirmed by variation of the magnetic field.

The reaction of lanthanum dicarbide with deaerated $4N$-sulphuric acid at room temperature was vigorous and exothermic. The gases evolved consisted mainly of acetylene, hydrogen, and ethylene, together with traces of carbon dioxide and methane as shown in Table 1. The higher hydrocarbon fraction contained virtually no C_3 compounds and was mainly C_4 hydrocarbons (Table 2). In addition to the gaseous products, which contained 1.46 g.-atoms of carbon per mole of LaC_2, a further 0.56 g.-atom of carbon was precipitated as the element,

[5] Pettersson, *Ber.*, 1895, **28**, 2419.
[6] Moissan, " The Electric Furnace," Chem. Publ. Co., Easton, Pa., 2nd edn., 1920.
[7] Damiens, *Compt. rend.*, 1913, **157**, 214; *Ann. Chim. (France)*, 1918, **10**, 137.
[8] Villelume, *Compt. rend.*, 1950, **231**, 1497; 1951, **232**, 235.
[9] Vickery, Sedlacek, and Ruben, *J.*, 1959, 498.
[10] Delépine, *Thèse Pharmacie, Paris*, 1904, as quoted by Pascal, " Nouveau Traité de Chimie Minérale," Vol. VII, p. 857, Masson et Cie, Paris, 1959.
[11] Stalinski, *Bull. Acad. polon. Sci., Classe III*, 1957, **5**, 997.
[12] Lock, *Proc. Phys. Soc.*, 1957, **70**, B, 566.

making 2·02 g.-atoms in all. The material balance on carbon (involving 150 mg. in a typical experiment) was therefore correct to 1%; this confirmed the infrared and chromatographic methods used to analyse the complex mixture of products, and also indicated the degree of absolute accuracy obtained.

Lanthanum sesquicarbide reacted even more vigorously with 4N-sulphuric acid and more carbon was precipitated (1·14 g.-atoms per mole of La_2C_3). Table 1 shows that the gases

TABLE 1. *Gaseous products of hydrolysis (volume %).*

System	H_2	CH_4	C_2H_2	C_2H_4	Higher hydrocarbons	CO	CO_2	N_2O	NO
LaC_2–H_2SO_4	17·9	0·2	68·3	8·9	4·2	—	0·4	—	—
La_2C_3–H_2SO_4	47·1	2·0	36·6	5·6	1·3	5·6	1·8	—	—
LaC_2–HNO_3	3·4	—	59·0	3·1	1·7	—	0·5	19·2	13·2
La_2C_3–HNO_3	16·4	1·4	50·3	3·8	7·6	—	0·3	16·9	3·6

TABLE 2. *Composition of the higher hydrocarbon fractions (volume %).*

System	C_3	Butane	But-1-ene	But-2-ene cis	But-2-ene trans	Buta-1,2-diene	Buta-1,3-diene	But-1-yne
LaC_2–H_2SO_4 ...	3·0	7·9	1·3	13·1	9·8	4·6	55·8	4·6
LaC_2–HNO_3 ...	2·6	2·6	8·0	5·5	8·0	2·6	70·8	—
La_2C_3–HNO_3 ...	26·6	4·4	3·4	6·2	4·4	1·3	49·4	4·2

evolved contained proportionately more hydrogen and less acetylene than the hydrolysis products from the dicarbide and there was also an appreciable amount of carbon monoxide, The higher hydrocarbons, which comprised 1·3% of the gases evolved, contained propane. propene, butane, but-1-ene, *cis*- and *trans*-but-2-ene, and traces of two other hydrocarbons. In all, the gaseous products contained 1·95 g.-atoms of carbon per mole of La_2C_3, making a total of 3·09 g.-atoms. In a control experiment, technical grade calcium carbide (containing calcium oxide as impurity) was hydrolysed with 4N-sulphuric acid under the same conditions; the reaction was much less vigorous and acetylene was evolved quantitatively. There was no other hydrocarbon, no oxides of carbon, and no hydrogen, nor was free carbon precipitated.

