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HYDROLYSIS OF URANIUM CARBIDES BETWEEN 25°C AND 100°C.

I. URANIUM MONOCARBIDE*

By

Mildred J. Bradley and Leslie M. Ferris

ABSTRACT

High-purity uranium monocarbide, when allowed to react with water at temperatures between 25° and 99°C., yielded a gelatinous, hydrous, tetravalent uranium oxide and a gas (93 ml. (STP) per gram of UC hydrolyzed) consisting of 86 vol. % methane, 11 vol. % hydrogen, 1.8 vol. % ethane, and small quantities of saturated C₃-to C₆-hydrocarbons. The gaseous products contained all the carbon originally present in the carbide. Hydrolysis, at 80°C., of monocarbide specimens containing dispersed uranium metal yielded the expected gaseous products and an additional 2 moles of hydrogen per mole of uranium metal. The rate of hydrolysis was studied briefly.

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INTRODUCTION

Since the hydrolysis of uranium carbides in aqueous systems has received little attention in earlier work, a program was initiated in this Laboratory to study the process (1). The results of the first phase of

(1) M. J. Bradley and L. M. Ferris, U. S. Atomic Energy Comm. Report.

ORNL-3101 (1961)

this program, on the hydrolysis of uranium monocarbide between 25° and 99° C., are given in this paper. Previously, Litz (2) studied this reaction; -----
(2) L. M. Litz, "Uranium Carbides; Their Preparation, Structure, and Hydrolysis," Ph. D. Thesis, Ohio State University, 1945. -----
however, he worked only at temperatures above 83°C. and did not measure the quantity of gas evolved or analyze the solid residue for carbon compounds.

EXPERIMENTAL

Materials. - The uranium monocarbide specimens were prepared by arc-melting high-purity uranium metal (less than 400 p.p.m. total impurities) and spectroscopic grade graphite. Specimens 2A, 2B, and 2C were nearly single phase stoichiometric uranium carbide as shown by chemical analysis (Table 1), metallographic examination, and X-ray analysis. The metallographic examination revealed traces of uranium metal at the grain boundaries and a higher carbide in the form of dark needles dispersed homogeneously throughout the grains. The uranium metal concentration, according to the elemental analyses, was 3.3 wt. %, based on a U-UC binary
Specimen 6B consisted of uranium metal dispersed throughout a uranium monocarbide matrix; traces of a third phase were also present. The uranium concentration was 17 wt. % considering the specimen as a U-UC binary (Table 1). No free carbon was detected in any of the specimens.

Apparatus and Procedure. - The apparatus consisted of a mercury-filled gas buret and a 250-ml. round bottom reaction vessel with a helium inlet

TABLE 1
COMPOSITION OF URANIUM MONOCARBIDE SPECIMENS

Specimen	Composition, ^a wt. %					
	Synthesis		Chemical Analysis			
	U	C	U	Total C ^b	O	N
2A	95.23	4.77	95.38	4.71	0.11	0.01
2B	95.23	4.77	95.43	4.59	0.02	0.01
2C	95.23	4.77	95.39	4.64	0.11	0.01
6B	96.00	4.00	96.03	4.01	0.06	0.01

^aCalculated for UC: U, 95.20; C, 4.80 wt. %.

^bNo free carbon detected.

and a funnel for introducing the water sealed to one side (3). The

(3) M. J. Bradley and L. M. Ferris, U. S. Atomic Energy Comm. Rept. ORNL-TM-38 (1961).

reaction vessel and the funnel were immersed in a constant temperature bath (a water-glycerol mixture) controlled to $\pm 0.1^\circ\text{C}$.

In each experiment, a 3- to 4-gram carbide specimen was placed in the reaction vessel and the funnel was filled with 50 ml. of water. As the reactants were preheated to the desired temperature, the reaction vessel and the water were flushed with helium to remove air from the system. The reaction was initiated by adding water to the carbide. The evolved gases were first collected in the gas buret, where the volume was measured, and then transferred to an evacuated sample bulb. After gas evolution had ceased, the gas remaining in the reaction vessel was sampled by using the gas buret as a Toepler pump. The gelatinous residue was dissolved in either 6 M HCl or 12 M H₃PO₄ and analyzed for both total and tetravalent uranium.

