

ORNL
MASTER COPY
OAK RIDGE NATIONAL LABORATORY

operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION



ORNL - TM - 462

COPY NO. - 41

DATE - January 21, 1963

HYDROLYSIS OF URANIUM CARBIDES BETWEEN 25 AND 100°.*
II. AS-CAST ALLOYS CONTAINING 2 TO 10 WT. % CARBON

By

Mildred J. Bradley and Leslie M. Ferris

ABSTRACT

Reactions with water of as-cast uranium-carbon alloys containing 2 to 10 wt. % carbon ($UC_{0.4}$ to $UC_{2.2}$) were investigated by using gas-chromatography for analysis of the gaseous products. Uranium metal-uranium monocarbide alloys yielded 2 moles of free hydrogen per mole of free metal, in addition to methane, small quantities of higher molecular weight gaseous hydrocarbons, and a solid, hydrous, tetravalent uranium oxide. The gaseous products contained all the carbon originally present in the alloy. Uranium dicarbide ($UC_{1.86}$; this combined-C/U atom ratio was the maximum which could be obtained) yielded a mixture of 36 hydrocarbons (methane, 15 vol. %; ethane, 28%; C_3 - to C_8 -alkanes, 7%; alkenes, 8%; alkynes, 0.6%; and unidentified unsaturates, 1%), free hydrogen (40 vol. %), a water-insoluble wax, and a solid, hydrous, tetravalent uranium oxide. Forty % of the combined carbon was found in the gas and 25% in the wax. The gaseous products from the hydrolysis of both UC and $UC_{1.86}$ were not affected by changes in the reaction temperature between 25 and 99°. The composition of the gases evolved at 80° from as-cast alloys with compositions between UC and $UC_{1.86}$ varied linearly with the combined-C/U atom ratio of the alloy, however, the amounts of methane produced were lower than expected from the UC concentrations in the alloys.

*For review by Inorganic Chemistry.

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

- A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or
- B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

(Contribution from the Chemical Technology Division, Oak Ridge
National Laboratory, Oak Ridge, Tennessee¹)

(1) Operated by Union Carbide Nuclear Co. for the U. S. Atomic Energy
Commission.

HYDROLYSIS OF URANIUM CARBIDES BETWEEN 25 AND 100°.
II. AS-CAST ALLOYS CONTAINING 2 TO 10 WT. % CARBON

By

Mildred J. Bradley and Leslie M. Ferris

Reactions with water of as-cast uranium-carbon alloys containing 2 to 10 wt. % carbon ($UC_{0.4}$ to $UC_{2.2}$) were investigated by using gas-chromatography for analysis of the gaseous products. Uranium metal-uranium monocarbide alloys yielded 2 moles of free hydrogen per mole of free metal, in addition to methane, small quantities of higher molecular weight gaseous hydrocarbons, and a solid, hydrous, tetravalent uranium oxide. The gaseous products contained all the carbon originally present in the alloy. Uranium dicarbide ($UC_{1.86}$; this combined-C/U atom ratio was the maximum which could be obtained) yielded a mixture of 36 hydrocarbons (methane, 15 vol. %; ethane, 28%; C_3 - to C_8 -alkanes, 7%; alkenes, 8%; alkynes, 0.6%; and unidentified unsaturates, 1%), free hydrogen (40 vol. %), a water-insoluble wax, and a solid, hydrous, tetravalent uranium oxide. Forty % of the combined carbon was found in the gas and 25% in the wax. The gaseous products from the hydrolysis of both UC and $UC_{1.86}$ were not affected by changes in the reaction temperature between 25 and 99°. The composition of the gases evolved at 80° from as-cast alloys with compositions between UC and $UC_{1.86}$ varied linearly with the combined-C/U atom ratio of the alloy, however, the amounts of methane produced were lower than expected from the UC concentrations in the alloys.

INTRODUCTION

Reactions with water of as-cast uranium-carbon alloys containing 2 to 10 wt. % carbon ($UC_{0.4}$ to $UC_{2.2}$) were investigated at temperatures between 25 and 99° as part of a systematic study of the hydrolytic be-

havior of uranium and thorium carbides. Several studies of the hydrolysis of sintered uranium carbides have been conducted, but no data were available on the behavior of as-cast UC-UC_{1.86} or low-carbon alloys. Earlier results of this study have been reported on the hydrolysis of UC and a UC_{0.8} alloy.²

(2) M. J. Bradley and L. M. Ferris, *Inorg. Chem.*, 1, 683 (1962).

