CONTRIBUTION FROM THE CHEMICAL TECHNOLOGY DIVISION,
OAK RIDGE NATIONAL LABORATORY, OAK RIDGE, TENNESSEE[1]

Hydrolysis of Uranium Carbides between 25 and 100°. III. Uranium Sesquicarbide and Mixtures of the Sesquicarbide with Monocarbide or Dicarbide

BY MILDRED J. BRADLEY AND LESLIE M. FERRIS

Received November 15, 1963

Reactions with water of heat-treated (60 hr. at 1600°) uranium carbides with total-C:U atom ratios varying from 1.0 to 2.0 were investigated using gas chromatography for analysis of the gaseous products. Uranium sesquicarbide [$U_4(C_2)_3$] yielded a gas containing hydrogen (59 vol. %) and hydrocarbons (methane, 2 vol. %; ethane, 26%; C_3 to C_8 alkanes, 6%; alkenes, 7%; alkynes, 0.6%; and unidentified unsaturates, 0.8%), a water-insoluble wax, and a hydrous uranium(IV) oxide. Fifty per cent of the carbon was found in the gas and 10% in the wax. Varying the reaction temperature between 25 and 99° caused no change in the hydrolysis products. Uranium monocarbide–sesquicarbide mixtures (UC to $UC_{1.5}$) produced less methane and more C_2 to C_8 hydrocarbons than expected, indicating that polymerization involving single carbon units from the monocarbide had occurred. Hydrolysis of sesquicarbide–dicarbide mixtures ($UC_{1.5}$ to $UC_{1.85}$) yielded the products expected from the behavior of the separate compounds—principally C_2 to C_8 hydrocarbons with some hydrogen and a little methane. No uranium sesquicarbide was formed when an as-cast specimen with a combined-C:U atom ratio of 1.86 was heat treated under conditions where uranium sesquicarbide should have formed if the as-cast specimen were a mixture of UC and $UC_{2.0}$. This further confirms prior work showing that $UC_{1.85\pm0.03}$ is the composition of the dicarbide.

Introduction

Three compounds exist in the uranium–carbon system: uranium monocarbide (UC), uranium sesquicarbide [$U_4(C_2)_3$], and uranium dicarbide[2] ($UC_{1.85\pm0.03}$). The monocarbide and dicarbide are thermally stable to short heat treatments.[3] Uranium sesquicarbide forms slowly at temperatures below about 1780°, while above that temperature it decomposes into the monocarbide and dicarbide.[3,4] The specimens prepared for this study by heat treating at 1600° include the sesquicarbide ($UC_{1.5}$), mixtures of the sesquicarbide with the monocarbide ($UC_{1.0}$ to $UC_{1.5}$), and mixtures of the sesquicarbide with the dicarbide ($UC_{1.5}$ to $UC_{1.85}$). The hydrolysis of as-cast specimens containing the high-temperature stable monocarbide and dicarbide phases which are quenched from the melt has been reported previously.[2,5]

Little is known about the chemistry of uranium sesquicarbide. The hydrolysis of a "U_2C_3" composition was reported by Moissan[6]; however, the sesquicarbide phase was not identified by X-ray or other techniques and the thermal treatment was not specified.

Mallett, Gerds, and Vaughn,[7] who were the first to identify uranium sesquicarbide by X-ray diffraction and metallography, reported that it did not react with water at either room temperature or 75°.

Experimental

Preparation of the Carbides.—Specimens were prepared as buttons 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 melted until visual examination showed that all the carbon had dissolved in the melt and then were melted an additional eight times (2-min. melts) to ensure complete reaction. Buttons were heated for 60 hr. at 1600° in a Brew high vacuum furnace, No. 424B. Temperatures were measured with an accuracy of ±20° with a Leeds and Northrup optical pyrometer. Graphite crucibles were used for heating specimens having carbon-to-uranium atom ratios of 1.4 or greater, while beryllia crucibles were used for specimens where this ratio was less than 1.4. Under these conditions there was no significant reaction of the specimens with the crucibles.

