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Hydrolysis of Uranium Carbides between 25 and 100°.

II. Uranium Dicarbide, Uranium Metal-Monocarbide Mixtures, and Uranium Monocarbide-Dicarbide Mixtures²

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Reactions with water of as-cast uranium carbides with total-C:U atom ratios varying from 0.4 to 2.2 were investigated using gas chromatography for analysis of the gaseous products. Uranium metal-uranium monocarbide mixtures yielded 2 moles of free hydrogen per mole of free metal, methane, small quantities of higher molecular weight gaseous hydrocarbons, and a hydrous uranium(IV) oxide. The gaseous products contained all the carbon originally present in the mixtures. Uranium dicarbide ($UC_{1.85 \pm 0.03}$) yielded a mixture of 36 hydrocarbons (average composition (vol. %): methane, 15%; 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 hydrous, uranium(IV) oxide. Forty per cent of the combined carbon was found in the gas and 25% in the wax. Varying the reaction temperature between 25 and 99° caused no change in the hydrolysis products from either uranium mono- or dicarbide. Hydrolysis of uranium monocarbide-dicarbide mixtures resulted in a linear decrease in the volume % of methane and linear increases in the percentages of hydrogen and C_2 to C_3 hydrocarbons in the gas as the combined-C:U atom ratio increased from 1.0 to 1.85. Less methane was evolved from monocarbide-dicarbide mixtures than expected from the monocarbide concentrations, indicating that some polymerization of C units had occurred.

Introduction

Three compounds exist within the uranium-carbon system: uranium monocarbide, uranium sesquicarbide, and uranium dicarbide. The monocarbide and dicarbide are thermally stable to short heat treatments,³ but at about 1780° the sesquicarbide decomposes by a peritectic reaction into monocarbide and dicarbide. Since the rate of formation of sesquicarbide is slow, the high temperature monocarbide and dicarbide phases are quenched from the melt in as-cast specimens. This study, which was conducted with as-cast specimens containing 2 to 10 wt. % C, therefore includes the hydrolysis of uranium monocarbide (UC), uranium dicarbide ($UC_{1.85 \pm 0.03}$), mixtures of the monocarbide with uranium metal or uranium dicarbide, and mixtures of the dicarbide with graphite. Earlier results of this study, on the hydrolysis of uranium monocarbide and a uranium monocarbide-17 mole % uranium metal specimen, have been reported.⁴

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.⁴⁻⁶ Litz,⁷ however, reported that the methane concentration of the gas decreased and the hydrogen concentration increased with increasing temperature. Several studies to determine the gaseous products from the hydrolysis of specimens which were

nominally uranium dicarbide have been conducted^{5,7-9}. These studies showed that the major reaction products were hydrogen, methane, and ethane, with significant amounts of alkenes and higher alkanes; however, there was considerable variation in the concentrations found. For example, hydrogen varied from 14.1%⁵ to 49.6%.⁹ The compositions of the carbides used by both Litz⁷ and Lebeau and Damiens⁹ are unknown since chemical analyses for uranium, combined carbon, and oxygen were not given. Only Lebeau and Damiens measured the volume of gas evolved. Kempter⁵ and Besson, Blum, and Spitz⁸ analyzed their gas samples by mass spectroscopy, which is more accurate than the cold trap procedures used by Litz⁷ and Lebeau and Damiens,⁹ but still does not provide for separation of similar compounds such as butene-1 and butene-2. Compositions between UC and UC_2 were studied by Moissan¹⁰ (" U_2C_3 ") and Besson, *et al.*⁸ (6.1 and 7.2% carbon, *i.e.*, $UC_{1.3}$ and $UC_{1.6}$); however, the compounds present in these mixtures were not identified. Depending upon the thermal treatment, monocarbide, dicarbide, and sesquicarbide could have been present.

Experimental

Preparation and Characterization 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. Chemical analyses for uranium, total carbon, free carbon, and the major constituents as identified by X-ray analysis are given in Table I. There was less than 0.1 wt. % tungsten contamination.

