

CHROMATOGRAPHIC STUDIES ON THE HYDROLYSIS OF CARBIDES

PART II. THE HYDROLYSIS OF URANIUM CARBIDES

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(Received November 4th, 1963)

INTRODUCTION

Both uranium mono- and di-carbides are well known, particularly because of the interest of the atomic energy authorities of the world¹. The dicarbide UC₂ was first prepared by MOISSAN² by heating the metal and carbon. Later the compound was prepared by heating an oxide with graphite, with evolution of carbon monoxide³⁻⁵; usually uranium dioxide was preferred to U₃O₈ as the source of uranium. LITZ, GARRETT AND CROXTON⁴ prepared uranium monocarbide UC by passing methane over the finely divided metal, and it has also been prepared from the metal and graphite at 2100°⁴. It is reported that the dicarbide is formed at higher temperatures from both types of reaction⁶.

Uranium monocarbide is a face-centred cubic lattice structure^{3,4}, $a_0 = 4.955 \text{ \AA}$, whilst the dicarbide is a body-centred tetragonal system^{4,7}. $a_0 = 3.517 \text{ \AA}$, and $c_0 = 5.987 \text{ \AA}$ with a carbon-carbon bond distance of 1.34 Å.

The results of hydrolysis of UC as described by MOISSAN^{2,8} were 0.5 % acetylene, 6 % ethylene, 79 % methane, 14 % hydrogen, the gaseous products representing one-third of the combined carbon, and the two-thirds remaining were liquid and solid hydrocarbons. The observations of LEBEAU AND DAMIENS⁹ differ considerably from this, when 29 % hydrogen, 20 % methane, 23 % ethane and other gaseous hydrocarbons were reported after 23 days reaction. Recently BRADLEY AND FERRIS¹⁰ and KEMPTER¹¹ have reported observations on these systems. The results for uranium monocarbide at 25° agree; the approximate percentages being 10 % hydrogen, 87 % methane, 2 % ethane. KEMPTER reports for UC₂, 14 % hydrogen, 17 % methane, 5 % ethylene, 39 % ethane, 2 % propane, 16 % C₄'s (mainly *n*-butane), with smaller amounts of C₅- and C₆-hydrocarbons.

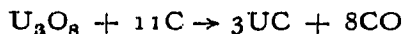
The work described here, was nearing completion when the latter two papers were published.

EXPERIMENTAL

Preparation

Uranium monocarbide. U₃O₈ (21.66 g) was mixed with carbon (3.40 g) finely ground and pelleted at 3 tons/sq. in. The pellets were placed in a previously outgassed graphite crucible and heated in a Wild Barfield/NRC vacuum resistance furnace (Model No. 2904B). The reaction,

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observed by the evolution of carbon monoxide, commenced at 1460° and was complete at 1690° . The temperature was taken up to 1760° for 90 min, when the pressure dropped to below 1μ . The pressure was never allowed to rise above 100μ . A grey crystalline, highly pyrophoric product was obtained. Yields *ca.* 92%. Analysis of a sample showed 95.3% uranium (UC requires 95.2%). An X-ray powder photograph showed the product to have face-centred cubic lattice with $a_0 = 4.958 \text{ \AA}$.

Uranium dicarbide. 10 g of uranium dicarbide were a gift from the U.K.A.E., R.E., Harwell. Analysis showed the carbide to contain 90.2% uranium (UC_2 requires 90.8%), and an X-ray powder photograph showed a body-centred tetragonal lattice with $a_0 = 3.52 \text{ \AA}$, and $c_0 = 6.00 \text{ \AA}$.

Hydrolysis

A simple all-glass apparatus was constructed which allowed the hydrolytic reagents used (2.5 ml) to be dropped on to the heated carbides (0.5 g) maintained at 100° by an oil bath. The resultant gases passed over a calcium chloride drying tube. The gases were then passed through a gas-sampling valve on to a gas-liquid chromatography column (25 ft. of 20% tetraisobutylene on 36-60 Silocel $\frac{1}{4}$ in. O.D. copper tubing) and detected using a flame ionisation detector, after the design of ONGKIEHONG¹². Temperature of the column was 20° , carrier gas nitrogen, 40 ml/min, hydrogen 20 ml/min, and air 400 ml/min. Fuller details of the apparatus were described previously¹³.

RESULTS

Tables I and II show the nature and composition (%) of the hydrolysis products of both carbides at 100° with 3 reagents, water, 4 N sulphuric acid and 4 N nitric acid

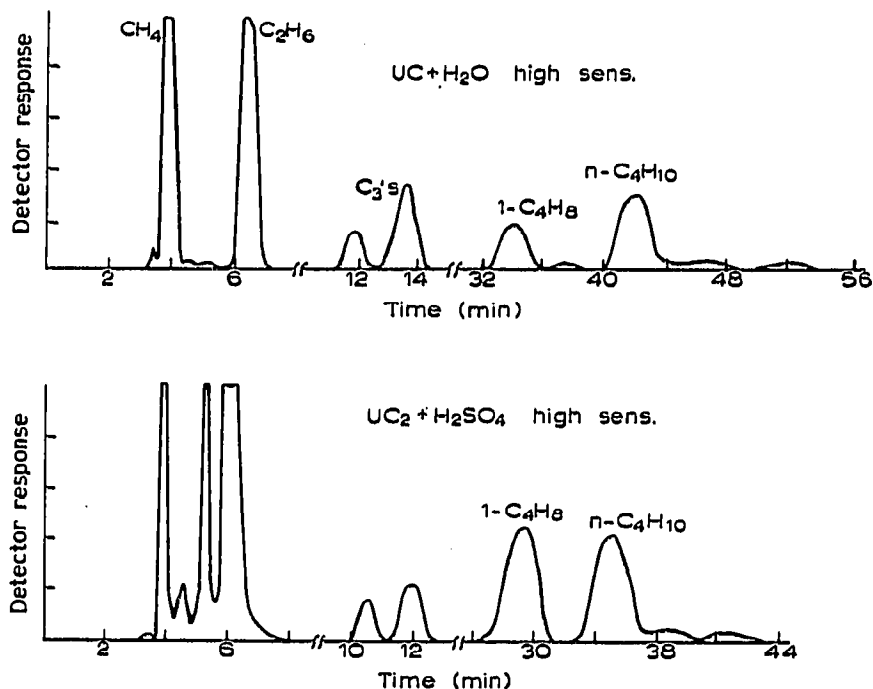


Fig. 1. Elution patterns for the hydrolysis of uranium mono- and dicarbides.