Characterization of the Carbides.—Chemical analyses for uranium, total carbon, free carbon, and the major carbide constituents as identified by X-ray analysis are given in Table I. Tungsten contamination, from the electrodes, was less than 0.1% in all specimens except UC_2-17A, which contained 0.31%, probably because of the longer melting time required. Specimens were also analyzed for oxygen (<0.1%) and nitrogen (<40 p.p.m., except specimen 2H, which contained 84 p.p.m.). Spectroscopic analyses found about 40 p.p.m. nickel, 25 p.p.m. calcium, and 15 p.p.m. copper; the concentrations of all other metallic impurities were less than 5 p.p.m. The monocarbide and dicarbide ($UC_{1.85}$) X-ray powder patterns were the same as those reported by Litz, Garrett, and Croxton[8] for UC and UC_2, while the sesquicarbide pattern corresponded to that of Mallett, Gerds, and Vaughn.[7] Metallographic examination[9] at magnifications of 250 and 1000× showed that specimen 2H ($UC_{0.98}$) was essentially single phase uranium monocarbide with traces of uranium metal at the grain boundaries. Specimens 8A ($UC_{1.25}$) and 11A ($UC_{1.39}$) were two-phase mixtures of the monocarbide and sesquicarbide, while specimens 12A ($UC_{1.59}$) and 10A ($UC_{1.70}$) were two-phase mixtures of the sesquicarbide and dicarbide. Although X-ray analysis indicated that specimen U_2C_3-1A ($UC_{1.47}$) was relatively high purity uranium sesquicarbide, metallography showed a uranium sesquicarbide matrix with about 5% of the area covered by two impurity phases which were presumed to be unreacted monocarbide and dicarbide. Specimen UC_2-17A was predominantly uranium dicarbide ($UC_{1.85}$) with some graphite as a rod-shaped precipitate and traces of an unidentified precipitate visible at 1000×.

---

[1] Operated by Union Carbide Nuclear Co. for the U. S. Atomic Energy Commission.

[2] M. J. Bradley and L. M. Ferris, *Inorg. Chem.*, **3**, 189 (1964).

[3] M. J. Bradley, unpublished data.

[4] F. A. Rough and W. Chubb, "Progress on the Development of Uranium-Carbide Type Fuels," BMI-1554 (1961).

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

[6] H. Moissan, *Ann. chim. phys.*, (7) **9**, 302 (1896).

[7] M. W. Mallett, A. F. Gerds, and D. A. Vaughn, *J. Electrochem. Soc.*, **98**, 505 (1951).

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

[9] M. J. Bradley, R. J. Gray, and L. M. Ferris, "Correlation of Composition and Heat-Treatments with the Microstructures of Uranium Carbides," ORNL-3515 (in preparation).

TABLE I

COMPOSITION OF URANIUM CARBIDES AFTER HEAT TREATING FOR 60 HR. AT 1600°

	Analyses, wt. %			Combined-C:U atom	X-Ray powder pattern[b]		
Specimen	U	Total C	Free C	ratio	UC	U_2C_3	$UC_{1.85}$
2H	95.2	4.76	...	0.99	P		
8A	94.0	5.96	0.03	1.25	P	P	
11A	93.4	6.55	0.02	1.39	P	P	
U_2C_3-1A[a]	93.0	6.93	0.04	1.47	Q[c]	P	Q[d]
12A	92.5	7.44	0.01	1.59		P	P
10A	92.0	7.98	0.08	1.70		P	P
UC_2-17A	90.8	9.14	0.64	1.86	Q[e]		P

[a] Heated briefly at 1680°. [b] P, present; Q, questionable. [c] Based on relative intensity of common line with $UC_{1.85}$ at 2.48 Å. [d] Based on one very faint line at 3.04 Å. [e] Based on one very faint line at 2.87 Å.

