CHROMATOGRAPHIC STUDIES ON THE HYDROLYSIS OF CARBIDES

PART I. THE PREPARATION
AND HYDROLYSIS OF RARE EARTH DICARBIDES

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INTRODUCTION

PETTERSON[1] first prepared the dicarbides of lanthanum and yttrium in an electric arc-furnace from the oxides by reduction with carbon. $(M_2O_3 + 5C \rightarrow MC_2 + 3CO)$ MOISSAN's pioneering observations[2-5] in this field have stimulated many examinations (some detailed), of the preparation of the carbides of the rare-earth elements.

By 1900 MOISSAN had prepared the following:
  (i) yttrium dicarbide by reducing yttria with carbon[2],
 (ii) lanthanum dicarbide by reducing the oxide with sugar charcoal[3],
(iii) cerium dicarbide by reducing the dioxide with sugar charcoal[4],
 (iv) praseodymium, neodymium, and samarium dicarbides by reducing their oxides with graphite[5,6] in an electric arc furnace.

In a similar electrolytic process, using carbon rods immersed in cerium dioxide in a copper crucible, cerium dicarbide was prepared[7]. STERBA[8] suggested that the reduction of cerium dioxide by carbon at high temperatures proceeds via the intermediate $CeC_2 \cdot 2CeO_2$, which was claimed to be produced after one minute of heating. DAMIENS[9] later denied the existence of this compound, stating it to be a mixture of carbides and oxides of cerium. The existence of a carbide CeC_3 has more recently been reported by WARF[10], but again denied by SPEDDING, GSCHNEIDER AND DAANE[11]. It seems most likely that the reaction proceeds with a step involving such a carbide. WARF's compound was probably a mixture of dicarbide in solid solution with excess carbon. A more likely intermediate is the free metal which combines with carbon to form the dicarbide in the final stage of the reaction[12], and preparation must be carried out under vacuum, or in an inert or reducing atmosphere, but not nitrogen[13] (due to formation of a nitride).

Reaction of the metal with graphite can also form the sesquicarbides M_2C_3, a carbide M_3C, as well as the dicarbide[11]. Indeed, ATOJI[14] reports that cerium dicarbide must always contain at least 5 % w/v sesquicarbide. The dicarbide and sesquicarbide of lanthanum have been prepared by reacting the hydride with graphite[15].

The structures of the dicarbides have been found by neutron-diffraction[12] and X-ray methods[11] to be body-centred tetragonal. The carbon–carbon bond lengths are about 1.3 Å, which is longer than in the acetylide ion. The metal atom is also known,

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TABLE I

ANALYSIS OF LIGHT FRACTION OF HYDROLYSIS GASES

	H_2	CH_4	C_2H_2	C_2H_4	CO	CO_2	N_2O	NO	High fraction
LaC_2/H_2SO_4	17.9	0.2	68.3	8.9	—	0.4	—	—	4.2
LaC_2/HNO_3	3.4	—	59.0	3.1	—	0.5	19.2	13.2	1.7

to exist in the trivalent state in the carbide, and the odd electron is assigned to a 5d conduction bond.

MOISSAN's hydrolysis results[2-6] indicate a large percentage (*ca.* 70 %) of acetylene produced from each dicarbide, and the work of DAMIENS[9] confirms this. More recent observations of DE VILLELUME[16] are not in general agreement with these results, although the discrepancy is probably due to catalysis or polymerisation effects at the high temperature (200°C). GREENWOOD AND OSBORN[15] hydrolysed lanthanum dicarbide and sesquicarbides using 4 N nitric and sulphuric acids. The major component found was acetylene and results are given in Tables I and II. Gas chromatography was used to analyse the gases produced.

Lanthanum and cerium dicarbides have been hydrolysed by PALENIK AND WARF[17] (for results see Table III), who reported ethane as well as the other products of GREENWOOD AND OSBORN[15].

TABLE II

ANALYSIS OF HIGH FRACTION OF HYDROLYSIS GASES

	C_3 hydrocarbons	n-C_4H_{10}	1-Butene	2-Butene		1,2-Butadiene	1,3-Butadiene	1-Butene
				cis	trans			
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	—

No figures were reported for non-condensable gases except that they probably amounted to 5 % at room temperature and 15 % at 200°C. Such gases must consist mainly of hydrogen and methane. No solid carbon is reported, and the similarity of results from LaC_2 and CeC_2 lead to the conclusion that the metals in these carbides are in the same oxidation state (III). The solid product of hydrolysis was reported to be amorphous hydroxides showing no X-ray pattern.