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

(2) Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

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

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

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

(8) J. Besson, P. Blum, and J. Spitz, *Compt. rend.*, **256**, 681 (1963).

(9) P. Lebeau and A. Damiens, *ibid.*, **156**, 1987 (1913).

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tion from the electrodes in the specimens containing 2.0 to 8.0 wt. % carbon but 0.2 to 0.3 wt. % in those containing 8.8 to 10 wt. % carbon. The higher tungsten contamination in the high-carbon specimens probably resulted from the longer melting times required to incorporate all the carbon into the buttons. The specimens were also analyzed for oxygen (<0.1 wt. %) and nitrogen (<65 p.p.m.). Spectroscopic analysis 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 ($UC_{1.85 \pm 0.03}$) X-ray powder patterns were the same as those reported by Litz, Garrett, and Croxton for UC and UC_2 .¹¹ There was no detectable change in the monocarbide pattern as the total-C:U atom ratio increased from 0.8 to 1.5 or in the dicarbide pattern as the ratio increased from 1.5 to 2.2. The seven specimens with total-C:U atom ratios of 1.9 to 2.2 had identical patterns except that the faint line at 2.87 Å. was missing from the UC_2 -16A pattern. Metallographic examination¹² at magnifications of 250X and 1000X showed that specimen 2E was nearly single phase uranium monocarbide but contained traces of uranium metal at the grain boundaries and small amounts of uranium dicarbide within the grains. Specimens 7A and 6B ($UC_{0.4}$ and $UC_{0.8}$) were mixtures of uranium monocarbide with uranium metal at the grain boundaries and within the grains. Specimens 3B, 4B, and 5B, which had compositions between UC and $UC_{1.85}$, were two-phase mixtures of the mono- and dicarbides. Even at a magnification of 1000X, specimen UC_2 -16A ($UC_{1.91}$; combined-C:U atom ratio of 1.88) was virtually singlephase. Specimen UC_2 -13A ($UC_{1.91}$; combined-C:U ratio of 1.87) contained a trace of spherical graphite. Specimen UC_2 -4A ($UC_{1.98}$; combined-C:U ratio of 1.86) contained a small amount of graphite as spherical and rod-shaped particles, while specimens UC_2 -1A, -2A, and -5A ($UC_{1.99}$) and UC_2 -6A ($UC_{2.15}$) contained large amounts of rod-shaped graphite particles.

Procedure.—The hydrolyses were conducted in a helium atmosphere using the technique described previously.⁴ When there was no further gas evolution over a 16-hr. period, the gas was sampled. Nonvolatile products were treated in two ways. The gelatinous uranium oxide residue was dissolved *in situ* under a helium atmosphere in either 6 M HCl (residues from specimens containing no uranium metal) or 12 M H_3PO_4 (U-UC residues which were not readily soluble in HCl), the solution filtered, and the filtrate analyzed for both total and tetravalent uranium. Nonvolatile, acid-insoluble waxes, found when the specimens contained uranium dicarbide, were recovered by washing the reaction vessel and filter with acetone and then ether and subsequently removing the solvents by evaporation. Any free carbon was collected on the filter. An alternative procedure was to remove the water from the uranium oxide by filtration and analyze both the solid and filtrate for carbon. Water-insoluble waxes from the dicarbide hydrolysis were removed from the reaction vessel by dissolution in acetone and ether.

Analytical.—The carbide specimens were analyzed for uranium, total carbon, oxygen, and nitrogen by procedures described previously.⁴ Free carbon was determined after the sample was dissolved in refluxing 6 M HCl and the solution filtered through a Leco disposable filtering crucible (No. 528-30, Laboratory Equipment Corp., St. Joseph, Michigan). The residue was washed with acetone and ether to remove any wax, dried, and burned, and the carbon was measured as CO_2 . Tungsten was determined by neutron activation analysis.¹³ The carbide was first fused with KNO_3 - K_2CO_3 , the resulting glass dissolved in water, and this solution irradiated for 5 min. in a neutron flux of 6×10^{11} n./cm.²/sec. The activated tungsten was precipitated with a tungsten carrier as $WO_3 \cdot H_2O$, the precipitate purified, ignited to WO_3 , and the γ -abundance observed with a multi-