There is general agreement that hydrolysis between 25 and 99° of uranium monocarbide yields principally methane with some hydrogen and small quantities of higher hydrocarbons.²⁻⁴ Litz,⁵ however, reported

(3) C. P. Kempter, *J. Less-Common Metals*, 4, 419 (1962).

(4) G. Baudin, J. Besson, P. Blum, and J. Spitz, *Compt. rend.*, 254, 4179 (1962).

(5) L. M. Litz, "Uranium Carbides; Their Preparation, Structure, and Hydrolysis," Ph. D. Thesis, Ohio State University (1948).

that the methane concentration decreased and the hydrogen increased with increasing temperature. Moissan⁶ studied the reaction of water with a

(6) H. Moissan, *Compt. rend.*, 122, 274 (1896).

sintered carbide having the composition "U₂C₃"; however, later work⁷

(7) P. Lebeau and A. Damiens, *Compt. rend.*, 156, 1987 (1913).

showed that his reported results were probably in error because methane could not be separated from the higher hydrocarbons according to his procedure. Lebeau and Damiens⁷ also investigated the hydrolysis of sintered "UC₂" (which was only partially analyzed) and obtained 32-36 ml. of gas per gram of "UC₂" consisting of 30-50% hydrogen, 12-20% methane, 23-25% ethane, 3-10% higher alkanes, 8-15% alkenes, and 1-3% alkynes. The composition of the carbide was determined solely by elemental analysis by both Moissan⁶ and Lebeau and Damiens.⁷ Litz⁵ studied the hydrolysis of sintered uranium dicarbide, finding at 85°, 17% hydrogen, 30% methane, 38% higher alkanes, 12% alkenes, and 2% alkynes; and, at 95°, 39% hydrogen, 18% methane, 31% higher alkanes, 9% alkenes, and 1% alkynes. It should be noted however, that Litz reported no elemental analyses. Kempter³

investigated the reaction of arc-melted uranium dicarbide (combined-carbon/uranium atom ratio of 1.87) with water at room temperature in a closed system (pressure unspecified) and obtained 14% hydrogen, 17% methane, 39% ethane, 8% higher alkanes, 20% alkenes, and 2% alkynes. Neither Litz⁵ nor Kempter³ measured the volume of gas evolved.

EXPERIMENTAL

Materials. - The uranium-carbon alloys were prepared by arc-melting high-purity uranium metal (less than 400 p.p.m. total impurities) and spectroscopic grade carbon, using nonconsumable tungsten electrodes. Buttons were remelted an additional eight times (2-minute melts) to ensure complete reaction after visual examination had shown that all the carbon had dissolved in the melt. Chemical analyses for uranium, total carbon, and free carbon, and the major constituents as identified by X-ray analysis are given in Table 1. The dicarbide specimens had identical X-ray powder patterns except that the faint UC line was missing from the UC₂-16A pattern. The alloys were also analyzed for oxygen (0.1%), nitrogen (65 p.p.m.), and tungsten (0.2%). Metallographic examination at magnifications of 250X and 1000X showed that UC specimen 2E was nearly single phase, with traces of uranium metal at the grain boundaries and a higher uranium carbide within the grains. The UC_{0.4} and UC_{0.8} alloys (specimens 7A and 6B) were mixtures of α -uranium at the grain boundaries and uranium monocarbide. Specimen 6B also contained a trace of a third phase within the monocarbide grains. The contrast between the α -uranium phase and the monocarbide in the photomicrographs of specimen 7A was so great that the presence of additional phases within the monocarbide grains would probably not have been detected. Specimens 3B, 4B, and 5B, which had compositions between UC and UC_{1.86}, were two-phase mixtures of the mono- and dicarbides. Even at a magnification of 1000X, specimen UC₂-16A (nominally UC_{1.91}; combined-C/U atom ratio of 1.88) appeared to be virtually single phase. Specimen UC₂-13A (nominally UC_{1.91}; combined-C/U ratio of 1.87) contained a trace of a second phase. Specimen UC₂-4A (nominally UC_{1.93}) contained spherical particles of graphite, while specimens UC₂-1A, -2A, and -5A