In this work, four rare-earth dicarbides have been prepared, and hydrolysed by water and mineral acids at 100°C.

EXPERIMENTAL

Materials

Lanthanum, cerium and yttrium oxides (99.9 % pure); gadolinium and dysprosium oxides (96 % pure) were purchased (New Metals and Chemicals Ltd., London). Neodymium and samarium oxides at least 99 % pure, were isolated from 100 g batches didymium oxide (Thorium Limited, London) using cation-exchange techniques[18,19] and analysed spectrophotometrically[20].

TABLE III
ANALYSIS OF HYDROLYSIS GASES[17]

	LaC_2 25°C	CeC_2 25°C	CeC_2 100°C	CeC_2 200°C
C_2H_6	24.3	19.7	16.3	11.2
C_2H_4	8.45	6.56	4.96	39.6
C_3H_8	0.21	6.03	1.03	13.5
C_3H_6	0.03	0.05	0.53	12.4
n-C_4H_{10}	0.51	6.83	2.32	1.96
C_2H_2	61.5	67.3	63.9	0
1-C_4H_8	1.13	1.39	1.20	1.76
iso-C_4H_8	0	0	0	0.58
Unknown I	0	0	0.37	0.89
$trans$-2-C_4H_8	0.66	0.84	1.49	3.64
cis-2-C_4H_8	0.72	0.87	1.84	3.74
n-C_5H_{12}	0.05	0	0	3.17
Unknown II	0.03	0.03	0.37	0
1,3-Butadiene	0.05	0.07	2.70	3.56
Unknown III	0	0	0	2.38
1,2-Butadiene	0.26	0.22	0.42	1.48
Unknown IV	2.14	2.10	2.51	0

The carbon was coconut charcoal, and was used throughout the preparations. 1.0000 g of this carbon when heated in a muffle furnace for 10 h at 700°C, gave 0.005 g unburnable residue. Charcoal was finely ground in a pestle and mortar, suitable for mixing with the powdered oxides.

Preparation

15 g of the rare-earth oxide was mixed with the stoichiometric weight of carbon, very finely ground together, and pelletted at 3 tons per sq. inch. The pellets were placed in a carbon crucible, in a Wild Barfield/NRC vacuum resistance furnace Model 2904B. After the pressure had dropped to below 0.01 μ the heating cycle was started, and initiation of the reaction noted by the sudden rise in pressure due to the evolution of carbon monoxide. Reaction occurred at temperatures ranging from 1260°C for lanthanum to 1600°C for gadolinium. Samarium oxide would not react at temperatures obtained in the furnace (1900°C), and dysprosium oxide reacted only very slowly.

TABLE IV
ANALYSIS DATA ON YTTRIUM CARBIDE AND FOUR RARE-EARTH DICARBIDES

	% Yield	% Metal		X-ray analysis		
		Found	Theoretical	a_0 (Å)	c_0 (Å)	Structure
YC_2	72.4	82.2	78.8	3.66	6.15	b.c.t.[§] [*]
LaC_2	80.6	85.5	85.3	3.93	6.57	b.c.t.
CeC_2	88.2	84.9	85.4	3.87	6.48	b.c.t. [**]
NdC_2	80.3	86.0	85.7	3.82	6.40	b.c.t.
GdC_2	79.3	87.2	86.7	3.71	6.24	b.c.t.

[§] b.c.t. = body-centred tetragonal (*cf.* ref. 14).
[*] Metal rich. Several lines not indexed, showed presence of other phases, possibly Y_2C_3, YC, and Y_3C.
[**] Two stray lines, most probably due to Ce_2C_3.

Four rare earth dicarbides and an yttrium carbide were prepared, however, and Table IV shows the yields, chemical analysis by oxalate precipitation and the structures as found by X-ray powder analysis. Deposits formed on cooler parts of the furnace, dissolved in dilute hydrochloric acid and were checked by precipitation with oxalate solution. Such deposits accounted for the low yields of products.