TABLE I
COMPOSITION OF URANIUM CARBIDES

Specimen	Analyses, wt. %			Combined-C:U atom ratio	X-Ray powder pattern ^a		
	U	Total C	Free C		U	UC	$UC_{1.85 \pm 0.03}$
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		q	p
UC_2 -16A	91.2	8.80	0.14	1.88			p
UC_2 -4A	91.2	8.88	0.30	1.86		q	p
UC_2 -1A	90.9	9.12	0.70	1.84		q	p
UC_2 -2A	90.9	9.18	0.74	1.84		q	p
UC_2 -5A	91.0	9.06	0.62	1.84		q	p
UC_2 -6A	90.3	9.78	1.54	1.81		q	p

^a p, present; w, weak; q, questionable based on one very faint line at 2.87 Å.

channel pulse height analyzer. The specific activity was compared to reference tungsten standards which had been treated similarly.

The X-ray powder patterns were determined with a Debye-Scherrer 114.59-mm. diameter powder camera using $CuK\alpha$ radiation.

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 used: 5A Molecular Sieve, tricresyl phosphate, silica gel-3 wt. % squalane, and di-2-ethylhexyl sebacate.¹⁴ 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.¹⁵ The amount of each unknown compound was estimated using 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, 3-methylbutene-1, 2-methylbutene-1, 2-methylbutene-2, pentyne-1, pentyne-2, 2-ethylbutene-1, heptene-1, or heptene-3. The compounds erroneously called branched hexane isomers in our first paper⁴ are now believed to be unsaturates except for a small amount of 3-methylpentane. Three of the major constituents in the gas samples were also determined by mass spectroscopy and the total carbon as calculated from the chromatographic analyses was corroborated by burning gas samples in oxygen over a hot platinum wire using an Orsat apparatus.

Total and tetravalent uranium in solution were determined potentiometrically. Persulfate oxidation was used to test the water for dissolved organic products,¹⁶ while carbon in the uranium oxide residues and the waxes was determined by combustion analysis.

Results

The maximum combined-C:U atom ratio which could be obtained by nonconsumable arc melting with tungsten electrodes was 1.85 ± 0.03 with an average deviation of 1 part per hundred based on chemical analyses for total and free carbon, metallography, X-

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TABLE II
 GASEOUS PRODUCTS FROM THE REACTION OF AS-CAST URANIUM CARBIDES WITH 80° WATER

	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
Vol. of gas evolved, ml. (STP)/g. of carbide	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
Methane	18	60	84	60	48	32	13	10	14	17	16	15	12
Ethane	1.14	1.78	1.76	11	18	24	22	36	29	31	27	28	23
Propane	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
Butanes ^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
Pentanes ^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
Hexanes ^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
Ethene	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
<i>cis</i> -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
<i>trans</i> -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
Hexenes ^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
Propyne	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 REACTION OF AS-CAST URANIUM CARBIDES WITH 80° WATER

	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
Carbide ^a (elemental anal.)													
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 ^a													
Methane	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
Ethane	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 ^{a,b}													
Wax	0.2	0.7	1.3	1.6	2.4	1.6	1.7	1.7	2.2	2.1
Graphite residue	0.2	0.1	0.2	0.6	0.6	0.7	1.3
Unaccounted for	1.1	1.5	2.2	2.9	2.3	2.8	2.5	2.8	1.9	2.4

^a Mg.-atoms of carbon per gram of original specimen. ^b After dissolving the uranium oxide in HCl.

ray powder patterns, and hydrolysis studies. Heat-treating produced no effect on the combined-C:U ratio, X-ray powder pattern, or hydrolysis properties,^{8,12} further indicating that UC_{1.85} is the composition of a true compound and is not a mixture of UC and UC₂. This is in agreement with work of Leitnaker and Witteman,¹⁷ who reported that UC_{1.86} is the formula for uranium dicarbide.

