

## STUDIES ON HYDROLYZABLE CARBIDES. VII.\*

DECOMPOSITION OF SOME DICARBIDES OF THE TYPE  $M^{III}C_2$  AND OF SCANDIUM CARBIDE WITH DEUTERIUM OXIDE

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Dicarbides of lanthanum, cerium, neodymium, samarium, gadolinium, terbium, holmium and yttrium and scandium carbide were prepared and decomposed using water or deuterium oxide. In both cases the same gaseous products were formed. The abundance of different hydrocarbon components and of hydrogen varies in dependence on the conditions of decomposition, however, the atomic ratio of hydrogen to carbon in the gaseous products remains the same, being  $\sim 1.5$  with pure dicarbides. Yttrium, holmium and scandium carbides show a different character, indicated by the presence of methane and hydrocarbons with odd number of carbon atoms, especially of allylene, in the gaseous hydrolytic products. In the latter cases the H : C ratio is higher than 1.5. According to the purity of the deuterium oxide used, either totally or partially deuteriated hydrocarbons of the series  $C_1-C_{10}$  are formed, predominantly olefins and acetylenes. Their IR spectra display a distinct low-frequency shift.

In our papers<sup>1-9</sup> as well as in the papers of other authors it was established that in hydrolysis of some carbides, in particular of those of elements of the third subgroup of the periodical system, mixtures of hydrocarbons are formed, containing in addition to acetylene, ethylene and ethane and in the case of mono- and sesquicarbides also to methane, hydrocarbons (linear) of the series  $C_4-C_{10}$ , or  $C_3$ ,  $C_5$  etc.

The present work has been devoted to the study of decomposition of some dicarbides of the type  $M^{III}C_2$  and of scandium carbide with deuterium oxide for two reasons: first in this way it is possible to obtain higher completely deuteriated hydrocarbons which otherwise are difficult to prepare. The second reason was to compare decomposition with water with that performed with deuterium oxide in searching for a possible isotope effect. The experiments were carried out with the following dicarbides:  $YC_2$ ,  $LaC_2$ ,  $CeC_2$ ,  $NdC_2$ ,  $SmC_2$ ,  $GdC_2$ ,  $TbC_2$ ,  $HoC_2$  and with the carbide  $ScC_{2-x}$ . All samples were prepared under absolutely identical experimental conditions, to allow comparison from several different aspects.

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## EXPERIMENTAL

*Working Procedure*

The following starting chemicals were used for the preparation of the respective carbides:  $\text{La}_2\text{O}_3$  (BHD, England),  $\text{CeO}_2$  (Lab., Apolda, GDR),  $\text{Nd}_2\text{O}_3$  99.9% (Sojuzchimexport, USSR),  $\text{Sm}_2\text{O}_3$  99.9% (Koch-Light Lab., England),  $\text{Gd}_2\text{O}_3$  99.9% (Lachema, Brno, ČSSR),  $\text{Tb}_2\text{O}_3$  99.9% (Johnson Matthey, London),  $\text{Ho}_2\text{O}_3$  99.9 (Johnson Matthey, London),  $\text{Sc}_2\text{O}_3$  99% (Serva, Heidelberg, BDR) and  $\text{Y}_2\text{O}_3$  99.99% (Lachema, Brno). Granulated carbon black (Pramet, Šumperk) of the content 99.99% C was used. Mixtures of oxides of the mentioned elements with carbon (in 1 : 7 mol ratio) were mixed in a rotating glass homogenizer and then were pressed into pellets of 5 mm diameter and 5–10 mm height, using a pressure of  $20 \text{ NM} \cdot \text{m}^{-2}$ . The pellets were placed in graphite crucibles (8 mm). All nine crucibles with the weighed samples were put simultaneously in a large graphite crucible along its periphery so that all crucibles lay in the same distance of the thermal zone of the furnace. The crucible was then placed in the furnace (Degussa, Wolfgang bei Hanau, type Hvota 6.5/13) which was evacuated to  $5 \cdot 10^{-2}$  Torr and heated to  $2150^\circ\text{C}$  for 3 hours. After cooling in Ar atmosphere, sintered black lustrous products were obtained. Because with all elements, except for scandium, at most dicarbides  $\text{MC}_2$  are formed in an excess of carbon, the products were not analyzed, for they always contain a certain amount of dissolved free carbon. The presence of dicarbides was confirmed by roentgenographic analysis (apparatus Mikrometa, Chirana). Owing to the rather high hygroscopicity of the samples only those containing scandium, yttrium, lanthanum, cerium, neodymium and gadolinium could be evaluated roentgenographically. The other decomposed during exposure to amorphous oxido-hydroxides.