The products of hydrolysis of the lanthanum carbides are not independent of the aqueous acid used. For example, Table 1 indicates that hydrolysis of the dicarbide with 2N-nitric acid results in the evolution of considerable amounts of nitrous oxide and nitric oxide, and that this is accompanied by a reduction in the amount of hydrogen and ethylene evolved. The effect is only slightly less marked with the sesquicarbide; but, with calcium carbide, only acetylene and carbon dioxide (0·3% by volume) were evolved and there was no trace of oxides of nitrogen or of free carbon. The composition of the higher hydrocarbon fractions is summarized in Table 2. Butadiene is again seen to be the main constituent and, in the case of the sesquicarbide, the C_3 fraction is prominent, forming 26·6% of the higher hydrocarbons and therefore 2% of all the gaseous products of hydrolysis (cf. 0·04% of C_3 obtained on hydrolysis of the dicarbide with nitric acid). Less free carbon was precipitated in the nitric acid hydrolyses than in the sulphuric acid hydrolyses; the dicarbide gave 0·41 g.-atom of carbon per mole of LaC_2 and the sesquicarbide 0·73 g.-atom per mole of La_2C_3.

Anhydrous sulphuric acid reacted differently from the aqueous acid. At room temperature, calcium carbide gave a gas consisting of acetylene (98%) together with traces of carbon dioxide and sulphur dioxide. The amount of acetylene evolved corresponded to 89% of the carbon in the carbide, the rest being precipitated as free carbon. Reaction with lanthanum dicarbide was much slower and, after 30 min., only 5% of the C_2 units had reacted to give acetylene. A small amount of hydrogen was also evolved but no other gases were detected. The reaction appeared to be retarded by the formation of an insoluble film of lanthanum sulphate on the carbide. Control experiments indicated that the sulphate was moderately soluble in hot anhydrous sulphuric acid and could, in fact, be recrystallized from this solvent. Accordingly a reaction was run at 100°; gas was evolved over a period of 5 hr. after which time 35% of the carbide remained unchanged. The gas proved to be pure sulphur dioxide, all the carbon that reacted appearing as the free element or tar. Lanthanum sesquicarbide reacted rather more vigorously. The initial gases evolved were acetylene and hydrogen together with a trace of sulphur dioxide, but when the reaction had proceeded for 3 days (after which time 25% of the

3 N 2

carbide remained unchanged) only hydrogen and sulphur dioxide were detected. Small amounts of water in the sulphuric acid had no apparent effect on any of these reactions, the products from 99·8% and 96% sulphuric acid being the same as those from the 100% acid.

It was shown in separate series of experiments that acetylene reacted slowly with anhydrous sulphuric acid at room temperature to give sulphur dioxide as the only gaseous product; the reaction was faster at 100°, being complete in about 15 hr. This suggests that the sulphur dioxide appearing in the above reactions arose from the reduction of sulphuric acid by acetylene rather than from the direct reaction of sulphuric acid with the carbide, *e.g.*, $2LaC_2 + 6H_2SO_4 =$ $La_2(SO_4)_3,6H_2O + 4C + 3SO_2$. The actual composition of the gases evolved depended on the temperature, and on the rate of removal of the products under vacuum from the reaction region. The absence of ethylene, even in the cold, does not necessarily imply that this gas was not formed initially since it is rapidly absorbed by anhydrous sulphuric acid and would not be expected to be evolved.

Chlorosulphonic acid reacted extremely vigorously with technical grade calcium carbide, but only slowly and incompletely with the carbides of lanthanum. With calcium carbide the main volatile product (87%) was hydrogen chloride, but acetylene, carbon monoxide, carbon dioxide, carbon oxysulphide, and sulphur dioxide were also produced in amounts which depended on the reaction temperature. Thus, when the reaction rate was moderated by intermittent cooling at −78°, the amount of acetylene evolved was more than doubled, but only two-thirds of the amount of carbon dioxide and sulphur dioxide, one-seventh of the amount of carbon oxysulphide and no carbon monoxide were formed. It was clear that acetylene was undergoing a secondary reaction with the chlorosulphonic acid and it was established that pure acetylene, when treated with chlorosulphonic acid at 100°, rapidly charred and evolved a mixture of the above gases. The formation of carbon oxysulphide is noteworthy.