The hydrolysis of uranium carbides yielded 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 (or 12 *M* H₃PO₄) gave a uranous chloride solution

without any gas evolution, showing that the uranium residue was UO₂·*x*H₂O. Nonvolatile waxes were also formed when the specimens 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 1.85 ± 0.03 (Table II).

Hydrolysis of uranium monocarbide⁴ yielded principally methane (86 vol. %), with some hydrogen (11 vol. %) and small quantities of higher hydrocarbons. The uranium metal-monocarbide mixtures, as expected, yielded 2 moles of hydrogen per mole of free metal in addition to the monocarbide hydrolysis products. The gaseous hydrolysis products of as-cast specimens having compositions between UC_{0.4} and UC_{1.0} con-

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

tained all the carbon originally present in the alloys (Table III).

The reaction of uranium dicarbide ($UC_{1.85 \pm 0.03}$) with water produced a water-insoluble wax and a gas containing about 40 vol. % hydrogen and a complex hydrocarbon mixture (composition, vol. %): methane, 15%; ethane, 28%; propane, 1.0%; butanes, 4.6%; C_5 to C_8 alkanes, 1.1%; ethene, 1.6%; butenes, 4.7%; C_5 to C_7 alkenes, 2.0%; alkynes, 0.06%; and unidentified unsaturated compounds, 1.2%. 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. Any free carbon in the original specimens was recovered as an insoluble residue which analyzed 99–100% carbon after dissolving the uranium oxide product in HCl and the wax in ether. Variation of the amounts of free carbon between 0.2 and 1.5 wt. % in specimens with combined-C:U ratios of 1.85 ± 0.03 and total-C:U ratios of 1.91 to 2.15 produced no change in the number of equivalents of the hydrocarbon gases evolved from a gram of carbide (Table III). Variations in the total volumes of gas and the equivalents of hydrogen have been confirmed by duplicate experiments and appeared to be related to the amounts of wax (H:C ratio of 1.2) and "unaccounted for" 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). Of the combined carbon present initially in the dicarbide specimens, about 37% was found in the evolved gas and about 25% in the wax after hydrolysis. No water-soluble organic products were found (limit of detection, 0.4% of the combined carbon) and no water-insoluble liquid organic films were observed visually on the surface of the water. After hydrolysis most of the wax was found on the surface of the reaction vessel with a small amount (2 to 7% of the initial combined carbon) mixed with the uranium oxide residue. Dissolving the oxide in HCl had no effect on the amount of nonvolatile hydrocarbons. The gas chromatographic analysis of the gases evolved upon hydrolysis of uranium dicarbide was checked by combustion of the gases to CO_2 and also by mass spectroscopic analysis. An example of a chromatographic analysis of a gas sample from specimen UC_{2-16A} for components other than helium (from the initial atmosphere in the system) and water (3%; calculated from the vapor pressure of water at 25°) is given in Table IV.

Combustion analysis found 0.66 ml. (STP) of CO_2 per ml. of this sample, which compared well with the 0.61 ml. calculated from the gas chromatographic analysis assuming ideal gas behavior. Mass spectroscopy found (vol. %): 40.4 % helium, 31.9% hydrogen, and 5.97% methane. 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 carbon "unaccounted for" (40%) in the uranium dicarbide hydro-

TABLE IV

Hydrogen	28.09 ^a	Unknown C_4	0.01
Oxygen	1.64 ^b	Pentene-2	0.02
Nitrogen	5.80 ^b	Unknown C_6-1	0.01
Methane	6.51	Unknown C_6-2	0.01
Ethane	13.26	3-Methylpentene-1	0.19
Ethene	0.89	3-Methylpentane	0.07
Propane	0.39	<i>n</i> -Hexane	0.08
Ethyne	0.04	Hexene-1	0.08
<i>n</i> -Butane	1.80	Hexene-2	0.05
Unknown C_6-1	0.23	Hexene-3	0.08
Isopentane	0.02	Hexyne-1	0.02
<i>n</i> -Pentane	0.12	Heptene-2	0.09
Butene-1	1.37	Unknown C_7-1	0.02
Propyne	0.11	Unknown C_7-3	0.06
<i>cis</i> -Butene-2	0.40	Unknown C_7-4	0.01
<i>trans</i> -Butene-2	0.35	Unknown C_8-2	0.41
Butyne-1	0.48	Total	62.71