Procedure.—The hydrolysis experiments and all analyses were conducted by the procedures developed in the study of the as-cast uranium carbides.[2]

Results

Hydrolysis of the heat-treated uranium carbides produced complex mixtures of gaseous hydrocarbons, hydrogen, and a hydrous uranium oxide which was amorphous to X-rays. Dissolution of the oxide in chlorine-free 6 *N* HCl yielded a uranous chloride solution without any gas evolution, showing the oxide to be $UO_2 \cdot xH_2O$. Nonvolatile waxes were also obtained from specimens containing sesquicarbide or dicarbide.

The reaction of uranium sesquicarbide (specimen U_2C_3-1A) with water at temperatures between 25 and 99° yielded a water-insoluble wax and 60 ml. (STP) of gas per gram of carbide consisting of 59 vol. % hydrogen, 2% methane, 26% ethane, 0.8% propane, 4% butanes, 0.7% C_5 to C_8 alkanes, 1.5% ethene, 4% butenes, 1% C_5 to C_7 alkenes, 0.6% alkynes, and 0.8% unidentified unsaturates (Table II). Of the total carbon present initially in the sesquicarbide, 50% was found in the evolved gas and 10% in the wax. There were no water-soluble organic products (limit of detection, 1% of the total carbon) and no water-insoluble liquid organic film was observed visually on the surface of the water. No insoluble residue remained after dissolving the uranium oxide in 6 *N* HCl and the wax in ether. When the water-insoluble residue was not dissolved in HCl, 5% of the total carbon was found in the uranium residue and 5% as an ether-soluble wax on the walls of the reaction vessel, showing that HCl dissolution of the uranium oxide residue did not affect the total amount of nonvolatile carbon products. The gas chromatographic analysis of the gases evolved on hydrolysis of uranium sesquicarbide was checked by combustion of the gases to CO_2 and also by mass spectroscopic analysis. A typical gas chromatographic analysis for components other than helium and water (3%; calculated from vapor pressure of water at 25°), together with mass spectroscopic analyses for helium, hydrogen, and methane, is given in Table III.

TABLE II

GASEOUS PRODUCTS FROM THE REACTION OF URANIUM SESQUICARBIDE (SPECIMEN U_2C_3-1A) WITH WATER AT TEMPERATURES FROM 25 TO 99°

Temp., °C.	25	40	80	99
Volume of gas evolved, ml. (STP) per g. of carbide	58	61	61	60
Gas composition, vol. %				
Hydrogen	62	60	58	56
Methane	1.24	1.81	2.46	2.29
Ethane	24	25	26	28
Propane	0.78	0.84	0.72	0.81
Butanes[a]	4.01	3.81	4.05	3.83
Pentanes[b]	0.56	0.29	0.31	0.23
Hexanes[c]	0.21	0.31	0.52	0.33
C_7 to C_8 alkanes	0.02	0.06	0.09	0.01
Ethene	1.42	1.38	1.19	1.93
Butene-1	2.12	2.51	2.61	2.40
cis-Butene-2	1.02	0.99	0.95	0.95
trans-Butene-2	0.72	0.69	0.68	0.79
Pentene-2	0.10	0.10	0.08	0.09
Hexenes[d]	0.80	0.85	0.90	0.76
Heptene-2	0.06	0.06	0.09	0.04
Ethyne	0.23	0.08	...	0.04
Propyne	0.05	0.03	0.06	0.07
Butyne-1	0.42	0.41	0.30	0.45
Hexyne-1 and -2	0.07	0.01	0.01	...
Unidentified unsaturates	0.73	0.79	0.93	0.77

[a] Includes 0.01 vol. % isobutane. [b] *n*-Pentane (83% of total C_5H_{12}) and isopentane (17%). [c] *n*-Hexane (72% of total C_6H_{14}) and 3-methylpentane (28%). [d] Hexene-1 (34% of total C_6H_{12}), hexene-2 (21%), hexene-3 (18%), and 3-methylpentene-1 (26%).