Hydrolysis

A simple all-glass apparatus allowed hydrolytic agents (2.5 ml) to be dropped on to 0.5 g carbide in a 5 ml flask at 100°C. The gases so released were passed over a small calcium chloride drying tube, and through a gas sampling valve where 1.4 ml samples were extracted and swept on to a gas-chromatographic column. The column was 25 ft. of 20 % w/w tetra-isobutylene on Silocel 36–60 mesh at 19°C. The detector was a flame-ionization type which could detect components comprising 0.001 % v/v of the mixture[21]. The flow rates of the gases used in the analysis were 40 ml/min for nitrogen, 20 ml/min for hydrogen and 400 ml/min for air. Fig. 1 shows a schematic diagram of the chromatographic unit.
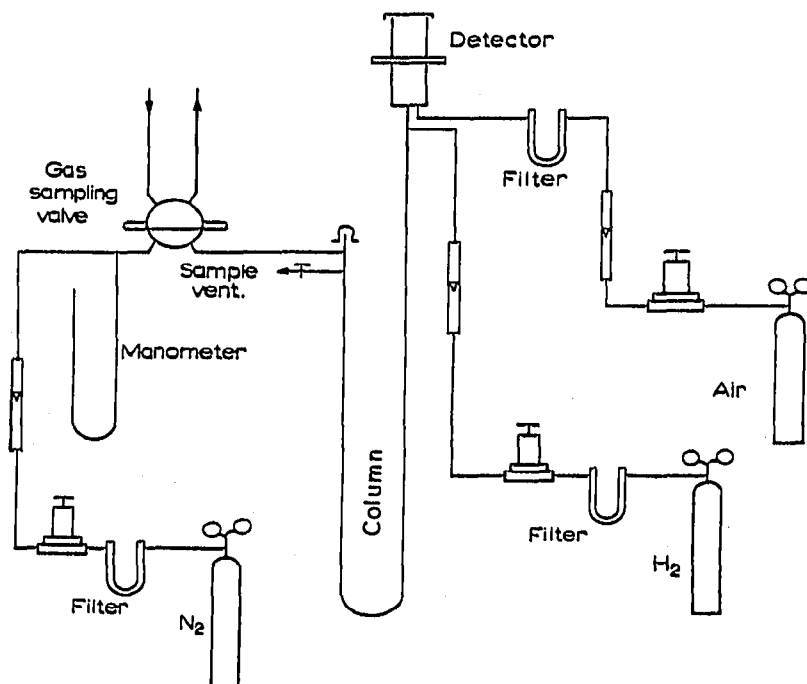

Fig. 1. Schematic diagram of chromatographic analyser unit.

RESULTS

Tables V, VI, and VII show the quantitative breakdown of the hydrolysis products from water, 4 N sulphuric acid, and 4 N nitric acid, respectively, at 100°C, in volume %. Fig. 2 shows the type of elution patterns obtained from lanthanem dicarbide and water, under differing sensitivities.

The data in Table VIII were obtained under the following conditions:

Temperature 19°C; flow rate, hydrogen 21 ml/min, nitrogen 42 ml/min, and air 400 ml/min; inlet pressure 13 p.s.i.; dead time (hydrogen) 3.7 min; column 25 ft. 20 % w/w tetra-isobutylene on Silocel 36–60 mesh.

TABLE V

HYDROLYSIS PRODUCTS FROM WATER AT 100°

Products	LaC_2	CeC_2	NdC_2	GdC_2	$YC_{1.9}$
Hydrogen	.5.64	1.79	2.21	5.07	2.50
Methane	o	0.01	0.28	0.14	4.50
Acetylene	67.72	69.72	66.45	68.23	67.30
Ethylene	7.42	8.67	9.16	8.48	7.15
Ethane	11.13	13.85	12.71	12.35	8.45
C_3H_4	o	o	o	o	0.71
Propylene	0.01	0.01	0.01	0.02	0.93
Propane	0.03	0.06	0.72	0.06	5.07
Isobutane	0.01	0.01	0.03	0.02	o
1-Butene	1.67	0.45	2.08	1.33	1.35
1,3-Butadiene	2.41	1.74	2.69	2.03	0.83
n-Butane	0.36	0.69	0.42	0.51	0.32
trans-2-Butene	0.50	0.87	0.64	0.65	0.34
cis-2-butene	0.55	0.92	0.60	0.65	0.01
1-Butyne	0.22	0.32	0.02	0.03	0.01
1,2-Butadiene	o	0.01	0.03	0.02	o
2-Butyne	o	0.06	0.01	o	o
Others	2.33	0.82	1.94	0.41	0.82

Fig. 3 shows the expected straight-line relationship between log retention time and carbon number for the alkanes and alkenes. Methane is not on the line, since as its short retention time indicates, ideal chromatographic conditions are not realised with this compound. It is also apparent that the true homologue of ethylene and propylene is cis-2-butene and the trans-2-butene, or 1-butene.