The prepared samples were decomposed using deuterium oxide (purity 99.5%, product of USSR) and for comparison also with distilled water. According to our previous experience

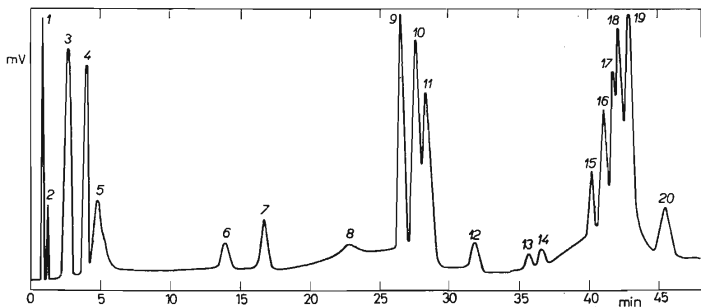


FIG. 1

Chromatogram of Gaseous Products of Yttrium Dicarbid Decomposition with Deuterium Oxide  
Reaction conditions see text, evaluation of the sequence of elution peaks see Table II.

and results the decomposition procedure was unified in such a way as to reduce the catalytic effect of the solid phase of the decomposing carbide. The carbide sample was placed in a 2 ml flask, closed by a rubber stopper with two glass inlets. One of them served for injecting water or deuterium oxide, till all air was expelled from the flask. The formed gaseous products were then exhausted through the second glass tube, using a syringe. Feed for chromatographic analysis was 0.5 ml of the gaseous mixture. Further amounts of gaseous products were used for mass analysis on an apparatus LKB 9000 Produkter Stockholm, as well as for measuring the infrared spectra on a UR Zeiss Jena apparatus (gas cuvette 100 mm) in the range 400–4000  $\text{cm}^{-1}$ .

The course of chromatographic analysis of the deuteriated hydrocarbons was checked on a mass spectrometer LKB 9000, the inlet of which was connected to the chromatographic column (2.5 m length) filled with Porapak Q and heated from 50 to 190°C (temperature gradient 3°C/min). The checking analysis was performed with the samples of yttrium and lanthanum dicarbides which were decomposed both with distilled water and with deuterium oxide. A characteristic chromatogram is shown in Fig. 1. Mass spectrum of the eluted fraction was registered at the maxima of the respective elution peaks with electron energies 14 and 70 eV.

With respect to the positive results of these preliminary analyses the analysis of the gaseous mixture obtained on decomposition of all prepared carbides was performed. To make the comparison with our earlier results easier, the column was filled with dimethylsulfolane and with poly(propylene glycol), on Chromosorb as carrier. This, however, allowed to evaluate only hydrocarbons up to  $\text{C}_4$ . Hydrocarbons of the series  $\text{C}_6$  to  $\text{C}_{10}$  whose content did not exceed 1.5% were not included into the over-all balance and were determined only qualitatively, from the mass spectra. All analyses were complemented by determining the D or H content as well as the ethane-ethylene ratio on a Janák chromatograph<sup>10</sup>.