TABLE III

COMPARISON OF GAS CHROMATOGRAPHIC AND MASS SPECTROSCOPIC ANALYSES

	Gas chromatography	Mass spectroscopy
Gaseous products, vol. %		
Hydrogen	20.62	21.4
Oxygen	0.43	
Nitrogen	1.20	
Methane	0.79	0.64
C_2 to C_8 hydrocarbons	13.71	
Helium	?	62.9
Total	36.75	

Combustion analysis found 0.42 ml. (STP) of CO_2 per ml. of this sample, which compared well with the 0.37 ml. calculated from the gas chromatographic analysis assuming ideal gas behavior. Therefore, the total carbon in the gas as determined by gas chromatography and the volume of gas evolved during the hydrolysis appears to be accurate within 10%, and the components found by chromatography plus the helium and the water vapor account for all of the gas sample. The missing 40% of the total carbon in the uranium sesquicarbide hydrolysis probably was lost as volatile species when the acetone and ether used to recover the wax from the reaction vessel were evaporated.

Although varying the reaction temperature between 25 and 99° had no detectable effect on the gas composition (Table II), the rate of uranium sesquicarbide hydrolysis increased markedly with increasing temperature (Fig. 1). The time required for complete reaction of a 3- to 4-g. specimen varied from 8 days at

Table IV

Gaseous Products from the Reaction of Heat-Treated Uranium Carbides with 80° Water

Specimens heated 60 hr. at 1600°

	Specimen						
	2H	8A	11A	U_2C_3-1A[a]	12A	10A	UC_2-17A
Combined-C: U atom ratio	0.98	1.25	1.39	1.47	1.59	1.70	1.86
Vol. of gas, ml. (STP)/g. of carbide	90	72	64	61	55	48	41
Gas composition, vol. %							
Hydrogen	9	28	41	58	62	45	34
Methane	88	45	23	2.46	4.18	12	16
Ethane	1.51	17	24	26	23	28	34
Propane	0.26	1.11	0.98	0.72	0.62	0.83	1.00
Butanes[b]	0.18	2.56	3.83	4.05	3.28	4.27	4.67
Pentanes[c]	0.04	0.30	0.42	0.31	0.27	0.38	0.39
Hexanes[d]	0.01	0.32	0.36	0.52	0.31	0.42	0.47
C_7 to C_8 alkanes	...	0.01	0.07	0.11	0.04	0.01	0.05
Ethene	0.03	0.85	1.21	1.19	1.18	1.60	1.70
Butene-1	0.06	1.43	1.91	2.61	2.02	2.54	3.12
cis-Butene-2	0.03	0.65	0.83	0.95	0.79	0.94	0.93
trans-Butene-2	0.02	0.57	0.63	0.68	0.58	0.78	0.74
Pentene-2	...	0.09	0.08	0.08	0.10	0.10	0.10
Hexenes[e]	0.02	0.50	0.80	0.90	0.81	0.84	1.16
Heptene-2	...	0.02	0.06	0.09	0.08	0.10	0.07
Ethyne	...	...	0.12	...	0.12	...	0.13
Propyne	...	0.03	0.04	0.06	0.06	0.12	0.13
Butyne-1	0.01	0.22	0.38	0.30	0.42	0.71	0.97
Hexyne-1 and -2	...	0.01	0.05	0.04	0.06	0.06	0.08
Unidentified[f]	0.13	0.36	0.76	0.93	0.64	0.77	0.83

[a] Heated briefly at 1680°. [b] Includes 0.01 to 0.02 vol. % isobutane. [c] *n*-Pentane (72% of total C_5H_{12}) and isopentane (28%). [d] *n*-Hexane (60% of total C_6H_{14}) and 3-methylpentane (40%). [e] Hexene-1 (30% of total C_6H_{12}), hexene-2 (20%), hexene-3 (24%), and 3-methylpentene-1 (26%). [f] At least 11 components, all unsaturated.