It will be noticed in Fig. 4 that retention data are related to boiling points, i.e. the phase separates the gases according to volatility and not structure. Acetylene appears as an exception, having no true boiling point, but subliming at —83.6°C.

TABLE VI

HYDROLYSIS PRODUCTS FROM 4 N H_2SO_4 AT 100°C

| Products	LaC_2	CeC_2	NdC_2	GdC_2	$YC_{1.9}$
Hydrogen	8.52	6.17	2.22	4.76	4.63
Methane	o	0.01	0.64	0.32	4.63
Acetylene	70.10	70.23	63.84	63.04	69.42
Ethylene	7.42	8.11	10.06	10.47	7.36
Ethane	10.92	11.62	13.86	13.46	8.17
C_3H_4	o	o	.o	o	0.36
Propylene	o	0 01	0.01	0.02	0.57
Propane	0.03	0.07	0.57	0.04	2.57
Isobutane	0.01	0.01	0.08	0.01	0.01
1-Butene	0.82	1 03	1.64	1.93	0.77
1,3-Butadiene	0.79	1.18	2.16	2.22	0.55
n-Butane	0.27	0.48	0.35	0.31	0.26
trans-2-Butene	0.41	0.44	0.43	0.42	0.16
cis-2-Butene	0.42	0.48	0.49	0.51	0.34
1Butyn-e	0.17	0.01	0.05	0.05	0.05
1,2-Butadiene	o	o	o	0.02	o
2-Butyne	o	o	0.02	o	o
Others	0.12	0.15	3.58	2.42	0.15
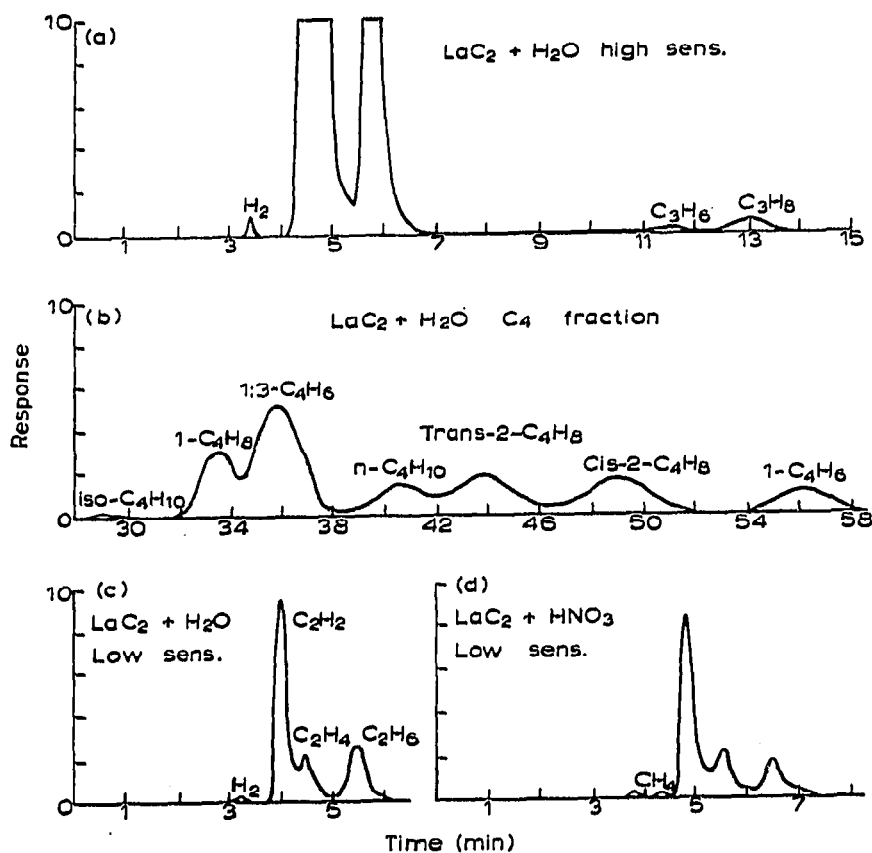
Fig. 2. Elution patterns for the hydrolysis of lanthanum dicarbide with various sensitivities and reagents.
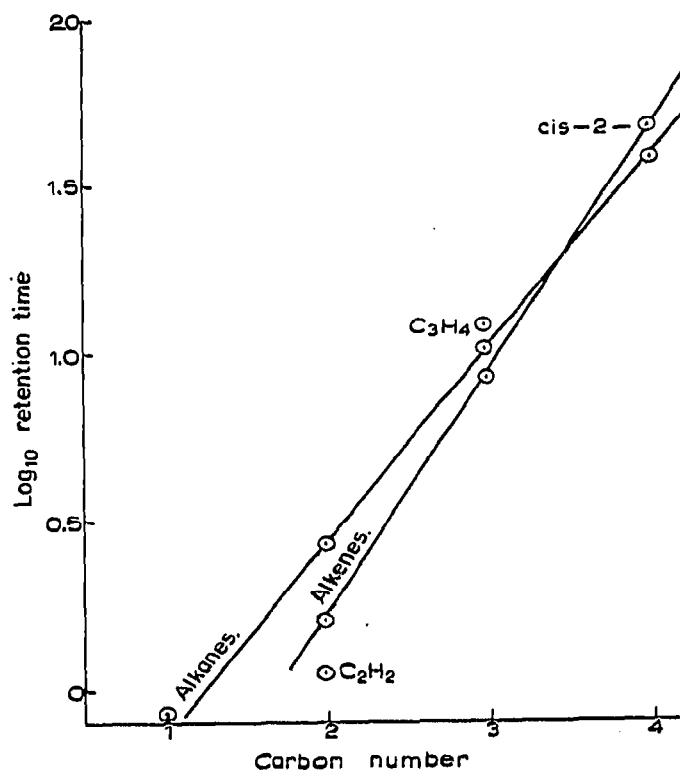
Fig. 3. Relationship between log retention time and carbon number for (i) alkanes and (ii) alkenes.