TABLE I.
COMPOSITION OF URANIUM CARBIDE SPECIMENS

Specimen	Analyses, wt. %			Combined C/U Atom Ratio	X-ray Powder Pattern ^a		
	U	Total C	Free C		U	UC	UC ₂
7A	98.0	1.95	0.02	0.39	P	P	
6B	96.0	4.01	0.05	0.83	W	P	
2E	95.2	4.68	0.01	0.97		P	
3B	94.0	6.06	0.12	1.25		P	W
4B	93.1	7.00	0.05	1.48		P	P
5B	92.0	8.03	0.08	1.71		W	P
UC ₂ -13A	91.2	8.78	0.18	1.87		T	P
UC ₂ -16A	91.2	8.80	0.14	1.88			P
UC ₂ -4A	91.2	8.88	0.30	1.86		T	P
UC ₂ -1A	90.9	9.12	0.70	1.84		T	P
UC ₂ -2A	90.9	9.18	0.74	1.84		T	P
UC ₂ -5A	91.0	9.06	0.62	1.84		T	P
UC ₂ -6A	90.3	9.78	1.54	1.81		T	P

^a P, present; W, weak; T, faint trace based on one, very faint line at 2.87 Å.

(nominally UC_{1.99}) and UC₂-6A (nominally UC_{2.15}) contained large amounts of graphite which appeared as rod-shaped dark areas in the photomicrographs.

Procedure. - The hydrolyses were conducted in a helium atmosphere using the technique described previously.² When there was no further gas evolution over a 16-hr period, the gas was sampled and the gelatinous uranium oxide residue dissolved. Residues for alloys containing no uranium metal were dissolved in 6 M HCl, while 12 M H₃PO₄ was used for the U-UC residues since they were not readily soluble in HCl. Non-volatile, acid-insoluble waxes, found when the alloys contained uranium dicarbide, were recovered by washing them from the apparatus using acetone and then ether and subsequently removing the solvents by evaporation.

Analytical. - The carbide specimens were analyzed for uranium, total carbon, oxygen, and nitrogen by procedures described previously.² Free carbon was determined after the sample was dissolved in refluxing 6 M HCl and the solution was filtered through a Leco disposable filtering crucible (No. 528-30, Laboratory Equipment Corp., St. Joseph, Michigan). The residue was burned and the carbon was determined as CO₂. The X-ray powder patterns were determined with a Debye-Scherrer 114.59-mm. diameter powder camera using Cu K-α radiation. The monocarbide and dicarbide patterns were the same as those reported by Litz, Garrett, and Croxton.⁸

 (8) L. M. Litz, A. B. Garrett, and F. C. Croxton, J. Am. Chem. Soc., 70, 1718 (1948).

Specimens were prepared for metallography by the techniques described by Gray, Thurber, and DuBose.⁹

 (9) R. J. Gray, W. C. Thurber, and C. K. H. DuBose, Metal Progr., 74, 65 (1958).

Gas samples were analyzed by gas-chromatography using a Burrell Kromotog K-2 instrument modified with a Gow-Mac thermistor detector. For optimum peak separation and resolution, four column packings were necessary. The column packings and temperature programs used for determining the specific gases are given below:¹⁰

5-A Molecular Sieve
(75°)

hydrogen
oxygen
nitrogen
methane

Tricresyl Phosphate

(room temperature, 12 min;
nonlinear heating to ~80°, 12 min.)

n-hexane
hexene-1, -2, and -3
hexyne-1, and -2

Silica Gel--3 wt. % Squalane

(room temperature, 6 min.;
nonlinear heating to ~65°,
12 min.)

ethane
ethylene
propane
acetylene
n-butane
unknown C₅-1
isopentane

Di-2-ethylhexyl Sebacate

(25% on C-22 Firebrick; room temp. 12 min.
nonlinear heating to ~80°, 12 min;
nonlinear heating to ~110°, 12 min.)

isobutane
propyne
cis- and trans-butene-2
butyne-1
unknown C₄
unknown C₅-2
pentene-2

(Continued from page 5)

n-pentane	unknown C ₆ -1 and -2
butene-1	3-methylpentene-1
	3-methylpentane+hexyne-1-(one
	heptene-2 peak)
	unknown C ₇ -1, -2, -3, and -4
	n-heptane
	unknown C ₈ -1, and -2
	n-octane

(10) A. D. Horton, unpublished data.

The chromatographic peaks for all identified hydrocarbons were checked against known standards using at least two different packings. The hydrocarbons were also tested for unsaturation with a mercuric perchlorate column.¹¹ The amount of each unknown compound was estimated using

(11) R. L. Martin, Anal. Chem., 34, 896 (1962).

the calibration constant for the n-alkane which was eluted after the unknown. All the unknown compounds were sorbed by mercuric perchlorate, indicating unsaturation. They did not correspond to any of the following standards: propene, isobutylene, 1,3-butadiene, butyne-2, pentene-1, pentyne-1, pentyne-2, 2-ethylbutene-1, heptene-1, or heptene-3. The compounds erroneously called branched hexane isomers in the first paper,² are now believed to be unsaturates except for a small amount of 3-methylpentane.