^a Vol. %. ^b High oxygen and nitrogen values resulted from small leak in gas sampling bulb which stood under vacuum for 24 hr. Air contamination was usually ~1%.

lysis was probably lost as volatile species when the acetone and ether used to recover the wax from the reaction vessel were evaporated.

Hydrolysis of uranium monocarbide-dicarbide mixtures resulted in a linear decrease in the volume % of methane and linear increases in the percentages of hydrogen and C_2 to C_8 hydrocarbons in the gas as the combined-C:U atom ratio increased from 1.0 to 1.85 ± 0.03 (Tables II and III). The amount of wax also increased with increasing dicarbide concentration in the specimens.

Varying the reaction temperature between 25 and 99° produced no detectable effect on the composition of the gas in the hydrolysis of the dicarbide (Table V). Variation in temperature also did not affect the gas composition in the hydrolysis of uranium monocarbide.⁴ 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 the dicarbide varied from 3.5 days at 25° to about 3 hr. at 99° (Fig. 1). During the first 5 hr. 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.⁴ Relative reaction rates were $UC > UC_{1.85} \gg U$ metal. Uranium monocarbide was completely hydrolyzed in 3 hr. at 80° compared to 5 to 15 hr. 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.¹⁸ Similarly, uranium dicarbide,

TABLE V
EFFECT OF TEMPERATURE ON THE COMPOSITION OF THE GASEOUS PRODUCTS FROM THE HYDROLYSIS OF URANIUM DICARBIDE (Specimen UC₂-16A)

Temperature, °C.	25	40	80	99
Vol. 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
Methane	9	10	10	10
Ethane	24	26	26	26
Propane	0.8	0.9	0.8	0.7
Butanes	3.9	3.8	3.8	3.0
Pentanes	0.25	0.21	0.21	0.19
Hexanes	0.19	0.44	0.36	0.57
<i>n</i> -Heptane	0.05	0.08	0.06	0.05
<i>n</i> -Octane	0.02	0.02	0.02	0.03
Ethene	1.7	1.8	1.8	1.2
Butenes	4.5	4.8	4.6	4.3
Pentene-2	0.14	0.07	0.16	0.12
Hexenes	1.0	1.1	1.4	0.3
Heptene-2	0.18	0.12	0.18	0.37
Propyne	0.13	0.13	0.13	0.14
Butyne-1	1.0	1.0	1.0	1.2
Hexynes	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.

which contains pairs of carbon atoms with a C-C distance of 1.34 Å. (approximately the double bond distance)^{18,19} on hydrolysis gives gaseous hydrocarbons containing predominantly 2, or multiples of 2, carbon atoms in addition to a more highly polymerized wax. The formation of methane and hydrocarbons containing an odd number of carbon atoms indicates that the dicarbide contains some single C units as well as C₂ 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 which is 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), ethene might be expected as a primary product: $UC_2 + 2H_2O \rightarrow UO_2 + C_2H_4$. The reaction products actually formed indicate a more complex mechanism. In preference to the formation of ethene (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 and hydrogenation 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