By contrast, there was little reaction between chlorosulphonic acid and lanthanum dicarbide, and the presence of lanthanum oxide failed to accelerate the reaction. At 100° hydrogen chloride, sulphur dioxide, and small amounts of carbon dioxide and carbon oxysulphide were formed but no acetylene was evolved. When the excess of chlorosulphonic acid was removed and fractionated, more hydrogen chloride and sulphur dioxide were obtained, and also a trace of acetylene, equivalent to 0·5% of the C_2 units in the carbide. The residue contained free carbon, unchanged carbide, and lanthanum sulphate, but no chloride. In this, lanthanum dicarbide differed from calcium carbide which gave a residue of calcium chlorosulphonate. The reaction of lanthanum sesquicarbide with chlorosulphonic acid was slow and incomplete. After 3 hr. at 100°, 40% of the carbide remained unchanged; only hydrogen chloride and sulphur dioxide were evolved and all the carbon in the carbide which had reacted appeared as the free element.

The reaction of the carbides with molten iodine in a sealed tube at 190° provides a further example of differing reactivities. After 5 hr., calcium carbide had reacted completely to give calcium iodide and tetraiodoethylene, C_2I_4, m. p. 187°, whereas the carbides of lanthanum reacted only to the extent of about 40%, the products being yellow crystals of anhydrous lanthanum tri-iodide and free carbon. No iodides of carbon were produced. The smooth reaction of calcium carbide with molten iodine also contrasts with the reaction of this compound with the other halogens. Thus, there was no reaction with liquid chlorine at −35° or with gaseous chlorine at room temperature though at 200° an exothermic reaction occurred which produced calcium chloride and free carbon quantitatively. With molten iodine monobromide at 100° there was 25% reaction to give free carbon, but no carbon–halogen compounds were detected. Liquid bromine, after 6 weeks at room temperature, gave a small amount of hexabromoethane. The reactions of bromine and iodine with calcium carbide confirm the observations by Biesalski and von Eck.[13]

Liquid ammonia was investigated as a typical basic protonic solvent but appeared to be unreactive; for example, lanthanum dicarbide when sealed with liquid ammonia in a glass bomb showed no reaction after three months at room temperature.

DISCUSSION

In addition to the well-known lanthanum dicarbide, the recently reported sesquicarbide [3,4] has been confirmed. There was no evidence for a third carbide, LaC,[9] the

[13] Biesalski and von Eck, *Z. angew. Chem.*, 1928, **41**, 741.

X-ray powder pattern for which suggests that it is an interstitial solution of lanthanum in the dicarbide.

Interpretation of the magnetic-susceptibility measurements involves an estimate of the inherent diamagnetism of the ions present. The two most recent values for the diamagnetic susceptibility of lanthanum sesquioxide (in units of 10^{-6} e.m.u.) are -39 [14] and -46 [11] per mole of $LaO_{1.5}$ and these, together with the accepted value of -11.25 for the susceptibility of the oxide ion,[15] lead to values of -22.1 and -29.1 for the susceptibility of the La^{3+} ion. The mean of these figures is close to the theoretical value of -27.1,[15] and this is preferred to the currently accepted value of *ca.* -20.[16] The diamagnetic susceptibility of the acetylide ion, $(C\equiv C)^{2-}$, can be calculated from the value for two carbon atoms (-12.0) together with a correction for the triple bond and the two negative charges. The value for the triple bond is usually taken to be $+0.8$ but, when two negative charges are also present on the ion, $+0.3$ has been considered more appropriate,[17] leading finally to -11.7 for the susceptibility of the acetylide ion. The total correction for the inherent diamagnetism of lanthanum dicarbide is thus $+38.8$, which converts the experimental value of -7.2 into a weak paramagnetic susceptibility of $+31.6$. This can reasonably be ascribed to a delocalized valency electron and is negligibly small when compared with the value of *ca.* $+1250$ expected for the bivalent ion La^{2+} (cf. also the values of $+96$ [11] and $+101$ [12] for the paramagnetism of metallic lanthanum which has three delocalized electrons).

