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The Hydrolysis of the Rare-Earth Carbides*

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Studies of the hydrolytic reactions of the rare-earth carbides have been reported by Moissan (1, 2), by Damiens (3), by Zambonini (4), by Villelume (5), by Greenwood, and Osborn (6), by Atoji et al. (7), and recently by Palenik and Warf (8). All of these studies deal primarily with the rare-earth dicarbides except that of Atoji, et al. (7) which alludes briefly to the hydrolysis of lanthanum sesquicarbide and some methanides of the form R_3C . This report concerns the hydrolysis of rare-earth dicarbides, sesquicarbides, solid solutions of carbon in rare-earth metals as well as rare-earth carbon alloys of varying compositions. Many of the carbide samples used in this study were those which had been studied by Gschneidner (9)(7) and had been preserved in evacuated, sealed tubes. Some additional preparations of the sesquicarbides were made especially for these studies. The hydrolytic reactions were carried out in water and hydrochloric acid solutions of varying concentrations. Assay of the gaseous products was by mass spectrometry and gas chromatography. Both instruments were carefully calibrated with pure hydrocarbons and hydrogen and mixtures thereof.

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Experimental

Preparation of the Carbide Samples. The methods of preparing the samples have been described by Gschneidner (9). Great pains were taken to homogenize the arc melted samples by repeated rotation and turning-over of the rare-earth metal carbon buttons in the arc furnace. Samples were checked for purity of the particular carbides by x-ray analysis employing all precautions described by Atoji et al. (7). Chemical analyses of these preparations were carried out by ignition to the corresponding oxide. Details of the procedure have been described by Spedding, Gschneidner, and Daane (10).

Hydrolysis of the Carbide Samples. The hydrolysis reactions were carried out in special reaction vessels which could be attached directly to the inlet system of the mass spectrometer or gas chromatograph. Provisions were made to quickly introduce the various carbides and alloys into the vessel after breaking the storage tubes. The air was pumped from the vessel via the instrument inlet systems and then a volume of degassed water or hydrochloric acid was introduced over the carbide through a mercury covered diaphragm by means of a hypodermic syringe. Provisions were made to condense excess water vapor prior to making an assay of the evolved gases. Aliquots of the gas mixtures were assayed at various times during their evolution and after 24 hours during which time even the slowest reactions were complete. All

reactions were initiated at room temperature. Some rise in temperature was observed but this did not exceed 50°C in any cases due to the large amount of hydrolytic reagent employed and the rate of cooling of the vessel.

Results

An alloy of lanthanum containing 10.4 per cent carbon, which had been prepared in greater than usual quantity was used to study the effect of the acidity of the hydrolyzing medium upon the reaction products. X-ray powder photographs of this alloy indicated the presence of both LaC_2 and La_2C_3 with lines due to the latter being stronger than those due to the dicarbide. Results of the mass spectrometric assay of the gaseous products are given in Table I. Hydrocarbons containing 1, 2, 3, and 4 carbon atoms are shown and identified and compounds containing 5 and 6 carbon atoms are indicated as "peaks" 67 and 79. The latter were not identified except to ascertain that they were unsaturated and/or possibly cyclic in nature. In addition a small amount of a relatively non-volatile oil was observed floating on the top of the hydrolysis medium. No free carbon was observed.

The rate of the reactions was slow in water but was reasonably rapid in 1.0 N hydrochloric acid. Since many of the carbides of the heavier rare earths react even more slowly than the lanthanum carbides, the hydrolysis of these carbides was carried out routinely in 1.0 N

Table I

Hydrolysis of La- 10.4% C in Water and Hydrochloric Acid Solutions^a

<u>Gas</u>	<u>H₂O</u>	<u>0.6 N</u>	<u>1.0 N</u>	<u>2.5 N</u>	<u>6.6 N</u>	<u>10.6 N</u>
hydrogen	38.55	31.27	34.80	33.14	31.14	30.00
methane	0.53	0.63	0.37	0.72	0.52	0.20
ethane	9.18	13.18	13.29	12.37	11.74	11.55
ethene	2.53	4.77	4.86	6.35	8.35	10.35
ethyne	34.59	36.45	36.72	35.38	36.10	36.19
propane	0.40	0.35	0.23	0.29	0.23	0.25
propene	0.64	0.40	0.35	0.41	0.29	0.34
propyne	2.48	1.87	0.96	1.41	1.58	1.58
n-butane	0.90	0.91	0.59	0.37	0.23	0.19
butene's	3.15	3.34	2.67	2.95	2.88	2.81
1 butyne	7.04	6.85	5.15	6.71	7.10	6.59
peak 67 ^b	82	38	41	38	38	28
peak 79 ^b	53	37	29	37	40	30

^a Results are in volume - per cent as are all results in this paper.