TABLE VII

HYDROLYSIS PRODUCTS FROM 4 N HNO_3 AT 100°C

Products	LaC_2	CeC_2	NdC_2	GdC_2	$YC_{1.6}$
Hydrogen	4.64	5.78	2.72	2.76	5.86
Methane	1.50	1.79	0.36	0.72	7.53
Acetylene	60.87	58.45	58.80	58.70	50.53
Ethylene	9.81	10.86	10.35	10.45	10.71
Ethane	10.82	9.53	8.67	7.86	7.72
C_3H_4	0	0	0	0	0.36
Propylene	0	0.01	0.01	0.02	0.57
Propane	0.05	0.21	1.14	0.05	4.36
Iso-butane	0.34	0.25	0.53	0.07	0.01
1-Butene	0.28	0.42	1.13	1.15	0.49
1,3-Butadiene	0.72	1.10	1.53	0.78	0.43
n-Butane	0.09	0.04	0.29	0.45	0.17
trans-2-Butene	0.13	0.05	0.42	0.58	0.12
cis-2-Butene	0.20	0.25	0.46	0.54	0.25
1-Butyne	0.14	0.04	0	0.02	0.03
1,2-Butadiene	0	0	0.04	0	0
2-Butyne	0.01	0	0.03	0.01	0.01
Nitrogen oxides	10.40	11.26	13.52	15.84	11.26

Association between acetylene molecules has been postulated. Fig. 4 shows the relationship used to identify the unknown hydrocarbons. The diagrams shows the retention times of the three unknown hydrocarbons coupled with the boiling points of three unsaturated C_4 hydrocarbons. Their intersections are either on or very close to the line, identifying the three as 1-butyne, 1,2-butadiene, and 2-butyne in order of elution.