Gas volumes were converted to standard conditions, assuming ideal gas behavior, and were corrected for the vapor pressure of water. The average gas composition was calculated from the volume and analysis of each sample. Air contamination of the gas samples was generally less than 0.3 vol. % and frequently less than 0.1 vol. %.

Analytical. - Gas samples were analyzed by a gas-chromatographic technique using a Burrell Kromo-log K-2 instrument modified with a Gow-Mac thermometer detector. Hydrogen, oxygen, nitrogen, methane, and ethane were determined on a 5-A Molecular Sieve column, while Burrell di-2-ethylhexylsebacate, standard concentration, was used for the higher hydrocarbons. Helium was the carrier gas, and peak areas were determined by the integrator on the Burrell instrument.

The carbide specimens were analyzed for uranium and total carbon by combustion analysis, weighing the uranium as U_3O_8 and carbon as CO_2 . The specimens were tested for free carbon by dissolving them in 6 M HCl and burning any residue that remained. A fluorination procedure was used for the oxygen analysis. (4). Nitrogen was determined by dissolving the sam-

(4) G. Goldberg, A. S. Meyer, Jr., and J. C. White, Anal. Chem., 32, 314
(1960).

ple in a sulfuric acid-hydrogen peroxide solution, steam distilling the resulting ammonia after making the solution basic, and finally determining the ammonia spectrophotometrically with sodium phenate.

Total and tetravalent uranium in solution were determined potentiometrically.

RESULTS

Uranium Monocarbide.- Uranium monocarbide, when allowed to react with water at temperatures between 25^o and 99^oC., yielded an insoluble, gelatinous, greenish-brown tetravalent uranium compound and 93 ml. (STP) of gas per gram of carbide, consisting chiefly of methane (86 vol. %) and hydrogen (11 vol. %)(Table II). The gas also contained small quantities of the saturated hydrocarbons containing two to seven carbon atoms, including at least three, and probably all four, of the branched hexane isomers (2,3-dimethylbutane could not be differentiated from 2-methylpentane by the analytical technique used). In addition, unidentified peaks representing a total of about 0.02 vol. % were found in the chromatogram between the butanes and pentanes, and between the pentanes and hexanes.

The nonvolatile, gelatinous hydrolysis product was amorphous to X-rays. After dissolution of this material in chlorine-free 6 N HCl, 95 to 99% of the uranium was in the tetravalent state. Since some air oxidation of the solutions was inevitable and no carbon was associated with the material, the residue is probably a hydrous tetravalent oxide of uranium. No insoluble organic material remained after dissolution of the hydrous oxide in 6 N HCl.

Within the limits of experimental error, a material balance for carbon was obtained. Assuming that the gases were ideal, each gram of uranium monocarbide hydrolyzed yielded an average of 3.89 mg-atoms of carbon (3.58 mg-atoms in methane and 0.31 mg-atoms in C₂-to C₇-hydrocarbons) and 16.09 mg-atoms of hydrogen (0.92 mg-atoms as H₂, 14.32 in methane, and 0.85 in C₂-to C₇-hydrocarbons). The original monocarbide contained 3.87 mg-atoms of carbon per gram of sample, as determined by chemical

TABLE II
 PRODUCTS OF THE URANIUM MONOCARBIDE-WATER REACTION AT VARIOUS TEMPERATURES

(Specimen Compositions given in Table I)