^b Peaks due to ion currents at mass 67 and 79 are given in terms of parts per 10000 of the base peak of ethyne. Similar results are given in all tables of this paper.

acid. As can be seen in Table I, changing from water to acid did not affect the type of products produced and made only small changes in the relative amounts of particular hydrocarbons produced. This La-10.4C alloy is metallic in appearance and conducts an electric current almost as well as the metal. The large amount of hydrogen is attributed to the existence of $C_2^{=}$ units in the crystal structures of LaC_2 and La_2C_3 (11) with the extra La valence electrons in the conduction band supplying those needed to form hydrogen gas.

A second series of experiments supports this interpretation. In this series, several La-C alloys were prepared with increasing amounts of carbon. These were hydrolyzed in water. The results are given in Table II. A large amount of hydrogen forms but a sharp drop in the amount of evolved hydrogen occurs between the 6 and 10.5 per cent alloys due to the disappearance of free La metal. A second sharp drop occurs in the 13.1 per cent sample which is predominantly the less metallic LaC_2 with only a small amount of La_2C_3 present. The presence of free La metal in the 6 per cent alloy is dramatically illustrated by the results in column six which shows an enhanced amount of free hydrogen. Presumably, in this case, hydrogen is produced so rapidly that reduction of ethyne does not take place to the same degree observed in the water reactions. As cited before, a relatively non-volatile oil floated on the top of the hydrolysis media in all these experiments.

Table II

Hydrolysis of La-C Alloy of Varying Carbon Content in Water

	<u>6% C</u>	La-C in Water ^a			1.0 N HCl <u>6% C</u>
		<u>10.5% C</u>	<u>12.2% C</u>	<u>13.1% C</u>	
hydrogen	45.30	38.55	37.38	28.91	75.68
methane	0.59	0.53	--	--	0.36
ethane	9.57	9.18	8.16	10.00	6.54
ethene	0.85	2.53	4.63	4.64	1.48
ethyne	28.47	34.60	36.88	45.15	10.67
propane	0.70	0.41	0.19	0.21	0.17
propene	0.55	0.65	0.51	0.46	0.19
propyne	2.49	2.48	1.60	1.37	0.49
n-butane	1.34	0.90	0.70	0.60	0.49
butene's	3.22	3.15	3.20	2.91	1.43
1-butyne	6.90	7.04	6.75	5.72	2.50
67	122	82	85	66	66
79	86	67	65	56	43

^a Approximate compositions of these alloys according to the phase diagram by Spedding, Gschneidner, and Daane (10) are: 6% C, La + La₂C₃; 10.5% C, La₂C₃ + LaC₂; 12.2% C, La₂C₃ + LaC₂; 13.1% C, La₂C₃ + LaC₂.

Alloys of several rare earths and carbon corresponding to the stoichiometric compositions, MC , M_2C , M_3C , and M_4C were hydrolyzed in 1.0 N hydrochloric acid. The results are given in Table III. The results for the MC composition are similar to those observed when the 6 per cent carbon in La alloy was hydrolyzed in 1.0 N acid as shown in Table II. The decreased production of hydrogen and the enhanced production of ethyne in the "LaC" compared to that of the 6 per cent alloy can be attributed to the diminished La content in "LaC" which is however still a mixture of La and La_2C_3 . While the details of the Ce-C and Pr-C phase systems are not known, these results suggest that the expected similarity to the La-C system is actual.

In the other compositions of this series, further support is given to the thesis that carbon exists interstitially. Compositions corresponding to M_2C have a small amount of $C_2^{=}$ groups as indicated by the presence of the small amount of ethyne and higher condensation and reduction products. Compositions corresponding to M_3C and M_4C are predominantly methanide although the Nd_3C used here indicated the presence of residual Nd_2C_3 . This may well have been due to inhomogeneous sites in the Nd C button prior to arc melting which produced small amounts of Nd_2C_3 .