## RESULTS AND DISCUSSION

Roentgenographic analysis of lanthanum, cerium, neodymium, gadolinium and yttrium carbides has demonstrated that the formed products are dicarbides with tetragonal lattice of the  $\text{CaC}_2$  type, having the following parameters:  $\text{LaC}_2$   $a = 3.69 \text{ \AA}$ ,  $c = 6.97 \text{ \AA}$ ;  $\text{CeC}_2$   $a = 3.65 \text{ \AA}$ ,  $c = 6.60 \text{ \AA}$ ;  $\text{NdC}_2$   $a = 3.82 \text{ \AA}$ ,  $c = 6.25 \text{ \AA}$ ;  $\text{GdC}_2$   $a = 3.71 \text{ \AA}$ ,  $c = 6.24 \text{ \AA}$ ;  $\text{YC}_2$   $a = 3.62 \text{ \AA}$ ,  $c = 6.06 \text{ \AA}$ . The sample of scandium carbide was roentgenographically distinctly different from other products. Its Debye-gram displayed a number of lines which could not be evaluated in terms of a tetragonal system (Table I). An analogous Debye-gram was earlier found with  $\text{ScC}_{1.93-2.26}$  sample<sup>7</sup>. The analysis of deuteriated hydrocarbons in the checking series, performed on a column filled with Porapak Q showed that besides  $\text{C}_2$  and  $\text{C}_4$  hydrocarbons (whose elution times were studied earlier on a column with sulfolane and polypropylene glycol filling) further elution peaks could be detected at higher temperatures used, 50 to 190°C, which were assigned to  $\text{C}_6$  and  $\text{C}_8$  hydrocarbons. Chromatograms as well as elution times of deuteriated and non-deuteriated hydrocarbons are identical; the sensitivity of the method showed no differences. Evaluation of chromatograms from Porapak Q filled column in combination with the mass spectra of the separate elution peaks is presented in Table II. When using water with only 85% deuterium oxide and 5% DHO as decomposition agent the mass spectra revealed lines of corresponding relative intensity, at molecular masses assigned to normal

TABLE I

Interplane Distances of Scandium Carbide Sample, prepared at 2150°C  
Apparatus Mikrometa, Chirana, Cu K $\alpha$ .

$d$ , kX	$I/I_0$	$d$ , kX	$I/I_0$
3.70	1	2.00	1
3.36	3	1.88	1
3.07	2	1.72	2
2.78	3	1.68	3
2.52	3	1.60	2
2.36	2	1.44	1
2.34	1	1.38	1
2.14	1	1.19	1

TABLE II

Gaseous Products of YC $_2$  Decomposition with Deuterium Oxide  
Evaluation of the chromatogram in Fig. 1.

Peak No	Amplification factor	Component	Content vol. %
1	20	D $_2$ , air	3.36
2	20	CD $_4$	0.86
3	1	C $_2$ D $_2$	64.50
4	5	C $_2$ D $_4$	16.80
5	5	C $_2$ D $_6$	2.70
6	100	C $_3$ D $_6$	0.06
7	100	C $_3$ D $_4$	0.11
8	5	—	—
9	5	C $_4$ D $_8$ 1-butene	5.41
10	10	<i>trans</i> -C $_4$ D $_8$	2.38
11	10	<i>cis</i> -C $_4$ D $_8$	2.06
12	50	C $_4$ D $_6$ 2-butene	0.05
13	50	CD $_3$ CDO	0.02
14	50	C $_3$ D $_6$ O	0.02
15	100	C $_6$ D $_8$	0.05
16	50	C $_6$ D $_{12}$	0.20
17	50	C $_6$ D $_{10}$	0.28
18	50	C $_6$ D $_{12}$	0.50
19	50	C $_6$ D $_8$	0.46
20	50	C $_6$ D $_{10}$	0.12

D : C 1.53

hydrocarbons and to partially deuteriated products. In this way it was proved that the elution times of normal, partly deuteriated and totally deuteriated hydrocarbons are equal and cannot be chromatographically distinguished. Combination with mass spectrometry allows to determine their ratio, using a mixture of heavy and normal water. In addition to hydrocarbons whose presence in the gaseous products of dicarbide decomposition can be explained by primary or secondary reactions of acetylene with hydrogen, some further elution peaks were found when the column was heated gradually from 50° to 190°C. These peaks can be assigned to substances whose formation is quite unambiguously to be ascribed to subsequent effect of the reaction medium. This is the reaction of hydrocarbons with the decomposing liquid, in our case water or deuterium oxide. For the sake of information, we shall mention only two characteristics of the found reactions. Acetylene reacts with water to form acetaldehyde with molecular mass 44. The chromatogram taken on a column filled with Porapak Q showed a weak peak with elution time 36 min; when deuterium oxide was used for decomposition a peak of molecular mass 48 was found under the same elution time corresponding to totally deuteriated aldehyde. In the case of  $YC_2$  decomposition, among whose hydrolytic products methane and hydrocarbons of the series  $C_3$  especially allylene were found in the amount up to 2%, we have established that the peak appearing with elution time 37 min has the molecular mass 58 and a strong fragment ion of the mass 43. With deuterium oxide as decomposition agent the same peak has the molecular mass 64, the mass of the fragment being 46. This corresponds to acetone whose presence can be explained by the reaction of allylene with water.