Specimen	Temp., °C.	Total Vol- ume of gas, ml./g.	Total Carbon, mg-atoms per gram	Total Hydro- gen, mg-atoms per gram	Volatile Products								
					Composition of Gas Evolved, ^a Vol. %								
					H ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀ ^b	iso- C ₅ H ₁₂	n- C ₅ H ₁₂	Branch- ed C ₆ H ₁₄	n- C ₆ H ₁₄
2C	25	94.4	3.97	16.37	10.8	85.5	2.44	0.68	0.34	0.018	0.062	0.032	0.008
2C		93.8	3.98	16.33	8.9	88.7	1.38	0.55	0.29	0.009	0.054	0.033	0.004
Avg.		94.1	3.98	16.35	9.8	87.1	1.91	0.62	0.32	0.014	0.058	0.032	0.006
2A	40	92.2	3.87	15.95	10.8	86.4	1.73	0.65	0.33	0.013	0.075	0.018	0.005
2A		92.3	3.85	15.92	10.9	86.2	1.75	0.63	0.33	0.011	0.045	0.019	0.003
2C		91.9	3.85	15.89	10.8	86.3	1.85	0.61	0.32	0.013	0.072	0.036	0.006
2C		92.2	3.92	16.07	9.9	86.1	2.93	0.59	0.30	0.009	0.057	0.028	0.007
Avg.		92.2	3.87	15.96	10.6	86.2	2.06	0.62	0.32	0.012	0.062	0.023	0.005
2B	60	92.3	3.86	15.95	10.7	86.6	1.79	0.50	0.31	0.017	0.054	0.020	0.009
2B		91.8	3.82	15.66	12.3	84.8	1.89	0.53	0.30	0.011	0.067	0.020	0.005
2B		93.4	3.80	15.95	12.5	85.3	1.39	0.53	0.26	0.008	0.060	0.014	0.008
2B		93.9	3.91	16.19	10.6	86.6	1.72	0.58	0.26	0.016	0.059	0.019	0.006
2A		93.4	3.89	16.12	10.7	86.8	1.64	0.55	0.26	0.010	0.049	0.010	0.008
Avg.		93.0	3.86	15.97	11.4	86.0	1.69	0.54	0.28	0.012	0.058	0.017	0.007
2B	80	-	-	-	10.7	86.6	1.7	0.65	0.23	0.01	0.05	0.03	0.01
2B		93.6	3.93	16.19	10.1	87.0	1.8	0.73	0.31	0.02		0.006	0.004
2B		93.4	3.94	16.26	10.8	86.0	1.90	0.76	0.30	0.023	0.075	0.14	0.017
2B		91.9	3.86	15.92	10.4	86.7	1.8	0.69	0.27	0.009	0.050	0.045	0.010
Avg.		93.0	3.91	16.12	10.4	86.7	1.8	0.69	0.27	0.009	0.050	0.045	0.010
2A	90	93.7	3.92	16.18	10.4	86.9	1.70	0.62	0.26	0.016	0.066	0.013	0.008
2A		93.2	3.82	15.97	12.9	84.0	1.85	0.75	0.28	0.016	0.078	0.017	0.010
2A		91.3	3.77	15.68	12.0	85.1	1.64	0.66	0.32	0.016	0.068	0.024	0.009
2C		93.7	3.90	16.17	10.9	86.5	1.70	0.57	0.26	0.016	0.047	0.013	0.009
Avg.		93.0	3.87	16.00	11.6	85.6	1.72	0.65	0.28	0.016	0.065	0.017	0.009
2A	99	95.9	3.92	16.40	13.3	83.6	1.86	0.74	0.32	0.012	0.077	0.008	0.010
2C		93.0	3.95	16.19	10.1	86.8	1.70	0.80	0.40	0.016	0.10	0.031	0.019
2C		92.5	3.85	15.97	11.5	85.4	1.89	0.70	0.35	0.010	0.079	0.030	0.012
2C		95.6	3.95	16.44	12.6	84.1	2.12	0.69	0.32	0.013	0.078	0.032	0.016
Avg.		94.2	3.92	16.25	11.9	85.0	1.89	0.73	0.35	0.013	0.083	0.025	0.014
Overall Avg.		93.2	3.89	16.09	11.1	86.0	1.84	0.64	0.30	0.013	0.063	0.026	0.009

^aIn addition, 0.001% n-heptane and about 0.02% of unidentified compounds were present.

^bIncludes isobutane: concentration of isobutane varied from less than 0.001% to 0.03%.