RESULTS

The maximum combined-C/U atom ratio which could be obtained by non-consumable arc-melting with tungsten electrodes was 1.86 ± 0.02 based on chemical analyses for total and free carbon, metallography, and hydrolysis studies. Heat-treating of specimens with a nominal C/U atom ratio of 2.00 for 6 hours at 2000^o, 60 hours at 1600^o, and 240 hours at 1260^o produced no effect on the combined-C/U ratio or hydrolysis properties,¹²

(12) M. J. Bradley, unpublished data.

further indicating that uranium dicarbide is a nonstoichiometric compound. It is also significant to note that we have successfully prepared essentially single-phase UC_{1.86}. Leitnaker and Witteman¹³ also

reported that $UC_{1.86}$ is the formula for uranium dicarbide.

(13) J. M. Leitnaker and W. G. Witteman, J. Chem. Phys., 36, 1445 (1962).

The water hydrolysis of uranium carbides yielded complex mixtures of gaseous hydrocarbons and a gelatinous, hydrous, tetravalent uranium oxide. Nonvolatile waxes were also formed when the alloy contained uranium dicarbide. The volume of gas evolved decreased from 138 ml. (STP) per gram of carbide to 42 ml. per gram as the combined-C/U atom ratio increased from 0.39 to 1.86 (Table II).

Hydrolysis of uranium monocarbide² yielded principally methane (86 vol. %), with some hydrogen (11%) and small quantities of higher hydrocarbons. The U-UC alloys, as expected, yielded 2 moles of hydrogen per mole of free metal in addition to the expected UC hydrolysis products. The gaseous hydrolysis products of specimens having compositions of $UC_{0.4}$ to $UC_{1.0}$ contained all the carbon originally present in the alloy (Table III).

The reaction of $UC_{1.86}$ with water yielded a water-insoluble wax, and a gas containing about 40 vol. % hydrogen and a complex mixture of at least 36 hydrocarbons: methane, 15 vol. %; ethane, 28%; propane, 1.0%; butanes, 4.6%; C_5 - to C_8 -alkanes, 1.1%; ethylene, 1.6%; butenes, 4.7%; C_5 - to C_7 -alkenes, 2.0%; alkynes, 0.06%; and unidentified unsaturated compounds, 1.2%. Of the combined carbon present initially in the $UC_{1.86}$ specimens, 37% was found in the gas phase and about 25% in the wax. The remaining carbon presumably was dissolved in the water in concentrations too low to detect by conventional analytical procedures. No water-insoluble liquid hydrocarbons were observed. The wax had a H/C ratio of about 1.1. Preliminary infrared data indicated the presence in the wax of aromatic- and aliphatic double bonds, C=O (ester, aldehyde, ketone) bonds, and C-O-C (ester, ether) bonds. Varying the amounts of free carbon in specimens with a combined-C/U ratio of 1.86 did not change the number of equivalents of the various hydrocarbon gases from a gram of carbide (Table III). Variations in the total volumes of gas and the equivalents of hydrogen have been