1,2-Butadiyne has the same boiling-point as 1,2-butadiene (10.3°C) but it was not expected to be present in hydrolysis products which contain some hydrogen initially in a highly active state.
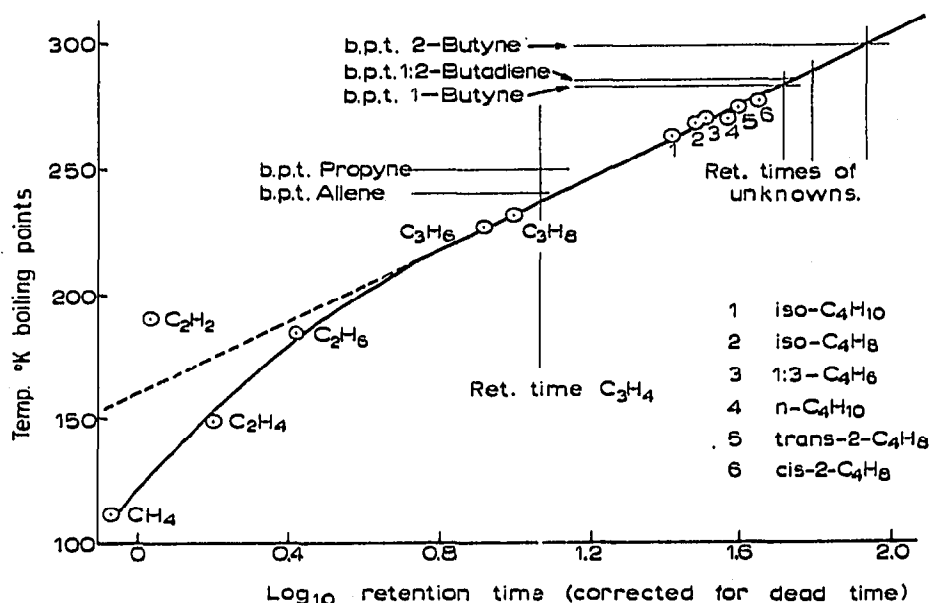

Fig. 4. Relationship between log retention time and boiling point (°K) for the alkanes and alkenes.

TABLE VIII

RETENTION TIMES OF HYDROCARBONS

Hydrocarbon	B.p. (°K)	Corrected retention time (R.T) (min)	$Log_{10}RT$
CH_4	111.7	0.25	0.70
C_2H_2	189.6	1.1	0.04
C_2H_4	149.3	1.6	0.20
C_2H_6	184.9	2.6	0.415
C_3H_6	226.2	8.25	0.92
C_3H_8	231	10.0	1.00
C_3H_4 (?)	—	11.85	1.074
iso-C_4H_{10}	263	26	1.415
1-Butene	26.8	30.3	1.48
1,3-Butadiene	270	32.5	1.51
n-Butane	270	37.1	1.57
trans-2-Butane	274.2	40.0	1.60
cis-2-Butene	276.9	45.1	1.65
1st unknown	—	52.6	1.72
2nd unknown	—	62.0	1.79
3rd unknown	—	87.0	1.94
Isopentane	301	91.0	1.96
n-Pentane	309	123.5	2.09

Another hydrocarbon, probably allene or methyl acetylene was found in the hydrolysis of yttrium carbide. The compound was eluted after propane but the intersections of the retention time with the boiling-points of allene (—32°C) and methyl acetylene (—23.3°C) did not lie on the line; although that due to allene was very close.

DISCUSSION

The results show general agreement with previous observations in this field[15], with close agreement in many instances, and discrepancies in others. Some general comments precede more detailed discussion on the individual carbides.

General comments

Composition of "others". Where water and sulphuric acid were used, this probably consisted of carbon monoxide, carbon dioxide, nitrogen and oxygen. With nitric acid, large quantities of nitric oxide and nitrogen dioxide were released. This is consistent with GREENWOOD AND OSBORN's results on lanthanum carbides[15], although there is a discrepancy over quantities.

Nitric acid. The percentage of C_4 hydrocarbons in the hydrolysis mixture was always less when nitric acid was used. For free radical type of reactions involving collisions of $C_2H \cdot$ radicals with subsequent hydrogenation to form C_4 hydrocarbons, a smaller percentage would be expected since NO is a chain-stopper. Reactions such as:

$$CH_3 \cdot + NO \longrightarrow CH_3NO$$

are well known in free radical reactions[22], and the analogous reaction with ethyl radicals is also known. Thus products such as nitro-compounds might be expected from the hydrolysis of carbides with nitric acid, but the conditions of operation of the

gas chromatography apparatus used for these results would not detect such products. EVERED AND POLLARD[23] have shown that alkyl nitrates and nitroalkanes can be satisfactorily eluted at about 110°C using dinonyl phthalate or squalane as solvents.