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analysis. These data also show conclusively that all the carbon originally present in the monocarbide was converted to gaseous products.

Although temperature had no detectable effect on the composition of the gaseous reaction products, the rate of hydrolysis increased markedly with increasing temperature (Fig. 1). The time required to hydrolyze completely a 3- to 4-gram irregularly shaped specimen decreased from a week to about 2 hr. when the reaction temperature was increased from 25° to 99°C. At the lower temperatures water first attacks cleavage planes in the crystals, so that extensive powdering of the sample occurs without much gas evolution. In one experiment at 25°C., the specimen disintegrated completely in 23 hr. to a -20 mesh powder which, by X-ray analysis, retained the UC crystal structure, while 50% of the carbon had been evolved as gaseous products. This behavior is similar to the stress-corrosion oxidation on cleavage planes when uranium carbides are exposed to moist air (5).

(5) F. A. Rough and W. Chubb, U. S. Atomic Energy Comm. Rept. BMI-1488 (1960).

Uranium Monocarbide - Uranium Metal Dispersion. - Hydrolysis, at 80°C., of specimen 6B, containing uranium metal (17 wt. % dispersed in a uranium monocarbide matrix, yielded an insoluble hydrous uranium oxide and 106 ml. (STP) of gas per gram of sample consisting of about 36 vol. % hydrogen, 60 vol. % methane, and small quantities of the higher hydrocarbons (Table III). More than 24 hr. was required for complete hydrolysis of a 5-g. specimen compared to only 3 hr. for the hydrolysis of the monocarbide at the same temperature (Fig. 1). The hydrogen concentration increased from 20 vol. % in the first 20% of the gas evolved to about