All the rare-earth sesquicarbides and that of yttrium except Eu and Yb were hydrolyzed in 1.0 N hydrochloric acid. The results are given in Table IV. Both mass spectrometric and gas chromatographic data

Table III

Hydrolysis of Lower Carbides of Some Rare Earths

	MC			M ₂ C		M ₃ C					M ₄ C
	<u>La</u>	<u>Ce</u>	<u>Pr</u>	<u>Y</u>	<u>Lu</u>	<u>Nd</u>	<u>Sm</u>	<u>Gd</u>	<u>Tb</u>	<u>Er</u>	<u>Nd</u>
hydrogen	61.05	59.20	60.78	34.05	26.40	51.63	84.64	75.22	77.19	51.08	80.03
methane	1.06	5.62	6.22	61.20	67.64	43.58	15.27	24.78	22.81	48.08	19.79
ethane	10.62	9.23	8.91	1.49	0.42	2.82	0.04	--	--	0.24	0.10
ethene	2.63	3.02	2.72	0.55	0.35	0.38	0.02	--	--	0.10	0.02
ethyne	16.56	11.52	12.42	1.60	1.07	0.81	0.05	--	--	0.18	0.03
propane	0.22	0.15	0.27	0.10	0.27	0.11	--	--	--	0.04	0.01
propene	0.28	0.50	0.40	0.16	0.88	0.11	--	--	--	0.07	0.01
propyne	0.60	0.70	0.80	0.27	2.40	0.17	--	--	--	0.07	0.02
n-butane	0.64	0.66	0.55	0.11	0.15	0.06	--	--	--	0.01	--
butene's	2.35	3.83	2.77	0.24	0.29	0.20	--	--	--	0.07	0.01
1-butyne	3.99	5.58	4.14	0.20	0.12	0.15	--	--	--	0.04	--
67	58	97	71	95	293	44	--	--	--	400	--
79	31	49	44	80	78	11	--	--	--	144	--

Table IV

Hydrolysis of Rare-Earth Sesquicarbides in 1.0 N HCl

	<u>La</u>	<u>Ce</u>	<u>Pr</u>	<u>Nd</u>	<u>Sm^a</u>	<u>Gd</u>	<u>Tb</u>	<u>Ho^b</u>	<u>Er^c</u>	<u>Er^c</u>	<u>Tm^d</u>	<u>Lu^e</u>	<u>Lu^e</u>	<u>Y</u>
hydrogen	39.43	21.20	32.67	27.66	59.85	27.92	36.98	15.18	39.89	33.23	5.13	13.86	4.24	23.90
methane	0.16	0.00	0.85	0.00	3.33	0.82	4.84	4.52	12.54	31.19	34.46	44.44	43.24	7.12
ethane	13.09	19.77	14.82	15.21	0.85	13.68	7.08	3.68	6.00	5.42	0.15	0.19	0.16	6.19
ethene	5.58	6.12	4.25	10.18	2.51	8.05	7.26	10.34	5.46	3.78	0.55	0.53	0.59	6.18
ethyne	31.78	34.79	32.59	32.79	28.11	34.08	31.29	58.25	23.44	13.89	4.01	3.51	2.34	47.31
propane	0.20	0.00	0.19	0.20	0.07	0.09	0.09	0.10	0.34	0.57	0.12	0.19	0.25	0.06
propene	0.42	0.46	0.60	0.71	0.24	0.57	0.55	0.84	1.49	2.03	2.74	3.02	3.26	0.62
propyne	0.73	0.89	1.34	0.85	1.38	0.71	0.89	0.06	3.79	4.97	51.83	31.88	44.49	1.97
n-butane	0.25	0.54	0.62	0.22	0.03	0.50	0.35	0.33	0.48	0.46	0.10	0.25	0.19	0.34
butene's	2.74	6.27	4.40	3.78	0.75	5.50	4.29	4.82	3.31	2.35	0.55	1.34	0.85	3.07
1-butyne	5.71	9.95	7.62	8.38	2.88	8.05	6.38	1.86	3.28	2.11	0.36	0.78	0.42	3.18
67	32	49	67	85	14	52	50	28	99	117	215	540	--	23
79	34	34	43	128	28	50	50	26	72	64	159	239	--	22
			cis-butene-2	1.66		cis-butene-2	1.94					cis-butene-2	0.00	
			trans-butene-2	0.94		trans-butene-2	1.32					trans-butene-2	0.78	
			n-butene-1	1.80		n-butene-1	2.24					iso-butylene	0.07	

^a Two faint SmC₂ lines and some faint lines due in Sm were found in x-ray powder diagram

^b Some HoC₂ lines in x-ray powder diagram

^c Samples made up from stoichiometric, 2 Er + 3 C. No x-ray data obtained. First sample contained no free carbon. Second sample contained free carbon

^d Sample made up from stoichiometric, 2 Tm + 3 C. Appearance - mottled green - much foaming during hydrolysis. No x-ray data obtained

^e Sample made up from stoichiometric, 2 Lu + 3 C. No x-ray data obtained

were obtained which were in good agreement with one another. The gas chromatograph was used primarily as a check on the mass spectral assays and to determine the composition of the butene fraction for selected preparations.