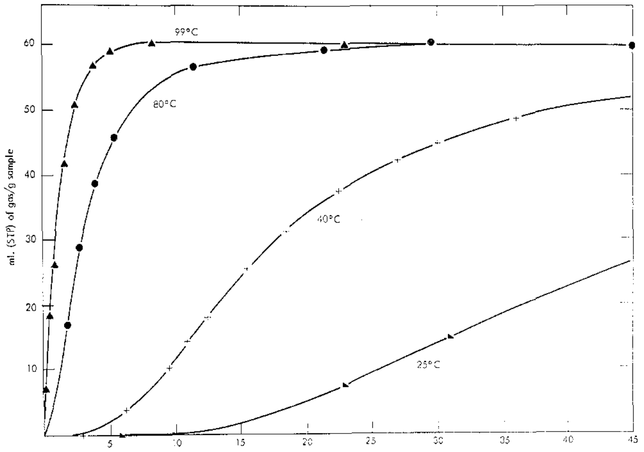

Fig. 1.—Effect of temperature on the rate of gas evolution in the reaction of 3- to 4-g. specimens of uranium sesquicarbide (sample U_2C_3-1A) with water.

25° to 8 hr. at 99°. As with uranium monocarbide and dicarbide, there was an induction period at the lower temperatures during which the carbide disintegrated without much gas evolution. For example, at 25° a 4-g. specimen was completely disintegrated after 24 hr., yet only 13% of the gas had been evolved. Uranium sesquicarbide reacted much more slowly than either the monocarbide or dicarbide; complete hydrolysis of 4-g. specimens at 99° required 2 hr. for the monocarbide, 3 hr. for the dicarbide, and 8 hr. for the sesquicarbide.

Hydrolysis of uranium monocarbide–sesquicarbide mixtures resulted in a linear decrease in the volume of gaseous products evolved per gram of carbide, a linear decrease in per cent methane in the gas, and increases in the percentages of hydrogen and C_2 to C_8 hydrocarbons as the C:U atom ratio in the mixtures increased from 1.0 to 1.5 (Table IV, Fig. 2). The amount of wax also increased with increasing sesquicarbide concentration in the specimens (Table V).

Table V

Carbon Distribution in the Reaction of Heat-Treated Uranium Carbides with 80° Water

Specimens heated 60 hr. at 1600°

Specimen	2H	8A	11A	U_2C_3-1A[a]	12A	10A	UC_2-17A
Combined-C:U atom ratio	0.99	1.25	1.39	1.47	1.59	1.70	1.86
	mg.-atoms of carbon per gram of original alloy						
Carbide[b]							
Total carbon	3.91	4.96	5.45	5.77	6.19	6.64	7.61
Free carbon	..	0.03	0.02	0.03	0.01	0.07	0.53
Gaseous products							
Methane	3.56	1.46	0.65	0.07	0.10	0.26	0.29
Ethane	0.12	1.12	1.36	1.40	1.11	1.23	1.23
C_3 to C_8 alkanes	0.07	0.55	0.66	0.65	0.45	0.56	0.49
Alkanes	0.03	0.51	0.61	0.70	0.54	0.57	0.56
Alkynes	..	0.03	0.06	0.04	0.06	0.08	0.09
Unidentified	0.03	0.06	0.12	0.14	0.09	0.09	0.09
Total	3.81	3.74	3.46	3.00	2.35	2.79	2.74
Nonvolatile products[c]							
Wax	..	0.2	0.2	0.5	0.7	1.1	1.7
Graphite residue	..	..	..	..	..	..	0.8
Unaccounted for	0.1	1.0	1.8	2.3	3.1	2.7	2.3

[a] Heated briefly at 1680°. [b] Elemental analysis. [c] After dissolving the uranium oxide in 6 *N* HCl.

Hydrolysis of uranium sesquicarbide–dicarbide mixtures resulted in linear decreases in the volume of gaseous products per gram of carbide and the volume % of hydrogen, a linear increase in the percentage of methane, and only a slight increase in the percentages of C_2 to C_8 hydrocarbons in the gas as the combined-

C:U atom ratio increased from 1.5 to 1.86 (Table IV). The amount of wax also increased with increasing dicarbide concentration in the specimen (Table V).