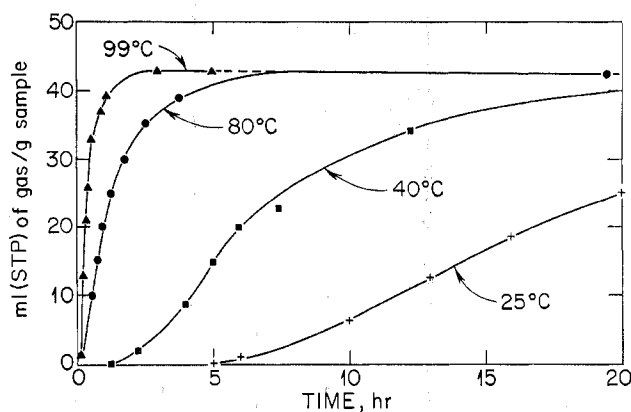


Fig. 1.—Effect of temperature on the rate of gas evolution in the reaction of 3- to 4-g. specimens of uranium dicarbide (sample UC₂-16A) with water.

those containing an even number of carbon atoms favored the 1- and 3-positions (butene-1, 65% of the total C₄H₈; hexene-1, 40%, and hexene-3, 39% of the *n*-C₆H₁₂). 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 C₆ 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 Warf²⁰ in the hydrolysis of lanthanum and cerium carbides, "the formation of equimolar amounts of the two 2-butenes does not represent thermal equilibrium 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 C₈ compounds (about 0.5 vol. %) and one of the C₇ compounds (about 0.2 vol. %), 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 nonvolatile products, particularly the "unaccounted for" ones, is needed before the hydrolysis of uranium dicarbide can be fully understood.

Although the hydrolysis at 80° of as-cast uranium carbides having compositions between UC_{1.0} and UC_{1.85±0.03} resulted in a linear decrease in the methane concentration and increases in the amounts of higher hydrocarbons, hydrogen, and wax as the combined-C:U atom ratio increased, the yields of methane were considerably lower than expected from the uranium monocarbide concentration in the specimen, basing the calculations on a UC-UC_{1.85} binary. For example, the calculated amount of uranium monocarbide present in UC_{1.25} is 2.79 mmoles/g., which should result in the

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TABLE VI
 COMPARISON OF URANIUM DICARBIDE HYDROLYSIS PRODUCTS^a

	Bradley and Ferris (av. for 7 specimens)	Besson, Blum, and Spitz ^b	Kempter ^b	Lebeau and Damiens ^b		Litz ^c	
Total-C:U atom ratio	1.9-2.2	2.19 ^b	2.05 ^b	<i>c</i>	<i>d</i>	?	?
Combined-C:U atom ratio	1.85	1.86 ^b	1.9	?	?	?	?
Temp., °C.	25-99	100	25	?	?	81	95
Gas vol., ml./g.	42	?	?	35.3 ^e	32.1	?	?
Gas composition, vol. %							
Hydrogen	41	25.4	14.1	49.6 ^e	28.9	17	39
Methane	15	19.0	17.3	13.0 ^e	19.8	30	18
Ethane	28	38.6	39.4	24.2 ^e	22.7	30	
Propane	1.0	2.1	2.0	2.7 ^e	5.6	0.7	
Butane	4.6	4.8	5.9	0.8 ^e	4.7	7.2	}31
Higher alkanes	1.1		
Ethene	1.6	4.4	5.3	2.3 ^e	1.4	2.5	
Propene			0.7	}9.1
Butene	4.7	5.8	9.5	}5.6 ^e	}14.4	}8.7	
Higher alkenes	2.0	...	4.6				
Alkynes	0.4	...	1.9	1.9 ^e	2.6	2.1	1.1
Unidentified unsaturates	1.2
Carbon oxides	1.1	0.9

^a Values rounded to nearest 0.1%. ^b Calculated from analyses. ^c "Sample 1": 1.47% free graphite. ^d "Sample 2": no graphite, 91.6% U. ^e The results of the two runs on specimen 1 were averaged.