TABLE II.
GASEOUS PRODUCTS FROM THE HYDROLYSIS OF AS-CAST URANIUM CARBIDES AT 80°

Specimen	7A	6B	2E	3B	4B	5B	UC ₂ -13A	UC ₂ -16A	UC ₂ -4A	UC ₂ -1A	UC ₂ -2A	UC ₂ -5A	UC ₂ -6A
Combined-C/U atom ratio	0.39	0.83	0.97	1.25	1.48	1.71	1.87	1.88	1.86	1.84	1.84	1.84	1.81
Volume of gas evolved ml. (STP)/g. of alloy	138	108	96	78	64	50	38	44	42	40	42	43	43
Gas composition, vol. %													
Hydrogen	79	37	13	23	24	30	36	48	40	34	41	40	51
CH ₄	18	60	84	60	48	32	13	10	14	17	16	15	12
C ₂ H ₆	1.14	1.78	1.76	11	18	24	32	26	29	31	27	28	23
C ₃ H ₈	0.50	0.48	0.43	1.01	1.38	1.13	1.02	0.84	1.02	1.04	1.04	1.00	0.80
C ₄ H ₁₀ ^a	0.18	0.03	0.18	1.72	2.96	4.39	5.58	3.85	4.53	5.06	4.58	4.36	3.92
C ₅ H ₁₂ ^b	0.08	0.16	0.06	0.25	0.30	0.37	0.40	0.27	0.42	0.40	0.32	0.28	0.25
C ₆ H ₁₄ ^c	0.03	0.02	0.02	0.21	0.34	0.57	0.71	0.36	0.69	0.71	0.63	0.84	0.51
C ₇ -C ₈ alkanes	--	--	--	--	0.07	0.05	0.10	0.08	0.11	0.11	0.10	0.12	0.10
C ₂ H ₄	0.05	0.02	0.04	0.46	0.68	0.70	2.10	1.84	1.45	1.58	1.46	1.45	1.27
Butene-1	0.09	0.06	0.06	0.87	1.64	2.76	3.44	2.94	3.48	3.27	2.97	3.17	2.80
Cis-butene-2	0.03	0.03	0.02	0.43	0.64	0.62	0.78	0.89	0.82	0.90	0.72	0.99	0.72
Trans-butene-2	0.03	0.03	0.02	0.29	0.54	0.57	0.68	0.80	0.69	0.79	0.63	0.82	0.68
Pentene-2	0.03	0.01	0.01	0.07	0.11	0.05	0.08	0.16	0.04	0.07	0.04	0.20	0.07
C ₆ H ₁₂ ^d	0.05	0.02	0.02	0.29	0.79	1.40	1.71	1.38	1.80	1.69	1.59	1.60	1.33
Heptene-2	--	0.01	--	0.01	0.05	0.25	0.31	0.18	0.35	0.28	0.26	0.38	0.13
C ₃ H ₄	--	--	--	--	0.02	--	--	0.13	--	0.02	--	0.02	0.02
Butyne-1	--	--	--	0.01	0.02	0.18	0.49	1.02	0.55	0.27	0.27	0.31	0.33
Hexyne-1 and -2	--	--	--	0.01	0.02	0.07	0.08	0.13	0.08	0.09	0.08	0.12	0.06
Unidentified ^e	0.20	0.29	0.13	0.47	0.63	1.11	1.33	1.20	1.38	1.18	0.94	1.12	1.15

^a Includes 0.01 to 0.02 vol. % isobutane.

^b n-Pentane (72% of total C₅H₁₂) and isopentane (28%).

^c n-Hexane (56% of total C₆H₁₄) and 3-methylpentane (44%).

^d Hexene-1 (25% of total C₆H₁₂), Hexene-2 (14%), Hexene-3 (25%), and 3-Methylpentene-1 (36%).

^e At least 11 components, all unsaturated.

TABLE III.
CARBON DISTRIBUTION IN THE HYDROLYSIS OF AS-CAST URANIUM CARBIDES AT 80°

Specimen	7A	6B	2E	3B	4B	5B	UC ₂ -13A	UC ₂ -16A	UC ₂ -4A	UC ₂ -1A	UC ₂ -2A	UC ₂ -5A	UC ₂ -6A
mg.-atoms of carbon per g. of original alloy													
Carbide (elemental analysis)													
Total carbon	1.62	3.33	3.90	5.05	5.83	6.69	7.31	7.33	7.39	7.59	7.65	7.54	8.14
Free carbon	0.02	0.04	0.01	0.10	0.04	0.07	0.15	0.12	0.25	0.58	0.62	0.52	1.28
Gaseous products													
CH ₄	1.14	2.90	3.61	2.08	1.37	0.70	0.23	0.20	0.25	0.31	0.31	0.29	0.23
C ₂ H ₆	0.14	0.17	0.15	0.80	1.12	1.06	1.10	1.02	1.09	1.13	1.00	1.08	0.88
C ₃ -C ₈ alkanes	0.18	0.12	0.10	0.43	0.58	0.59	0.54	0.42	0.52	0.55	0.51	0.54	0.45
Alkenes	0.07	0.04	0.03	0.33	0.53	0.62	0.62	0.64	0.68	0.64	0.59	0.70	0.55
Alkynes	--	--	--	0.01	0.01	0.02	0.07	0.10	0.05	0.03	0.02	0.04	0.03
Unidentified	0.06	0.07	0.03	0.08	0.11	0.14	0.13	0.14	0.15	0.12	0.11	0.13	0.13
Total	1.60	3.29	3.92	3.73	3.71	3.14	2.70	2.52	2.74	2.78	2.54	2.78	2.27
Nonvolatile products													
Wax	--	--	--	0.22	0.66	1.33	1.55	2.36	1.63	1.66	1.68	2.18	2.10
Insoluble residue	--	--	--	--	--	--	0.18	0.12	0.21	0.61	0.62	0.67	1.34
Unaccounted for	--	--	--	1.10	1.46	2.22	2.88	2.33	2.77	2.54	2.81	1.91	2.43

confirmed by duplicate experiments and are related to the amounts of wax (H/C ratio of 1.1) and "unaccounted" products (estimated H/C ratio of about 1.8 assuming total hydrogen for the system as 4H atoms per U atom because the uranium product is tetravalent).