Discussion

The composition of the C_2 to C_8 hydrocarbon mixtures produced in the reaction of uranium sesquicarbide with water was virtually identical with that from uranium dicarbide[2] (Table VI). Uranium sesquicarbide, like uranium dicarbide, produced more straight-chain isomers than branched chain. The isobutane concentration was always 0.01 to 0.02% regardless of the *n*-butane concentrations; the *n*-pentane concentration was about 75% of the total pentane concentration; and *n*-hexane accounted for about 65% of the total hexanes. The double bond was always in the 2-position in *n*-alkenes containing an odd number of carbon atoms (pentene-2, heptene-2), while the 1-position was favored in those containing an even number of carbon atoms (butene-1, 60% of the total C_4H_8; hexene-1, 43%, hexene-2, 28%, and hexene-3, 28% of the *n*-C_6H_{12}). As was the case with uranium dicarbide, approximately equal amounts of *cis*- and *trans*-butene-2, 57 and 43%, respectively, were formed. Again, 3-methylpentane was the only branched hexane found, and 3-methylpentene-1 the only branched hexene.

TABLE VI

C_2 TO C_8 HYDROCARBONS FROM THE HYDROLYSIS OF URANIUM SESQUICARBIDE AND URANIUM DICARBIDE

	Uranium sesquicarbide	Uranium dicarbide[a]
	Relative comp., vol. %[b]	
Ethane	66	63
Propane	1.80	2.16
Butanes	10.1	10.2
Pentanes	0.78	0.75
Hexanes	1.30	1.42
C_7 to C_8 alkanes	0.28	0.23
Ethene	2.97	3.56
Butene-1	6.52	7.05
cis-Butene-2	2.38	2.06
trans-Butene-2	1.70	1.63
Pentene-2	0.20	0.21
Hexenes	2.25	3.54
Heptene-2	0.22	0.60
Ethyne	0.22	. . .
Propyne	0.15	0.06
Butyne-1	0.75	1.03
Hexyne-1 and -2	0.10	0.20
Unidentified	2.32	2.65

[a] Data calculated from ref. 2. [b] Methane and hydrogen not included.