X-ray patterns of the sesquicarbide preparations of La, Ce, Pr, Nd, Gd, Tb, and Y indicated only the presence of M_2C_3 lines. Similar preparations from Sm and Ho showed faint lines due to SmC_2 and somewhat stronger lines due to HoC_2 in corresponding preparations. No reliable x-ray data were obtained for the preparations from Er, Tm, and Lu. However, analytical data indicated that all three of these preparations corresponded to M_2C_3 except for an excess of free carbon which in all cases was less than 0.5 per cent of the theoretical amount. It is unfortunate that good crystallographic data were not obtained for these particular sesquicarbides since the hydrolysis products showed large amounts of methane and propyne and greatly diminished amounts of ethyne.

In addition to the usual relatively non-volatile oily material, soft greases similar to petroleum jelly were also part of the hydrolysis products of the sesquicarbides. No attempts were made to identify these oils and greases.

The dicarbides of all the rare earths except Ce and Eu were hydrolysed in 1.0 N hydrochloric acid. In addition to the gaseous

Table V

Hydrolysis of Rare-Earth Dicarbides in 1.0 N HCl

	<u>La</u> ^a	<u>Pr</u>	<u>Nd</u>	<u>Sm</u>	<u>Gd</u>	<u>Tb</u>	<u>Dy</u>	<u>Ho</u> ^b	<u>Er</u> ^c	<u>Tm</u> ^d	<u>Yb</u>	<u>Lu</u>
hydrogen	17.95	29.85	10.14	16.63	12.63	12.60	28.27	18.31	16.61	32.30	31.26	25.58
methane	--	--	--	--	0.24	0.23	0.46	7.87	2.85	2.51	--	10.30
ethane	11.49	1.80	9.51	5.55	5.79	5.69	1.13	4.50	2.91	0.26	0.36	0.21
ethene	5.68	3.59	11.82	12.52	15.11	15.21	5.52	8.99	9.30	1.68	1.88	1.15
ethyne	58.60	63.53	64.59	62.23	60.40	61.49	61.40	51.13	58.89	60.36	65.45	42.49
propane	0.13	--	0.08	0.09	0.08	0.12	0.03	0.12	0.08	0.05	0.01	0.09
propene	0.17	0.07	0.21	0.13	0.43	0.32	0.25	0.93	1.00	0.35	0.01	1.13
propyne	0.30	0.01	--	--	--	0.01	0.06	0.51	--	0.60	0.01	17.58
n-butane	0.36	0.11	0.26	0.13	0.24	0.23	0.09	0.37	0.34	0.03	0.01	0.07
butene's	2.12	0.56	2.19	1.50	3.56	2.87	1.51	4.69	5.81	0.96	0.41	0.80
1-butyne	3.21	0.41	1.20	0.89	1.52	1.21	1.30	2.51	2.20	0.92	0.49	0.63
67	23	7	19	7	17	8	12	48	41	11	4	24
79	23	5	17	6	11	5	13	48	37	16	7	25

^a Some faint lines due to La_2C_3 were found in the x-ray powder diagram

^b X-ray powder diagrams showed both HoC_2 and Ho_2C_3 present. HoC_2 estimated to be main constituent

^c Very faint Er_2C_3 lines present in x-ray powder diagram

^d Sample appeared metallic although no lines due to Tm were observed in the x-ray powder patterns

products shown in Table V, oils and small amounts of soft greases were also formed. All of these dicarbides gave well characterized x-ray patterns and with the exception of La, Ho, and Er no lines other than those of the expected body-centered structure were observed. Faint lines due to La_2C_3 and Er_2C_3 were observed in the dicarbide preparations of these elements and both Ho_2C_3 and HoC_2 lines were present in the holmium preparations. The hydrolysis products of this preparation bear a striking similarity to those found for the "holmium sesquicarbide" preparation. More careful work on this carbide is warranted in the future.