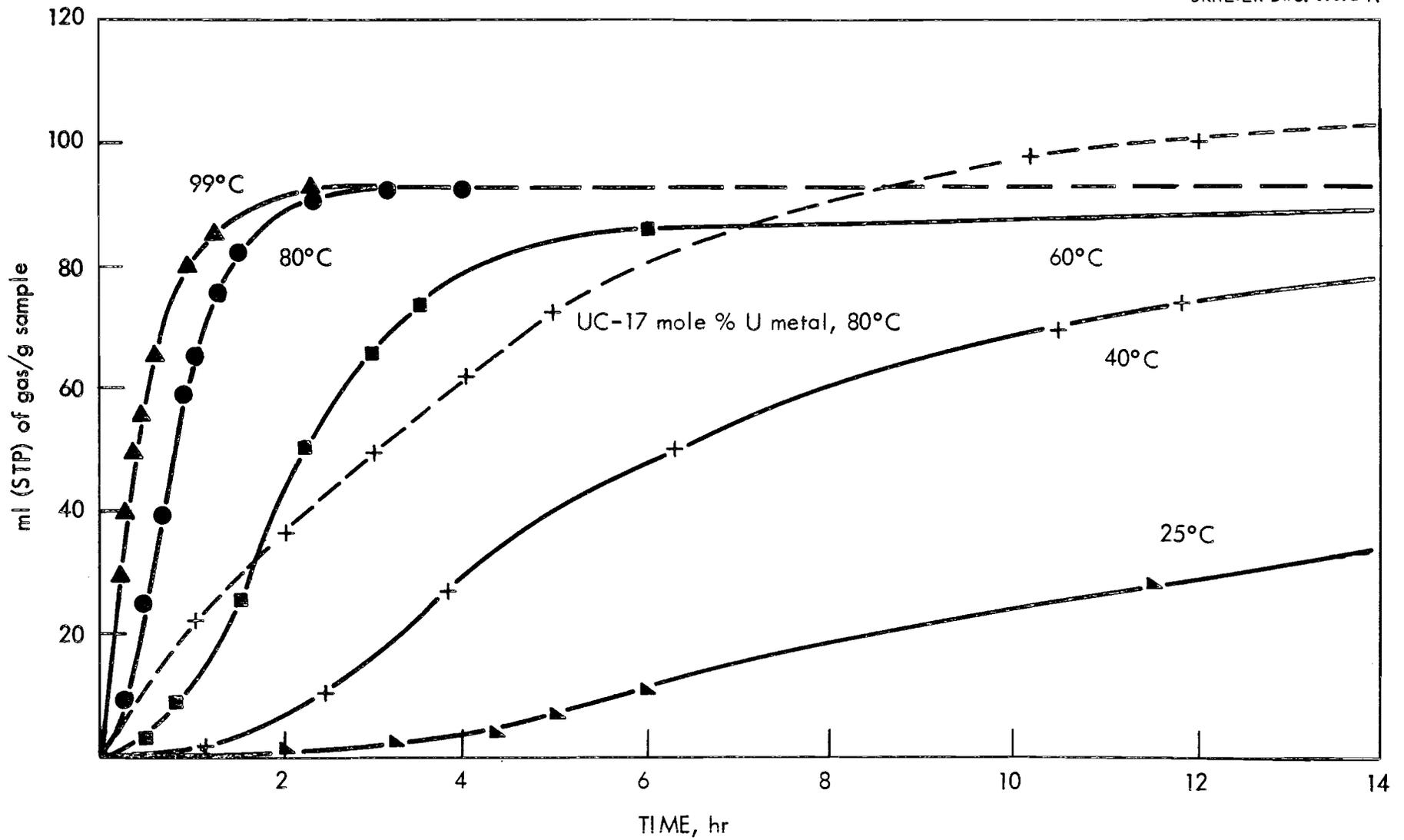


Fig. 1. Rates of gas evolution on hydrolysis of 3- to 4-g. uranium monocarbide and UC-U metal specimens.

TABLE III

REACTION OF URANIUM MONOCARBIDE-URANIUM METAL DISPERSION WITH
WATER AT 80°C.

Specimen 6B composition given in Table 1.

Run No.	Total Volume of Gas, ml./g	Total Carbon, mmoles per gram	Total Hydrogen, mmoles per gram	Volatile Products								
				Composition of Gas Evolved, ^a							Vol. %	
				H ₂	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₄ H ₁₀	C ₅ H ₁₂	C ₅ H ₁₂	iso-	n-
1	104.4	3.26	15.81	35.4	61.2	2.04	0.74	0.35	0.02	0.09		
2	106.2	3.29	16.06	40.1	55.2	1.86	1.62	0.73	0.05	0.22		
3	106.8	3.39	16.27	33.4	63.4	1.96	0.70	0.22	0.01	0.08		
Avg.	105.8	3.31	16.06	36.3	59.9	1.95	1.02	0.43	0.03	0.13		

^aIn addition to the values shown, 0.07% of branched hexanes, 0.04% of n-hexane, and 0.2% of unidentified compounds were evolved.

50 vol. % in the final 40% of the gas with a corresponding decrease in the methane concentration from 80 to 50 vol. %. These results indicate that the dispersed uranium metal reacts more slowly with water than the uranium monocarbide matrix.

The hydrous uranium oxide was not readily soluble in 6 N HCl at 80°C; after 2 hr. 10% of the uranium was undissolved and after 16 hr. 3% was still undissolved. In contrast, the solid hydrolysis product from uranium monocarbide dissolved completely in 6 N HCl at 80°C. within an hour. The residue from hydrolysis of the specimen containing 17 wt. % uranium metal was soluble in boiling 12 M H₃PO₄. Analysis of the resulting solutions showed that at least 95% of the uranium was in the tetravalent state.

As in the studies with high-purity monocarbide specimens, all the carbon present in the sample was converted to gaseous products. Hydrolysis of 1 g. of specimen 6B (4.03 mg-atoms of U and 3.33 mg-atoms of C)

yielded 3.31 mg-atoms of carbon (2.83 in CH_4 and 0.48 in C_2 - to C_6 -hydrocarbons) and 16.06 mg-atoms of hydrogen (3.43 as H_2 , 11.34 in CH_4 , and 1.29 in C_2 - to C_6 - hydrocarbons).