Nature of reaction. The initial stage of this highly exothermic process is possibly the chemisorption of water molecules on the surface of the carbide. The metal atom probably has a higher affinity for oxygen than hydrogen causing fission of the water molecule to give atomic or ionised hydrogen. Such an entity attacks the carbon in the crystal leading initially to C_2H radicals from acetylides, or CH_2 radicals from methanides, with the corresponding metal hydroxide or hydrated metal oxide. With water and sulphuric acid, the products found are very similar, hence the presence of hydrogen ions does not affect the nature of the reaction, which must therefore be concerned with reaction by the water molecule rather than the hydrogen ion. The carbide is eventually dissolved by acid, but with water there always remains a solid deposit which appears to contain little or no carbon. Uranium carbides showed an oily film on the water, indicating the presence of higher hydrocarbons[24].
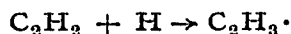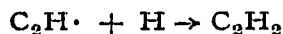
If the formation of radicals is assumed, and the undoubted presence of free or active hydrogen (which does not all combine to form hydrocarbons—since hydrogen gas is present in the hydrolysis products in every case), the course of the further reactions may have a wide variety of interpretations.

Rare earth carbides

The first observation that can be made is that there appears to be no trend along the rare earth series. From lanthanum and gadolinium the results are similar under the same conditions although there is a distinct variation in the ease of preparation of these carbides. Even cerium[III] dicarbide with the possibility of the formation of cerium[IV] during hydrolysis, does not give different results. Cerium is known to exist in the trivalent state in the dicarbide[14], and has been found to remain so in that valency state when hydrolysed with water or $4 N$ sulphuric acid, but to be oxidised to Ce^{IV} when hydrolysed with $4 N$ nitric acid.

The main difference (apart from the smaller C_4 hydrocarbons produced) between the reactions is the lower percentage of acetylene (58–60 %), and different percentages of ethylene (10–11 %) and ethane (8–11 %), formed with nitric acid when compared to the other two hydrolytic reagents. The results for water are acetylene (66–70 %), ethylene (7–9 %), and ethane (11–14 %) respectively. The higher ethylene figure, and lower ethane figure, is probably also a feature of the unusual reaction of nitric acid where the degree of hydrogenation is apparently curtailed.

Ethylene is probably produced by reactions such as:[25]

$$C_2H\cdot \ + \ H \rightarrow C_2H_2$$

$$C_2H_2 \ + \ H \rightarrow C_2H_3\cdot$$

$$H \ + \ C_2H_3\cdot \ \rightarrow \ C_2H_2 \ + \ H_2 \rightarrow C_2H_4$$

Ethylene can then combine with hydrogen atoms readily to form the ethyl radical, a reaction which may be surface-catalysed, leading to ethane[26]. The reduction in acetylene is only apparent since, if the percentage of "others" is excluded from the results (*i.e.* contain little or no carbon), the acetylene figure is brought up to a similar value

as those with water, the ethane and ethylene figures also increase. Thus with nitric acid, more carbon is released from the carbide as C_2 hydrocarbons than with water or sulphuric acid.

Very small percentages of methane and C_3 hydrocarbons are present, their complete absence is to be expected from carbides containing C_2 groups in the crystal. The appearance of such species may be due to the presence of a few single carbon atoms in the crystal which react to form methylene radicals. Such radicals could be further hydrogenated to form methane or react with acetylene or $C_2H \cdot$ radicals to form C_3 species[27].

$$CH_3 \cdot + C_2H_2 \rightarrow C_3H_5 \cdot$$

$$CH_3 \cdot + C_2H_4 \rightarrow C_3H_7 \cdot$$

The major C_4 hydrocarbon present is 1,3-butadiene which can be formed by the reaction of two C_2 entities followed by hydrogenation.