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 specimens were binary mixtures of uranium mono- and dicarbides. Therefore, it appears that some of the single C units from the monocarbide (which react mainly with hydrogen to form methane in the absence of uranium dicarbide) react with C₂ units from the uranium dicarbide to produce higher hydrocarbons. Since some single C units react with C₂ units in the hydrolysis of monocarbide-dicarbide mixtures, it seems probable that the small quantities of higher hydrocarbons produced in the hydrolysis of essentially pure uranium monocarbide⁴ arise from polymerization of C units from the monocarbide as well as from the trace of dicarbide impurity. With polymerization occurring in the system it must be emphasized that the results of this study apply to the intimate mixtures prepared by arc-melting and quenching. Mixtures of UC and UC_{1.85} prepared by other methods such as sintering or heat treating would not necessarily yield the same results.

Application of gas chromatography to the analysis of the uranium dicarbide hydrolysis products has made possible the separation and identification of 20 hydrocarbons which were not found in any previous study (for example, the separation of C₄H₈ into butene-1, *cis*-butene-2, and *trans*-butene-2). The values for the major gaseous products from the uranium dicarbide hydrolysis as determined in this investigation were within the range reported by Lebeau and Damiens⁹ (Table VI). Their lower gas volumes suggest the presence of UO₂ impurity in their carbide. The results of this study differ significantly from those obtained by Litz,⁷ who reported that the composition of the hydrolysis products changed markedly with temperature;

viz. 17% hydrogen at 81° vs. 39% at 95° with a decrease in the methane from 30 to 18%. Litz also reported that the uranium monocarbide hydrolysis products change markedly with temperature, a fact we were unable to confirm.⁴ In hydrolyzing the dicarbide we obtained considerably more hydrogen (34 to 50%) than did either Kempter⁵ (14.1%) or Besson, *et al.*⁸ (25.4%). Ignoring the hydrogen and calculating relative amounts of hydrocarbons, about 47% ethane, 2% propane, and 7% butane were found in the three most recent studies (Table VII). Kempter found more

 TABLE VII
 COMPARISON OF URANIUM DICARBIDE GASEOUS HYDROCARBON PRODUCTS

	Bradley and Ferris (av. of 7 specimens)	Besson, Blum, and Spitz ^b	Kempter ^b
Gaseous hydrocarbons, vol. % of total gaseous hydrocarbons ^a			
Methane	25	25.4	20.1
Ethane	47	51.7	45.9
Propane	1.7	2.8	2.3
Butane	7.8	6.4	6.9
Higher alkanes	1.9		
Ethene	2.7	5.9	6.2
Butene	8.0	7.7	11.1
Higher alkenes	3.4		5.4
Alkynes	0.7		2.2
Unidentified unsaturates	2.0		

^a Hydrogen not included.

alkenes (23% vs. 14% by Besson, *et al.*, and 14% plus a possible 2% as unidentified unsaturates by this study) and less methane (20% vs. 25% for both Besson, *et al.*, and this study). Since some variation in the amounts of wax and free hydrogen from specimens prepared under outwardly identical conditions was observed in this study, some spread in the hydrogen values is to be expected in comparing data of several

workers. Since neither Besson, *et al.*, nor Kempter measured the amount of gas evolved, the moles of hydrocarbons produced cannot be compared.

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Solubility Studies on Substituted Ammonium Salts of Halide Complexes.

III. Tris(tetramethylammonium) Ennechlorodibismuthate(III)^{1,2}

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Tris(tetramethylammonium)ennechlorodibismuthate(III) has been prepared and its solubility studied as a function of chloride ion concentration. The data indicate that BiCl_4^- and BiCl_6^{3-} are the only chlorobismuth complexes present in solution. $\beta_6/\beta_4 = 6.4$ at 25° and ion normality of 4.1. This result required re-examination and reinterpretation of spectrophotometric and potentiometric data previously obtained by other authors.^{3,4} All data are consistent with the existence of a single equilibrium $\text{BiCl}_4^- + 2\text{Cl}^- \rightleftharpoons \text{BiCl}_6^{3-}$ in acid solutions containing 0.4 to 4.0 *M* chloride ion.