Products of decomposition of carbide samples with deuterium oxide and the results of their gas-chromatographic analysis are summarized in Table III. For comparison, the same samples were also decomposed with normal water under otherwise identical conditions. Some differences in the values of deuteriated and non-deuteriated products of one carbide species and in the relative abundances in individual hydrocarbons for different carbides were not taken into account in this study, because the effect of the method and conditions of hydrolysis on the relative content of individual components has been pointed out earlier. The most important conclusion is that the hydrolysis products are, as to their hydrocarbon composition, the same, no matter whether the decomposition was performed with distilled water or with deuterium oxide. The fact that carbide samples prepared simultaneously and under the same experimental conditions from oxides of the elements of the 3rd subgroup of the periodical system, and hydrolyzed under very similar conditions show two entirely different forms, is in agreement with the thermodynamic conditions of oxide reduction. First, no methane was found in the decomposition products of  $LaC_2$ ,  $CeC_2$ ,  $NdC_2$ ,  $GdC_2$ ,  $SmC_2$  and  $TbC_2$  and all hydrocarbons formed may be derived from acetylene and hydrogen as primary products in terms of their hydrogenation and polymerization reactions. In contrast to this, a small but detectable amount of methane and  $C_3$  hydrocarbons was found among the decomposition products of yttrium

TABLE III

Products of Carbides Decomposition with Deuterium Oxide and Water (in vol.%)

Column temperature 35°C, hydrocarbons higher than C<sub>4</sub> are not included into the balance.

Component <sup>a</sup>	LaC <sub>2</sub>		CeC <sub>2</sub>		NdC <sub>2</sub>		SmC <sub>2</sub>		GdC <sub>2</sub>		TbC <sub>2</sub>		HoC <sub>2</sub>		YC <sub>2</sub>		ScC <sub>x</sub>		
	D <sub>2</sub> O	H <sub>2</sub> O	D <sub>2</sub> O	H <sub>2</sub> O	D <sub>2</sub> O	H <sub>2</sub> O	D <sub>2</sub> O	H <sub>2</sub> O	D <sub>2</sub> O	H <sub>2</sub> O	D <sub>2</sub> O	H <sub>2</sub> O	D <sub>2</sub> O	H <sub>2</sub> O	D <sub>2</sub> O	H <sub>2</sub> O	D <sub>2</sub> O	H <sub>2</sub> O	
Deuterium	11.00	7.60	3.30	6.10	4.70	12.60	10.30	10.50	12.00	6.90	6.60	7.00	14.30	10.10	8.10	6.50	10.30	—	—
Hydrogen	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Methane	64.80	61.20	64.20	60.30	67.60	66.80	62.90	63.40	64.15	63.30	61.20	62.50	58.50	62.00	59.00	60.20	33.80	36.20	—
Acetylene	10.55	14.50	20.50	20.25	18.80	—	—	—	10.40	12.65	—	—	—	—	17.20	16.15	—	—	—
Ethane	6.40	7.55	8.00	6.30	—	14.30	20.00	20.00	7.00	8.40	20.50	21.20	18.25	20.20	7.14	8.70	10.80	6.35	—
n-Butane	1.30	0.94	0.53	0.82	0.82	0.54	0.41	0.52	0.85	1.25	1.10	0.90	0.43	0.55	0.35	0.49	0.34	0.30	—
i-Butene	3.15	3.75	2.26	2.86	3.50	2.32	2.26	2.46	1.97	2.97	3.70	2.95	2.22	2.27	2.90	3.10	2.14	1.44	—
trans-2-Butene	0.40	1.02	0.26	0.80	0.52	0.60	0.80	0.56	0.45	0.95	1.23	1.12	0.55	0.56	0.70	0.93	0.20	0.20	—
cis-2-Butene	0.70	1.86	0.32	1.32	1.28	1.36	1.56	1.20	1.35	1.77	2.32	2.00	1.20	1.16	1.08	1.77	0.42	0.36	—
1,3-Butadiene	0.18	0.05	0.05	0.20	0.33	0.05	0.10	0.06	0.10	0.10	0.10	0.08	0.15	0.15	0.05	0.15	0.11	0.05	—
1,2-Butadiene	0.10	0.02	—	0.05	—	—	0.04	—	—	0.02	—	—	0.05	0.04	—	0.02	—	—	—
i-Butyne	1.20	1.40	0.53	0.95	2.40	1.33	1.20	1.20	1.63	1.60	3.20	2.25	2.20	1.82	1.00	1.05	2.36	1.30	—
Vinylacetylene	0.22	0.10	0.02	0.05	0.10	0.05	0.05	0.10	0.12	0.10	0.05	—	0.05	0.02	0.02	—	—	—	—
Propane	—	—	—	—	—	—	—	—	—	—	—	—	0.02	0.01	0.02	0.02	0.84	0.70	—
Propene	—	—	—	—	—	—	—	—	—	—	—	—	0.03	0.01	0.03	0.03	1.90	1.80	—
Allylene	—	—	—	—	—	—	—	—	—	—	—	—	0.15	0.05	0.05	0.06	18.30	22.30	—