Similarly, the corrected value for lanthanum sesquicarbide is $+61.0 \times 10^{-6}$ e.m.u. per mole of $LaC_{1.5}$, again indicating delocalization of the extra 1.5 electrons per lanthanum atom. These conclusions are consistent with the known metallic conductivity of the two carbides [4] and establish the fact that any localization of the supernumerary electrons must be less than 1% of their total concentration. Such localization cannot, therefore, be invoked to explain either the variations in C–C bond length [3] or the complexity of the hydrolysis products.[2,9]

The products obtained by hydrolysis of the carbides might be expected to reflect the presence of the C_2 units in their structure. Calcium carbide yields pure acetylene and it seemed possible that the variety of products reported to be obtained from lanthanum dicarbide resulted from the reducing influence of the extra valency electron. Pettersson [5] first observed that hydrocarbons were evolved but failed to identify them. Moissan [6,18] stated that the products were methane (27.9%), ethylene (1.5%), and acetylene (71.0%) together with a small residue of liquid and solid hydrocarbons, but Damiens,[7] in a more detailed study, reported the presence of hydrogen and the absence of methane. His gaseous products comprised hydrogen (10%), ethane (12.5%), higher paraffins (1.6%), ethylene (6.7%), higher olefins (2.0%), and acetylenes (67.2%). The work of Villelume [8] on the reaction of lanthanum dicarbide with steam at temperatures up to 500° is not comparable with these earlier investigations because of the occurrence of cracking and polymerization reactions amongst the products. The results for 4N-sulphuric acid in Table 1 tend to confirm Damiens's results rather than Moissan's, though there was a trace of methane and no ethane. The production of hydrogen, acetylene, ethylene, and C_4 hydrocarbons and the virtual absence of methane and C_3 hydrocarbons is consistent with the following sequence of reactions: Water molecules are oriented with the oxygen lone-pair electrons towards the La^{3+} ions. Two of each three water molecules then undergo proton transfer to the acetylide ion, the proton from the third molecule combining with an electron from the conduction band to give nascent hydrogen:

$$LaC_2 + 3H\cdot OH = La(OH)_3 + C_2H_2 + [H]$$
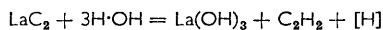
Most of the acetylene and hydrogen is evolved at this stage, these gases comprising 86.2%

[14] Blanchetais, Thesis, Paris, 1954.
[15] Angus, *Proc. Roy, Soc.*, 1932, *A*, **136**, 569.
[16] Landolt–Börnstein's Tabellen.
[17] Vickery, Sedlacek, and Ruben, *J.*, 1959, 503.
[18] Moissan, *Compt. rend.*, 1898, **127**, 911.

of the volatile products. However, some of the acetylene is reduced by the nascent hydrogen to ethylene before being evolved, though none is reduced as far as ethane. In addition, partial reduction of acetylene to the vinyl radical, $CH_2=CH\cdot$ accounts for the presence of C_4 and the virtual absence of C_3 units in the products. Thus dimerization of the vinyl radical gives buta-1,3-diene, which is the major component of the higher hydrocarbons. However, some of the butadiene is completely reduced to butane, whilst 1,2-addition of hydrogen produces but-1-ene and 1,4-addition gives *cis*- and *trans*-but-2-ene. It is hard to devise a convincing mechanism for the formation of the small amount of carbon dioxide (0·4%). It was not present in the reagents and any explanation must also account for the presence of this gas (1·8%) and carbon monoxide (5·6%) in the hydrolysis products of lanthanum sesquicarbide.

The only reference to the hydrolysis of the sesquicarbide [3] states that about 50% of the gas evolved was acetylene, that the amount of hydrogen liberated was $2\frac{1}{2}$ times that obtained from the dicarbide, and that small amounts of propane, propene, and propyne were formed. Our results with 4N-sulphuric acid were that 36·6% of the evolved gas was acetylene and that, per mole of LaC_2 and $LaC_{1\cdot5}$, the sesquicarbide gave three-fifths of the amount of acetylene and 3·06 times the amount of hydrogen. In addition, small amounts of propane and propene were found, but no propyne. The formation of the C_2 and C_4 hydrocarbons is consistent with the sequence of reactions outlined in the previous paragraph. The presence of 2% of methane may be a consequence of the fact that the C–C bond in the sesquicarbide (1·32 Å) is longer than that in the dicarbide (1·28 Å) and is therefore more easily ruptured during the vigorous reaction. This would also explain the presence of C_3 hydrocarbons ($C_2 + C_1$) and the greater deposit of free carbon from the sesquicarbide.