Spectrophotometric³ and electrometric⁴ studies of complexes BiCl_n^{3-n} have indicated complexes for $n = 1$ to 5 with some evidence for formation of BiCl_6^{3-} at high $[\text{Cl}^-]$. The unreliability of bismuth amalgam electrodes⁴ together with the number of assumptions required to interpret the spectrophotometric data³ prompted us to see what information, especially for complexes of $n \geq 4$, could be obtained from solubility studies. Our data indicate that for $[\text{H}^+] = 4.1$ and $[\text{Cl}^-] > 0.4$ *M*, only BiCl_4^- and BiCl_6^{3-} are present, contrary to the conclusions of Hume and Newman³ and Ahrlund and Grenthe.⁴ The spectrophotometric and potentiometric findings of the previous authors have been reinterpreted and their data shown to be consistent with an equilibrium involving only BiCl_4^- and BiCl_6^{3-} and the absence of BiCl_5^{2-} .

Experimental

Technical grade BiCl_3 , which was very wet, was hydrolyzed to BiOCl , which was twice dissolved and reprecipitated using reagent grade hydrochloric acid. $[(\text{CH}_3)_4\text{N}]_3\text{Bi}_2\text{Cl}_9$ was prepared by dissolving BiOCl in 3 *M* hydrochloric acid and adding a concentrated solution of reagent grade tetramethylammonium chloride. Large hexagonal crystals of $[(\text{CH}_3)_4\text{N}]_3\text{Bi}_2\text{Cl}_9$ precipitated, were filtered, dissolved in hot 3 *M* hydrochloric acid, and recrystallized at 0° from the same solution. The final product was washed with cold 3 *M* hydrochloric acid and dried in a vacuum desiccator over solid sodium hydroxide. The salt is stable in air and can be dried at 100° without decomposition. Analysis of the salt for carbon and hydrogen was made by the Clark Micro-analytical Laboratory, bismuth was determined spectrophotometrically by the method of Merritt, Hershenson, and Rogers in

6 *M* hydrochloric acid,⁵ and chloride was measured by titration with silver ion according to the familiar Mohr method after hydrolyzing the bismuth to BiOCl . One mole of chloride ion per mole of bismuth ion in the salt was added to the number of moles of chloride precipitated by silver ion.

Anal. Calcd. for $[(\text{CH}_3)_4\text{N}]_3\text{Bi}_2\text{Cl}_9$: C, 15.02; H, 3.78; Bi, 43.56; Cl, 33.26. Found: C, 15.26; H, 3.92; Bi, 43.5; Cl, 33.21.

The formula is of a general type $(\text{M}_I)_3(\text{M}_{II})_2\text{Cl}_9$ obtained by Wheeler⁶ and Cavalca⁷ where M_I is an alkali metal and M_{II} may be As, Sb, or Bi.

Standard solutions of Bi^{+3} for spectrophotometry were prepared by dissolving bismuth metal in nitric acid and destroying the nitrate ion with fuming sulfuric acid at 300° . Analysis for bismuth in solutions was done spectrophotometrically at 328 $\text{m}\mu$ in 6 *M* hydrochloric acid using a Beckman Model DU spectrophotometer.

All equilibrium studies were made in solutions which were 4 *M* in hydrogen ion to prevent hydrolysis. Varying concentrations of Cl^- were obtained by substituting sulfuric for hydrochloric acid, assuming H_2SO_4 to be a 1:1 electrolyte.^{1,2}

Solubility measurements were made with the aid of a Brönsted saturator.⁸ The salt was placed in a filter tube containing a medium fritted glass disk and connected by a capillary U-tube to a sampling tube. One pass of solvent over the salt was usually sufficient for saturation, although in practice several passes were employed. Suction from a water pump was used to pull solvent through the salt bed. Each sample of solvent was analyzed in duplicate by taking aliquots and at least two runs were made with each particular solvent employed. The saturator was maintained at $25.0 \pm 0.1^\circ$ in a thermostat during all manipulations.

The $[\text{Cl}^-]/[\text{Bi(III)}]$ ratio in 4 *M* H_2SO_4 saturated with the salt was unchanged from that in the salt, indicating that no change takes place in the solid phase.

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