Atomic ratio

D : C or

H : C

<sup>a</sup> On decomposition with deuterium oxides the hydrocarbons are totally deuterated.

and holmium carbides, in addition to the prevailing content of even-number chained hydrocarbons. In the case of scandium carbide methane and  $C_3$  hydrocarbons predominate in the gaseous decomposition products, in addition to  $C_2$  and  $C_4$  hydrocarbons. Evidently with scandium the prevailing amount is that of the other type of carbide, which with  $YC_2$  and  $HoC_2$  is present only in very small amount.

The hydrolysis revealed that decomposition of carbides with deuterium oxide is somewhat slower than when performed with normal water. Quantitative measurement was hindered, besides other factors, by the different surface areas of the starting substances. We have therefore verified this effect by means of infrared spectra. A compact piece of carbide was decomposed with a 1 : 1 mixture of deuterium oxide and water and infrared spectra were recorded in the regions characteristic for  $-C\equiv H$  and  $-C\equiv D$  bond, in dependence on time. It was confirmed that the intensity of vibration maxima of normal hydrocarbons is greater than that of deuteriated hydrocarbons in the same time of a simultaneously proceeding decomposition. Fig. 2 shows the spectra of deuteriated, mixed and nondeuteriated gaseous products

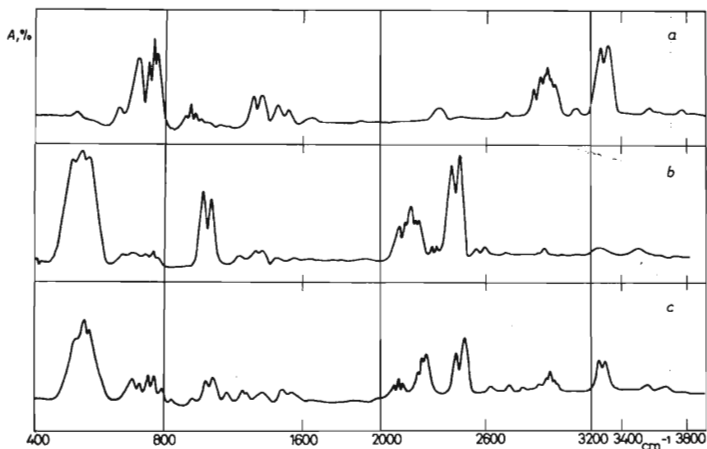


FIG. 2

Infrared Spectra of Gaseous Products of Cerium Dicarbide Decomposition *a* with Distilled Water, *b* with 99.9% Deuterium Oxide, *c* with 85% Deuterium Oxide  
Spectrophotometer UR-10 Zeiss, Jena, gas cuvette 100 mm length.

of cerium dicarbide decomposition. The other carbides display practically the same spectra. The only exception are the gaseous mixtures formed in the decomposition of scandium, yttrium and holmium carbides. Their spectra show a new, distinct absorption maximum of methane and  $\text{CO}_2$ , appearing at  $1305$  and  $2349\text{ cm}^{-1}$ , respectively. A strong shift towards lower frequencies, by c. 70% of its numerical value, can be seen in the spectra of deuteriated products. From Fig. 2c it is evident that when deuterium oxide with equilibrium contents of DHO and  $\text{H}_2\text{O}$  is used as decomposition agent, only low peaks are found at the original positions for normal hydrocarbons and a medium shift appears for partially deuteriated products.

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