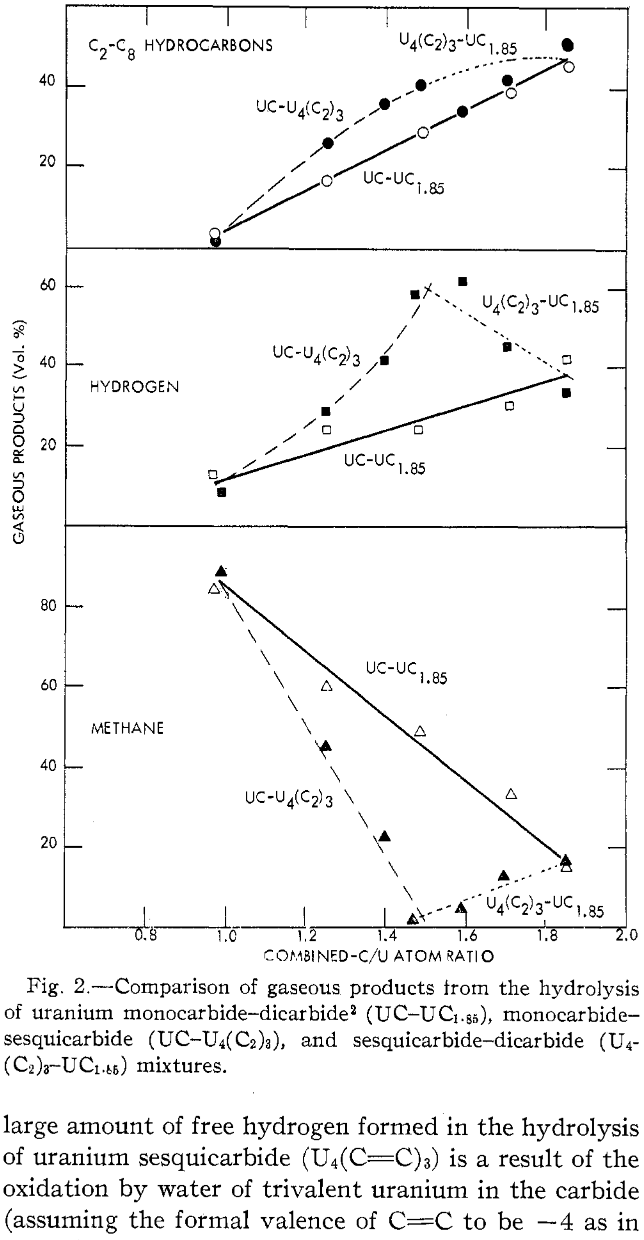

Fig. 2.—Comparison of gaseous products from the hydrolysis of uranium monocarbide–dicarbide[2] (UC–$UC_{1.85}$), monocarbide–sesquicarbide (UC–$U_4(C_2)_3$), and sesquicarbide–dicarbide ($U_4(C_2)_3$–$UC_{1.85}$) mixtures.

The similarity between the hydrolysis products from uranium sesquicarbide and uranium dicarbide is not completely unexpected since both crystal lattices contain C_2 units with similar C–C bond distances (approximately the double bond length; 1.30 Å. for the sesquicarbide and 1.34 Å. for the dicarbide).[10] The mechanism for the hydrogenation and polymerization of the C_2 groups to this complex mixture of C_2 to C_8 hydrocarbons is probably the same in both cases. The large amount of free hydrogen formed in the hydrolysis of uranium sesquicarbide ($U_4(C{=}C)_3$) is a result of the oxidation by water of trivalent uranium in the carbide (assuming the formal valence of C=C to be −4 as in ethene) to tetravalent uranium in the oxide product.

$$\begin{array}{c} -2 \\ 2U^{+3} + 4H_2O \longrightarrow 2UO_2 + H_2 + 6H^+ \\ +1 \times 2 \end{array}$$

The amount of free hydrogen obtained experimentally (0.81 g.-atom per g.-atom of uranium) was somewhat lower than the theoretical of 1 g.-atom per g.-atom of uranium; however, the sesquicarbide hydrolysis yielded more gaseous C_2 to C_8 hydrocarbons (0.75 g.-atom of C per g.-atom of U and 1.93 of H *vs.* 0.62 of C and 1.56 of H from the dicarbide), less wax (0.14 g.-atom of C per g.-atom of U and 0.22 of H *vs.* 0.49 of C and 0.59 of H from the dicarbide) and less "unaccounted for" carbon (0.58 g.-atom of C per g.-atom U *vs.* 0.66 from the dicarbide), indicating that part of the hydrogen from the uranium oxidation reacted with carbon-containing groups to form gaseous hydrocarbons. With such a large excess of hydrogen it is rather surprising that so many unsaturated hydrocarbons were found. Appar-

---

[10] A. E. Austin, *Acta Cryst.*, **12**, 159 (1959).

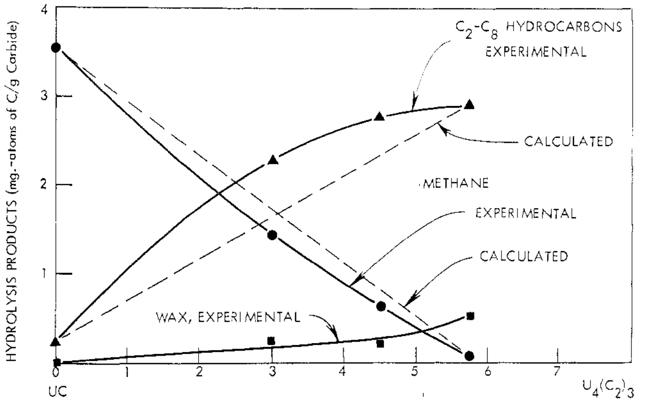

Fig. 3.—Hydrolysis products from uranium monocarbide–sesquicarbide mixtures showing deviation of experimental values from those calculated for a UC–$U_4(C_2)_3$ binary.

ently the uranium oxidation step is partially independent of the hydrogenation of the C_2 units. The uranium monocarbide impurity (about 2.5% according to metallography) was responsible for most if not all of the methane (0.02 g.-atom per g.-atom of uranium) produced in the hydrolysis of uranium sesquicarbide. Additional study of the nonvolatile products, particularly those "unaccounted for," is needed before the hydrolysis of uranium sesquicarbide and dicarbide can be fully understood.