Reactions with 2N-nitric acid were investigated after it had been found [19] that this reagent was reduced to lower oxides of nitrogen by uranium carbide. The reaction apparently depends on the presence of a metal in a lower oxidation state or the evolution of nascent hydrogen, since calcium carbide yielded only acetylene and a trace of carbon dioxide and did not reduce the nitrate ion. Reduction of nitric acid by lower-valent cations or nascent hydrogen is well known,[20] and, depending on conditions the products may contain nitrogen dioxide, nitric oxide, nitrous oxide, nitrogen, ammonium ions, or hydrazine. However, unless the acid is fairly concentrated or is heated, reaction is normally very slow, though the standard redox potentials for all these reactions are favourable.[21] The reduction of dilute nitric acid in the cold by the carbides of lanthanum is therefore unusually rapid, and the absence of nitrogen and nitrogen–hydrogen compounds from the products is also exceptional. The decrease in the amount of hydrogen and ethylene evolved when nitric rather than sulphuric acid is used for hydrolysis (see Table 1) can be understood in terms of the simultaneous reactions competing for nascent hydrogen. Thus, with dilute sulphuric acid, nascent hydrogen either is evolved as molecular hydrogen or is used to reduce the acetylene to ethylene and other products, but with nitric acid some of the nascent hydrogen is used in reducing the nitrate ions and less is available for reduction of acetylene or evolution of molecular hydrogen.

Secondary reactions also complicate the interpretation of the results obtained with anhydrous sulphuric acid and chlorosulphonic acid. The complexity is illustrated in the case of chlorosulphonic acid by the formation of carbon oxysulphide in addition to free carbon and the oxides of carbon; moreover, despite the release of large volumes of hydrogen chloride, no sulphur trioxide was detected even after evaporation of the excess of chlorosulphonic acid. As with anhydrous sulphuric acid the principal reduction product of the acid was sulphur dioxide.

[19] Toogood, unpublished observations in this laboratory.
[20] Gmelin's " Handbuch der Anorganischen Chemie," Syst. No. 4, " Stickstoff," Verlag Chemie, G.m.b.H., Weinheim/Bergstrasse, 1936.
[21] Latimer, " The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, New York, 1938.

EXPERIMENTAL

Compounds were handled either in a vacuum-frame or in a glove box which incorporated a wafter motor to circulate the oxygen-free nitrogen atmosphere continuously through a drying train containing phosphorus pentoxide.

Temperatures up to 1200° were obtained by a nichrome-wound silica furnace lagged with asbestos powder. Higher temperatures were obtained by means of a Radyne portable induction furnace. The temperature was measured on a chromel–alumel thermocouple (0—1200°) or by an optical pyrometer (up to 2200°).

X-Ray powder photographs were taken with a Unicam 9 cm. powder camera and copper-K_α radiation. Specimens for magnetic measurements were ground to a fine powder and compressed in a glass tube (5 × 40 mm.) which was closed at each end by glass plates sealed on with picein wax. The susceptibilities were kindly measured by Mr. R. Barnard of the Physics Department.

Lanthanum metal (Johnson Matthey and Co.) was 99·99% pure. Graphite powder was Harwell's grade A. Hydrogen was generated by heating degassed lithium aluminium hydride to 150°. The calcium carbide used in the control experiments was of commercial grade; on the basis of analysis for carbon (acetylene) and calcium (EDTA) the material contained 80% of CaC_2, the main impurity being calcium oxide. Anhydrous sulphuric acid was prepared as previously described.[22] Chlorosulphonic acid (b. p. 150—152°) was purified by fractionation at atmospheric pressure. Iodine monobromide was synthesized directly from the elements.

Lanthanum dihydride was prepared by warming lanthanum in the presence of the correct amount of hydrogen. Absorption was rapid at 40—50° provided that care was taken to avoid the formation of an oxide film on the metal. Samples were then annealed at 300° for 48 hr. before being ground. The hydride was pyrophoric and scrupulous care was necessary to avoid contact with oxygen. Powder photographs confirmed that the compound was face-centred cubic with $a_0 = 5\cdot660 \pm 0\cdot002$ Å (lit., 5·667,[23] 5·658 [24]).