Discussion

In all of the hydrolytic reactions studied a relatively large amount of hydrogen was evolved. This is attributed to the general metallic nature of the carbides and the electrons available in the conduction bands of the materials. Variations in the amount of hydrogen observed from one rare earth to another do not seem to bear any relationship to the possible oxidation state of the final residue but are probably due to the difficulty of preparing homogeneous materials. In those alloys containing an excess of metal (metal lines in the x-ray powder patterns), hydrogen as H_2 or in the form of reduction products of ethyne or its condensation products was the principal gaseous species evolved. Alloys which are solutions of carbon in the metal produce hydrogen and methane in

expected proportions. The small amounts of ethyne, ethene, and ethane shown in the M_2C , M_3C , and M_4C examples given in Table III are probably due to inhomogeneous preparations in which local production of M_2C_3 or MC_2 took place.

The observed inconsequential changes in gas composition as the strength of hydrochloric acid used to hydrolyze the La-10.4C alloy increased was unexpected. Greater quantities of the reduction products of ethyne were expected since the rate of reaction increased as the acid strength increased. The expected increase was manifested only in the production of ethene with the remainder of the products being little affected. No reason is apparent.

It is no surprise that a large number of even-numbered hydrocarbons are produced since Atoji and Williams (11) have shown that $C_2^{\equiv}$ units exist in both the rare-earth dicarbides and sesquicarbides. The C to C distance in the sesquicarbides is somewhat less than in the dicarbides but in all cases this distance is very much less than the C=C distance in unsaturated hydrocarbons. Even under the somewhat mild reaction conditions used here, some breakage of C_2 units occurs as is evident from the production odd-numbered hydrocarbons. These are produced in moderate amounts from all the samples studied, with propyne being most prevalent. Of considerable interest however are the preparations from lutetium and erbium. Two preparations of ' Lu_2C_3 ' produced large amounts of methane and propyne and only a small amount of ethyne. One

of two preparations of Er_2C_3 also produced these gases in about the same proportions (Tables VI and V). However, even the preparation of LuC_2 produced large amounts of methane and propyne along with ethyne. X-ray analyses of the sesquicarbides of Er and Lu were not successful because of experimental problems at the time and the apparent complexity of the patterns. However, the x-ray patterns of LuC_2 showed only dicarbide lines. Further study of Er and Lu carbides is in order since it appears that there is something unique about these rare-earth carbides. Certainly, study of the crystal structure of the carbides should be undertaken, especially to elucidate the disposition of carbon atoms in the crystal structures.

Several mechanisms for the formation of these hydrolytic products can be formulated which are in harmony with the observations. Certainly some free radicals involving $-\text{C}_2^-$, C_2H^- , CH_3^- , and H^- are precursors of the various C^- , C_2^- , C_3^- , C_4^- , and higher hydrocarbons that are produced. All of the rare-earth carbides hydrolyzed in water formed colloidal suspensions of hydrous rare-earth oxides which were evident by an observed Tyndall effect. In some cases, even those reactions carried out in 1.0 N hydrochloric acid indicated the presence of colloidal reaction products which are probably oxychlorides. However, those reactions in strong hydrochloric acid formed true solutions of rare-earth chlorides. Thus the presence of an external reactive surface substrate

for highly mobile radicals is not essential for the formation of the reduced or condensation products of ethyne. The surface of the reacting carbide itself may be considered sufficient substrate on which these reactions can occur.

No butadienes were positively identified in any of these experiments. This is the principal difference between the results reported here and comparable ones of Palenik and Warf. The absence of these hydrocarbons in this work may be due to the different reaction conditions since these authors observe only minor quantities of butadienes in their room temperature reactions. Since gas chromatographic assays were used here only to spot check the mass spectrometric assays, these compounds could have been missed. It is interesting to speculate that Unknown IV reported by Palenik and Warf might have been 1-butyne, and perhaps one of their other unknown compounds was propyne. Neither of these compounds is usually introduced in gas chromatographs used for conventional petroleum assays, thus these authors could have missed these compounds.

Many questions brought out in this research remain unanswered. Of primary importance is the problem of developing reliable methods of preparing these carbides. The arc-melting technique can certainly be improved upon since it is extremely difficult to obtain homogeneous preparations by means of its application in this particular work. A

technique which obviates having to turn partially melted buttons should be developed. Perhaps, for hydrolytic studies, smaller scale preparations in which the entire boule of carbide is melted in the arc would be preferable.

Another prime question concerns the apparent uniqueness of the hydrolytic products of holmium, erbium and lutetium carbides. Still another concerns the identity of the oils and greases observed in these studies.

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