Comparison of the behavior of as-cast[2] and 1600° heat-treated specimens with combined-C : U atom ratios between 1.0 and 1.85 shows that the volume of gas evolved during the hydrolysis was about the same, but the gas compositions, particularly the methane and hydrogen concentrations, from the heat-treated specimens containing uranium sesquicarbide were markedly different from the as-cast monocarbide–dicarbide mixture with the same C : U atom ratio (Fig. 2). As in the case of monocarbide–dicarbide mixtures, less methane and more C_2 to C_8 hydrocarbons were evolved from monocarbide–sesquicarbide mixtures than expected for a UC–$U_4(C_2)_3$ mixture (Fig. 3), indicating that some of the C units from the monocarbide had reacted with C_2 units from the sesquicarbide to form higher hydrocarbons. The sesquicarbide–dicarbide mixtures yielded the products expected from the behavior of the separate compounds (Fig. 4).

No uranium sesquicarbide was detected in specimen UC_2-17A by X-ray even though the specimen had a combined-C : U atom ratio of only 1.86 and had been heat treated under conditions where uranium sesquicarbide should have been formed if as-cast $UC_{1.85}$ were an equilibrium mixture of UC and $UC_{2.0}$. Furthermore this heat-treated sample yielded the same amount of methane as as-cast $UC_{1.85}$, whereas sesquicarbide mixtures yielded considerably less methane than monocarbide–dicarbide mixtures with the same C : U atom ratios. These observations further confirm that $UC_{1.85}$ is the composition of a true compound and not a mixture of UC and $UC_{2.0}$. Since there was little if any cleavage of C=C units during the hydrolysis of uranium sesquicarbide, the presence of methane in the products from $UC_{1.85}$ indicates that the dicarbide crystal probably consists primarily of C_2 units with a few C units substituted for C_2 units in the lattice, rather than a complete anion "hole". Additional neutron diffraction studies are needed to determine whether uranium dicarbide is a random carbon-deficient UC_2 structure or an oriented structure with a larger unit cell such as U_7C_{13}, in which case superlattice lines should be detected.

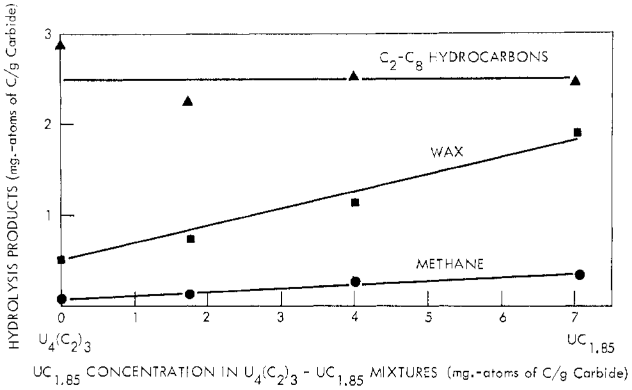

Fig. 4.—Hydrolysis products from uranium sesquicarbide–dicarbide mixtures; experimental values are the same as those calculated for $U_4(C_2)_3$–$UC_{1.85}$ binary.

Acknowledgment.—The authors wish to thank members of the ORNL Metals and Ceramics Division for their aid in this study: T. Hikido and L. Queener for arc melting the carbides, and J. P. Hammond and C. Hamby for heat treating the specimens. We are also indebted to the ORNL Analytical Chemistry Division, particularly A. D. Horton and J. L. Botts for developing the gas chromatographic procedure, R. L. Sherman for the X-ray analyses, the group of W. R. Laing for most of the chemical analyses, R. R. Rickard for the tungsten analyses, C. K. Talbott for gas combustion analyses, J. R. Sites for mass spectroscopy, and L. J. Brady for the carbon analyses of the water. The formula $U_4(C_2)_3$ for the sesquicarbide was suggested by C. F. Coleman, ORNL Chemical Technology Division.