Lanthanum sesquicarbide was prepared from accurately stoicheiometric amounts of lanthanum hydride and graphite. The two powders were ground together in an agate mortar for 30 min. and then slowly heated to 1000° in a previously degassed silica tube. Hydrogen, which was gradually evolved, was allowed to accumulate in the reaction system until a maximum pressure had been attained. There was no evidence from infrared spectra or molecular-weight determinations for the presence of hydrocarbons in the hydrogen evolved. The sample was then annealed at 1000° at 10^{-5} mm. Lanthanum dicarbide was prepared similarly, after which it was crushed, placed in a degassed graphite crucible, and heated to 2200° under a high vacuum. The sample did not melt but changed colour from dark grey to a metallic yellow, indicating that sintering had occurred.

Reactions of the carbides were carried out on a vacuum-frame which incorporated a constant-volume manometer, Töpler pump, molecular-weight bulbs, and fractionating traps. The reaction system consisted of a tipping unit which could be rotated in a vertical plane about a ground-glass joint to bring the reactants into contact, the unit having previously been charged with known weights of carbide and reagent in the glove box.

Because of the small quantities of material used in each reaction and the complexity of the hydrocarbon mixtures involved, conventional gas analysis would have been both complicated and incapable of identifying all the gases present. A simple method of analysing the various gaseous fractions was therefore developed, by using a combination of infrared spectroscopy and gas–liquid chromatography. Spectra were normally obtained on a Perkin–Elmer Infracord instrument in the range 667—4000 cm.$^{-1}$, but when higher resolution or more accurate wave numbers or intensities were required a Unicam S.P. 100 spectrometer was used. Authentic samples of each gas were obtained and spectra measured at various pressures. Suitable bands were selected and calibration graphs drawn to relate pressure to absorbance (log scale). These graphs normally comprised 6—10 points and were accurately linear. It was found that absorbance varied slightly with the presence of other gases and it was necessary to run calibrations on synthetic mixtures approximating to the composition of the products. In some mixtures absorption bands of two components overlapped to some extent and this necessitated the use of non-overlapping bands in other regions. For example, the strong band in nitrous oxide at

[22] Greenwood and Thompson, *J.*, 1959, 3474.
[23] Holley, Mulford, Ellinger, Koehler, and Zachariasen, *J. Phys. Chem.*, 1955, **59**, 1226.
[24] Stalinski, *Bull. Acad. polon. Sci., Classe III*, 1955, **3**, 613.

1285 cm.$^{-1}$ is superimposed on the strong acetylene band at 1328 cm.$^{-1}$. Table **3** summarizes the absorption bands selected and the pressure range in which each band was used.

TABLE 3. *Infrared spectra for analysis.*

Gas	Absorption band (cm.$^{-1}$)	Pressure range (mm.)	Gas	Absorption band (cm.$^{-1}$)	Pressure range (mm.)
C$_2$H$_2$	729	0—10	CO$_2$	2349	0—40
	3287	10—60		3660	40—80
	1328	10—100	SO$_2$	1361	0—20
C$_2$H$_4$	949	0—20		1151	20—60
	1444	20—50	COS	2051	0—12
CH$_4$	1306	0—24	N$_2$O	2224	0—50
HCl	2960	0—400		2564	0—200
	2886	0—400	NO	1876	0—300
CO	2143	0—400			

The gases listed in Table **3** were obtained from cylinders and purified by fractionation in the vacuum-line or were prepared by standard procedures.   Carbon oxysulphide was prepared by adding aqueous potassium thiocyanate to concentrated sulphuric acid.[25]

Gas–liquid chromatographic separations were obtained by using instruments constructed in this Department and we are indebted to Dr. T. F. Palmer and Mr. J. H. Morris for their assistance.   The stationary phases used were squalane, dimethylsulpholane, and 2,2'-diethoxy-diethyl ether–silver nitrate.

[25] Bartunck and Barker, *Phys. Rev.*, 1935, **48**, 516.