Hydrolysis of as-cast specimens with compositions between UC and UC_{1.86} produced a linear decrease in the methane concentration and increases in the amounts of free hydrogen, C₂- to C₈-hydrocarbons, and wax as the combined-C/U atom ratio of the alloy increased (Tables II and III).

Varying the reaction temperature between 25 and 99° had no detectable effect on the composition of the gas in the hydrolysis of UC_{1.86} (Table IV). These results differ markedly from those of Litz⁵ who reported that the free hydrogen concentration increased from 17 to 39% while the methane concentration decreased from 30 to 18% as the temperature was raised from 83 to 95°. Temperature also had no effect on the gas composition in the hydrolysis of uranium monocarbide.² Although the gas composition was not affected, the rates of hydrolysis increased markedly with increasing temperature. The time required for complete reaction of a 3- to 4-g. specimen of UC_{1.86} varied from 3.5 days at 25° to about 3 hours at 99° (Fig. 1). During the first 5 hours at 25°, there was no visible change in the carbide. After 16 hr., complete disintegration of the sample had occurred, yet only half of the gas had been evolved. This behavior is similar to that of uranium monocarbide at the lower temperatures where it is postulated that water first attacks cleavage planes in the crystals.² Relative reaction rates were UC > UC_{1.86} > U metal. Uranium monocarbide was completely hydrolyzed in 3 hours at 80° compared to 5 to 15 hours for the dicarbide specimens and 15 days for UC_{0.39}.

DISCUSSION

Uranium monocarbide, either in the pure state or alloyed with uranium metal, yields primarily methane on hydrolysis as expected from its crystal structure since each carbon atom is surrounded by six uranium atoms at a distance of 2.48 Å. while the closest C-C distance is 3.50 Å.¹⁴

TABLE IV.
EFFECT OF TEMPERATURE ON THE COMPOSITION OF THE GASEOUS PRODUCTS
FROM THE HYDROLYSIS OF UC_{1.86}
Specimen used: UC₂-16A

Temperature, °C	25	40	80	99
Volume of gas evolved, ml. (STP) per g. of carbide	43.2	43.2	43.7	43.1
Gas composition, vol. %				
Hydrogen	52	49	48	50
CH ₄	9	10	10	10
C ₂ H ₆	24	26	26	26
C ₃ H ₈	0.8	0.9	0.8	0.7
C ₄ H ₁₀	3.9	3.8	3.8	3.0
C ₅ H ₁₂	0.25	0.21	0.21	0.19
C ₆ H ₁₄	0.19	0.44	0.36	0.57
C ₇ H ₁₆	0.05	0.08	0.06	0.05
C ₈ H ₁₈	0.02	0.02	0.02	0.03
C ₂ H ₄	1.7	1.8	1.8	1.2
C ₄ H ₈	4.5	4.8	4.6	4.3
C ₅ H ₁₀	0.14	0.07	0.16	0.12
C ₆ H ₁₂	1.0	1.1	1.4	0.3
C ₇ H ₁₄	0.18	0.12	0.18	0.37
C ₃ H ₄	0.13	0.13	0.13	0.14
C ₄ H ₆	1.0	1.0	1.0	1.2
C ₆ H ₁₀	0.11	0.12	0.13	0.10
Unidentified ^a	0.9	1.1	1.2	1.1

^a At least 11 components, all unsaturated.

Similarly, uranium dicarbide, which contains pairs of carbon atoms with a C-C distance of 1.34 Å. (double bond distance)^{14,15}, on hydrolysis gives

(14) A. E. Austin, Acta Cryst., 12, 159 (1959).