DISCUSSION

Uranium monocarbide belongs to a class of reactive, heavy-metal carbides which includes PuC , Pu_2C_3 , UC_2 , ThC_2 , CeC_2 , etc. (6,7). Al-

(6) J. L. Drummond, B. J. McDonald, H. M. Ockenden, and G. A. Welch, J. Chem. Soc., 1957, 4785.

(7) G. J. Palenik, "Rare Earth Carbides: Structural and Hydrolytic Studies," Ph. D. Thesis, University of Southern California, 1960.

though these carbides yield mixtures of hydrocarbons on hydrolysis, they differ from the salt-like alkali metal and alkaline earth carbides in that they exhibit a metallic luster and high thermal and electrical conductivities; yet, they cannot be considered as interstitial carbides such as TiC , ZrC , and HfC which are inert to most chemical reagents except strong oxidants. Wells (8) places uranium monocarbide in the interstitial cate-

(8) A. F. Wells, "Structural Inorganic Chemistry," Oxford University Press, London, pp. 553 and 704, 1950.

gory and UC_2 in the salt-like class although the physical properties and the hydrolysis behavior of the two compounds are remarkably similar except for the type of hydrocarbons produced. Rundle's (9) fundamental premise

(9) R. E. Rundle, Acta Cryst., 1, 180 (1948).

that the properties of uranium monocarbide require octahedrally oriented, metal-non-metal bonds of considerable strength which, though directed, are not localized is probably basically correct. However, the implication that UC , like TiC , is chemically inert is not in agreement with the re-

sults of this study. Therefore, the metal-non-metal bonds must also have a considerable amount of ionic character to account for the high reactivity of uranium monocarbide.

Uranium monocarbide yields primarily methane on hydrolysis, as would be 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 (10). Although the principal reaction is $UC + (2 + x)$

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

$H_2O \longrightarrow UO_2 \cdot xH_2O + CH_4$, significant amounts of hydrogen and C_2^- to C_7^- hydrocarbons are also produced. Hydrogen can be obtained by reaction of uranium metal with water: $U + (2 + y)H_2O \longrightarrow UO_2 \cdot yH_2O + 2H_2$; however, more free hydrogen was obtained than expected on the basis of the C/U atom ratio in the specimens. For example, hydrolysis of 1 gram of high-purity uranium monocarbide yielded 0.46 mg-atoms of free hydrogen whereas only 0.27 mg-atoms would be expected from the chemical analysis assuming a U(3.4 wt. %)-UC binary. There are two plausible methods by which the higher hydrocarbons and the additional free hydrogen could be produced. The higher hydrocarbons could arise from the polymerization of free radicals produced during hydrolysis with the simultaneous evolution of free hydrogen. The alternative possibility is that the high-purity specimens contained about 5 wt. % U_2C_3 , and, necessarily, also about 5 wt. % uranium metal. The H/C atom ratio in the higher hydrocarbons was 2.7 as required: $U_2C_3 + (4 + 2z)H_2O \longrightarrow 2UO_2 \cdot zH_2O + 3CH_{2.7}$. In this case, all of the free hydrogen would have resulted from uranium metal. Impurities in these amounts could not be detected by X-ray methods. Photomicrographic examination did show traces of a third phase within the UC grains

in both the high-purity and the 17 wt. % uranium dispersion.

The results of this study differ significantly from those obtained by Litz (2), who reported that the composition of the hydrolysis products changed markedly with temperature; viz., 81% methane at 83°C., 72% at 90°C. and only 57% at 100°C. with a corresponding increase in the hydrogen concentration from 12 to 37%. Litz, however, did not report the mode of preparation and purity of his monocarbide, did not measure the volume of gas evolved, did not analyze the solid residue for carbon compounds, or give evidence that the reactions had gone to completion. One of the methods Litz investigated for preparing uranium monocarbide involved in situ conversion of uranium metal to uranium hydride and the subsequent conversion to carbide with methane. It is possible that carbide specimens prepared in this manner might still contain uranium metal and/or hydride which, on hydrolysis, would yield large quantities of hydrogen, particularly at the higher temperatures.

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