$$C_2H \cdot + C_2H_2 \rightarrow C_4H_3 \cdot [28]$$
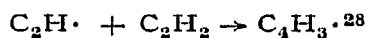
Other C_4 hydrocarbons might be formed by further reaction of this radical with hydrogen, or further free radical reactions, possibly

$$C_2H_5 \cdot + C_2H_2 \rightarrow C_4H_7 \cdot [29]$$

$$C_2H_5 \cdot + C_2H_4 \rightarrow C_4H_9 \cdot [30]$$
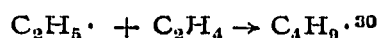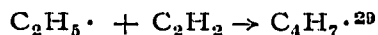
Polymerisation (probably catalysed) appears as a major factor in the hydrolyses at higher temperatures, forming high percentages of C_1 and C_3 hydrocarbons as reported by DE VILLELUME[30,31] and PALENIK AND WARF[17] when reacting cerium dicarbide at 200°C. Little or no acetylene is reported. Thus it is possible that the C_1 and C_3 species are formed through free radical mechanisms involving bond splitting which becomes prominent at higher temperatures. The exothermic nature of the reaction may produce local "hot zones" even though the general temperature is 100°C, and hence cause such reactions to proceed to a minor extent and give only minor yields of C_1 and C_3 species. Further work is necessary to resolve these problems.

Yttrium carbide

Chemical analysis of this carbide showed 82.2 % metal; YC_2 requires 78.8 %. Crystallographic examination showed that the carbide was mainly YC_2 but contained a number of unidentified X-ray lines probably due to another carbide phase. SAMSONOV, KOSOLAPOVA, AND MAKARENKA[32] have described the preparation of three yttrium-carbon phases, YC, Y_2C_3 and YC_2 (from the oxide with carbon *in vacuo*) at temperatures of 1800–1900°C, 1700–1800°C, and 1900°C, respectively. The structure of Y_2C_3 is known to be complex[34], explaining why the unidentified lines on the powdergram from the carbide prepared here could not be indexed. Y_2C is known to be cubic[11], while the structure of YC is not known. Assuming only YC_2 and Y_2C_3 were present, would demand the proportions 75 % Y_2C_3 and 25 % YC_2—this is not possible in view of the powdergram. A more reasonable proposition is that the carbide was mainly YC_2, containing metal, and Y_2C_3. The sesquicarbide (M_2C_3) contains C_2 groups in the

crystal which are therefore acetylides, but produce less acetylene and more methane and C_3 hydrocarbons than the dicarbides!

The same general remarks made for the rare-earth dicarbides can be made for this carbide, but the hydrolysis products were different, containing more methane, propane, propylene and showing the presence of another hydrocarbon, probably C_3H_4– allene or methyl acetylene.

The mechanism of the hydrolysis of the carbides which produce a mixture of hydrocarbons is still not certain, but accurate analyses of the products will certainly help to elucidate the problem. To prove that there is no trend down the rare-earth series, the remaining dicarbides should be hydrolysed, *i.e.* praesodymium, samarium, and dysprosium to lutetium. Europium dicarbide has to date defied preparation. Pure yttrium dicarbide must be prepared and hydrolysed to observe if the products are analogous to the rare-earth carbides. If a trend exists down the series, then yttrium should be compared to dysprosium and holmium—the position predicted from a consideration of atomic radii. More detailed studies on the hydrolysis at higher temperatures, *e.g.* passage of super-heated steam over the heated carbide, to study the effects of temperature on the products are necessary, in order to elucidate whether catalytic or free radical processes are involved. Studies on calcium carbide have already been initiated.

Relative studies of the rare-earth dicarbides and sesquicarbides will be stimulating, since in the sesquicarbides there are 1.5 unpaired electrons, and the carbon is present as C_2 groups. Apparently less acetylene is produced[11] but the reason is not clear.

SUMMARY

Four rare-earth dicarbides and a yttrium carbide (average composition $YC_{1.6}$) have been prepared and hydrolysed using water or mineral acids. The hydrolysis products, gaseous hydrocarbons, were determined using gas-liquid chromatography. The preparation from the oxide and carbon appears to proceed via the metal, and the results of hydrolysis are discussed from the nature of the carbide, the primary and subsequent free-radical reaction steps. In particular, the unusual results with nitric acid, due to the chain-terminating properties of nitric acid are mentioned.

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