(15) M. Atoji, J. Chem. Phys., 35, 1950 (1961).

gaseous hydrocarbons containing predominantly 2, or multiples of 2, carbon atoms in addition to the more highly polymerized wax. The formation

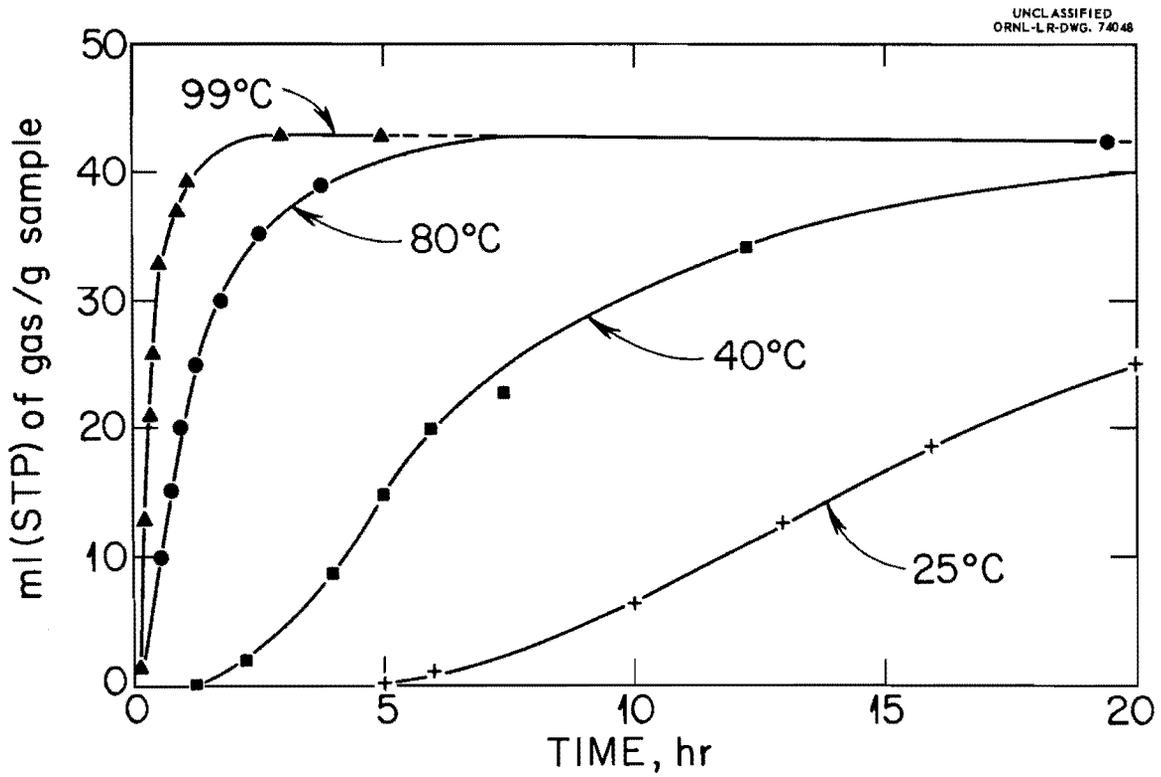


Fig. 1. Rates of gas evolution in the reaction of 3- to 4-g specimens of $UC_{1.86}$ (sample UC_2-16A) with water.

of methane and hydrocarbons containing an odd number of carbon atoms indicates that $UC_{1.86}$ contains some single C units as well as C_2 units in the crystal. One of the most interesting features of the uranium dicarbide hydrolysis reaction is the reproducible production of such a complex mixture of gaseous hydrocarbons independent of temperature between 25 and 99°.

With C=C units in the dicarbide crystal and 4 hydrogen atoms available for hydrogenation per uranium atom (because the final uranium product is tetravalent), ethylene might be expected as a primary product:



The reaction products actually formed indicate a complex mechanism. In preference to the formation of ethylene (0.8% of the combined carbon), the C=C units present in the crystal are either hydrogenated to ethane (15% of the carbon) or polymerized to higher molecular weight compounds. Straight-chain isomers predominate over branched chain. While the isobutane concentration was always 0.01 to 0.02%, independent of the n-butane concentration and the amount of dicarbide present in the original alloy, the n-pentane concentration was always about 72% of the total pentane concentration, and the n-hexane about 56% of the total hexanes. 3-Methylpentane, the only branched hexane found, is also the only one which could be formed by the polymerization of C=C units. The double bond was always in the 2-position in n-alkenes containing an odd number of carbon atoms (pentene-2, heptene-2), while those containing an even number of carbon atoms favored the 1- and 3-positions (butene-1, 65% of the total C_4H_8 ; hexene-1, 40%, and hexene-3, 39% of the n- C_6H_{12}). 3-Methylpentene-1, the only branched hexene identified to date (and probably the only one present in significant quantities since the two unidentified peaks in the C_6 range represent only about 0.1% of the total gas), like 3-methylpentane could be formed by the polymerization of C=C units. No 2-ethylbutene-1, which also would yield 3-methylpentane upon hydrogenation, was found. Approximately equal amounts of cis- and trans-butene-2, 54 and 46%, respectively, were formed. As noted by Palenik and Warf¹⁶ in the hydrolysis of lanthanum and cerium carbide, "the formation

of equimolar amounts of the two 2-butenes does not represent thermal equili-

(16) G. J. Palenik and J. C. Warf, Inorg. Chem., 1, 345 (1962).