TABLE I
HYDROLYSIS OF URANIUM MONOCARBIDE

	<i>Hydrolysing agent</i>		
	H_2O	$4N H_2SO_4$	$4N HNO_3$
Hydrogen	9.16	7.47	8.09
Methane	79.05	78.55	64.64
Acetylene	0.57	0.64	0.72
Ethylene	0.43	0.86	0.43
Ethane	5.49	5.86	5.57
Propylene	0.57	0.79	1.32
Propane	1.36	0.27	2.00
1-Butene	0.86	0.91	0.58
1,3-Butadiene	0.42	0.83	0.36
<i>n</i> -Butane	1.40	1.44	1.06
<i>trans</i> -2-Butene	0.31	0.57	0.15
<i>cis</i> -2-Butene	0.31	0.57	0.18
Others	0.07	1.24	
Nitrogen oxides	0	0	14.91

respectively. Fig. 1 shows the elution patterns obtained with the monocarbide and dicarbide respectively. The nature of the products was established using the techniques which have been described previously¹³.

TABLE II
HYDROLYSIS OF URANIUM DICARBIDE

	<i>Hydrolysing agent</i>	
	<i>Water</i>	$4N H_2SO_4$
Hydrogen	0.54	0.64
Methane	27.71	26.75
Acetylene	0.57	0.64
Ethylene	9.23	8.87
Ethane	44.31	45.62
Propylene	2.00	3.22
Propane	6.00	4.57
1-Butene	4.02	3.92
<i>n</i> -Butane	4.93	4.08
<i>trans</i> -2-Butene	0	0.25
<i>cis</i> -2-Butene	0	0.26
Others	0.69	1.28

With both carbides a small waxy deposit was observed, probably higher hydrocarbons, but insufficient material was available for further study. Work is in progress to elucidate the nature of these products.

DISCUSSION

The results for the uranium monocarbide hydrolysis at 100° agree quite well with those of BRADLEY AND FERRIS¹⁰ at 99°; although the methane content is lower, and the ethane figure is higher. There is agreement with KEMPTER'S¹¹ results, although

traces of acetylene, propylene and unsaturated C_4 hydrocarbons were also observed. However, the results from uranium dicarbide do not agree with those of KEMPTER at 25° , less hydrogen and methane were found, whilst the work of LITZ¹⁴ (with 47 % hydrogen at 100°) is in even more disagreement. Metal-rich samples would hydrolyse giving more hydrogen than expected, as would samples prepared from the hydride, where hydrogen remained in the lattice.

Tables I and II both show that the hydrolysis products from water and sulphuric acid are almost identical, which indicates that the reaction involves the water molecule, probably in a chemisorption process, rather than as an ionic species. Oxygen has a greater affinity for uranium than hydrogen has, leading to the formation of oxide or hydrated oxide, and the reaction of atomic hydrogen with the carbon in the lattice then follows. In the case of the monocarbide, this clearly results in the methylene radical, with an excess of hydrogen forming methane and ethane as the main products. The lack of ethylene is probably due to its ease of hydrogenation. Over 96 % of the gaseous products are saturated hydrocarbons.

With uranium dicarbide, the carbon is present as carbon-carbon bonded groups in the lattice, with a bond length of 1.34 \AA . However, a large percentage of methane (26 %) points to an easy cleavage of this bond (indeed 83 % of the products are saturated hydrocarbons) and can be compared with the rare-earth dicarbides. In these cases, less than 1 % methane is formed, and over 65 % acetylene. The C_3 hydrocarbons are probably formed by reaction of a methylene or methyl radical, with a C_2 entity, and the C_4 hydrocarbons by dimerisation of C_2 radicals.

The results in Table I using nitric acid are different from those using water, and are worthy of separate discussion. Some 15 % of oxides of nitrogen are formed, but even allowing for this, the methane and C_4 hydrocarbon figures are lower, again due to the chain terminating activity of nitric oxide. It is most probable that such compounds as nitromethane, or formaldoxime are formed by the reactions of NO and hydrocarbon radicals in this system, since the formation of oxalic acid has been communicated to us¹⁵. Work is in progress to elucidate the solutions to these problems.

ACKNOWLEDGEMENTS

We wish to acknowledge the receipt of a D.S.I.R. Student Scholarship to one of us (S.E.) during this work, and our thanks are extended to the Royal Society for financial help in the purchase of equipment. Acknowledgement is made to the Atomic Energy Research Establishment, Harwell, of the Atomic Energy Authority, for a gift of the uranium dicarbide, and to Dr. G. M. PHILLIPS for unpublished information concerning the dicarbide hydrolysis.

SUMMARY

The gaseous products of the hydrolysis of uranium mono- and dicarbides using water, nitric acid and sulphuric acid at 100° is reported. Gas-liquid chromatography was used to elucidate the products. The results are discussed with a view to justifying the number of hydrocarbon products with respect to the nature of the carbide.

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J. Chromatog., 15 (1964) 223-227