brium and, therefore, must be a consequence of the mechanism by which the two were formed." Identification of the 11 unidentified, unsaturated compounds is limited by the available standards. Except for one of the unknown C₅ compounds (about 0.5 vol. %) and one of the C₇ compounds (about 0.2%), all unidentified compounds were less than 0.1%. The reproducible production of such a complex mixture of gaseous hydrocarbons must reflect structural characteristics in the solid crystal, yet variations in the extent of polymerization to form wax also indicate that catalytic surfaces may be involved in the hydrolysis. Additional study of the non-volatile products, particularly the "unaccounted for" ones, is needed before the hydrolysis of uranium dicarbide can be fully understood.

Although the hydrolysis at 80^o of as-cast uranium carbides having compositions between UC and UC_{1.86} produced a linear decrease in the methane concentration and increases the amounts of higher hydrocarbons, hydrogen and wax with increasing combined-C/U atom ratio in the alloy, the yields of methane were considerably lower than expected from the UC concentration in the alloy, basing the calculations on a UC-UC_{1.86} binary. For example, the calculated amount of UC present in UC_{1.25} is 2.79 mmoles. per g. of alloy, which should result in the formation of about 2.6 mmoles. of methane per gram. Experimentally, the specimen yielded only 2.08 mmoles. of methane per gram. Both X-ray and metallographic examination indicated that the as-cast alloys were composed of binary mixtures of UC and UC_{1.86}. Therefore, it appears that some of the C units from the UC hydrolysis (which react mainly with hydrogen to form methane in the absence of UC_{1.86}) react with units from the UC_{1.86} to produce higher hydrocarbons. Since some C units react with C₂ units in the hydrolysis of UC-UC_{1.86} mixtures, it is possible that the small quantities of higher hydrocarbons produced in the hydrolysis of essentially pure uranium monocarbide² arise from polymerization of C units from the monocarbide as well as from the dicarbide impurity.

The composition of the gases evolved in the hydrolysis of $UC_{1.86}$, as determined in this investigation, was similar to that obtained by Lebeau and Damiens⁷ if allowance is made for the problems they encountered in separating similar gases by fractional distillation and chemical sorption. Their lower gas volumes (32 to 36 ml/g. vs. 38 to 44 ml/g.) suggest the presence of UO_2 and carbon in their carbide. The results of this study differ significantly from those obtained by Litz⁵ who reported that the composition of the hydrolysis products changed markedly with temperature between 83 and 95°. We obtained considerably more hydrogen (34 to 50%) than did Kempster³ (14%). Ignoring the hydrogen and calculating relative amounts of hydrocarbons, about 47% ethane, 2% propane, and 7% butane were found in both studies; however, Kempster found more alkenes (22% vs. 14% plus a possible 2% as unidentified unsaturates) and less methane (20% vs. 25%). The difference in the hydrogen concentration in the two studies may reflect a pressure effect on the reaction, since Kempster probably did not hydrolyze his specimens at atmospheric pressure, or his specimens may have yielded less wax and, therefore, less hydrogen than ours did. Some variation in the amounts of wax and free hydrogen from specimens prepared under outwardly identical conditions was observed in this study. Since neither Litz nor Kempster determined the amounts of gaseous hydrocarbons and wax formed, no quantitative comparison with their data can be made.

ACKNOWLEDGEMENT

The authors wish to thank several members of the ORNL Metals and Ceramics Division for their aid in this study: T. Hikido and L. Queener for preparing the specimens, and R. J. Gray for supervising the metallographic examinations. We are also indebted to the ORNL Analytical Chemistry Division, in particular A. D. Horton for developing the gas chromatographic procedure, J. L. Botts for analyzing the gas samples, and W. R. Laing and R. L. Sherman for supervising the chemical and X-ray analyses.



DISTRIBUTION

1. E. L. Anderson, AEC, Wash.
2. R. E. Blanco
- 3-28. M. J. Bradley
29. F. L. Culler
30. F. R. Dowling, AEC, Wash.
- 31-32. L. M. Ferris
- 33-34. E. J. Murphy
35. J. W. Nehls
- 36-37. CR Library
38. Document Reference Section
- 39-40. Laboratory Records
41. Laboratory Records - RC
- 42-56. DTIE
57. Research and Development Div, ORO

1
2
3

4
5
6

7
8
9