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HYDROLYSIS OF URANIUM CARBIDES BETWEEN 25° AND 100°C. I. URANIUM MONOCARBIDE*

By

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ABSTRACT

High-purity uranium monocarbide, when reacted with water at temperatures between 25° and 99°C., yielded a gelatinous, tetravalent, hydrous uranium oxide and a gas (93 ml. (STP) per gram of UC hydrolyzed) consisting of 86 v/o methane, 11 v/o hydrogen, 1.8 v/o ethane, and small quantities of saturated C_3 to C_6 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 of 3- to 4-g. specimens of the monocarbide was markedly temperature-dependent; the time required for complete hydrolysis varied from a week at 25° to about 2 hr. at 99°C.

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INTRODUCTION

Uranium, thorium, and plutonium carbides offer great promise as nuclear reactor fuels because of their high densities, thermal conductivities, and melting points (1). Uranium monocarbide in solid solution with zirconium

(1) U. S. Atomic Energy Comm. Rept. TID-7603 (1961).

carbide can also be used as a component in plasma thermocouples (2). Knowledge

(2) G. M. Grover, Nucleonics, 17, No. 7, 54 (1959).

of the chemical reactivity of these carbides is essential to persons involved in their preparation, handling, and processing. Since their behavior in water and other aqueous systems was virtually unknown, a program was initiated at this Laboratory to supply some of the desired information (3). The results

(3) M. J. Bradley and L. M. Ferris, U. S. Atomic Energy Comm. Rept. ORNL-3101 (1961).

of the first phase of this program, on the hydrolysis of uranium monocarbide between 25° and 99°C., are given in this paper. Previously, Litz (4)

(4) L. M. Litz, "Uranium Carbides: Their Preparation, Structure, and Hydrolysis," Ph.D. Thesis, Ohio State University, 1945.

studied this reaction; 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 (5). Specimens 2A, 2B, and 2C were nearly single-phase,

(5) D. T. Bourgette, ORNL Metallurgy Division, personal communication.

stoichiometric uranium carbide as shown by chemical analysis (Table I),

metallographic examination (Fig. 1), and X-ray analysis. The metallographic examination revealed traces of uranium metal and a higher carbide in the specimens. The uranium metal concentration, according to the elemental analyses, was 3.4 m/o, based on a U-UC binary composition. Specimen 6B consisted of uranium metal dispersed throughout a uranium monocarbide matrix (Fig. 2). The uranium metal concentration was 17 m/o considering the specimen as a U-UC binary (Table I). No free carbon was detected in any of the specimens.

TABLE I

COMPOSITION OF URANIUM MONOCARBIDE SPECIMENS

	Composition,[a] w/o					
	Synthesis		Chemical Analysis			
Specimen	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

[a]Calculated for UC: U, 95.20; C, 4.80 w/o.
[b]No free carbon detected.

Procedure.- The hydrolysis experiments were conducted as follows: The carbide specimen (3-4 g.) was placed in the reaction vessel, 50 ml. of water was placed in the funnel, and the apparatus was assembled as shown in Fig. 3. The reactants were preheated to the desired temperature in the constant-temperature bath (a water-glycerol mixture) controlled to $\pm 0.1^{\circ}$C., while the main 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. Since the initial rate of hydrolysis was low, the helium displaced by addition of the water to the reaction vessel was vented through the pressure equalizer

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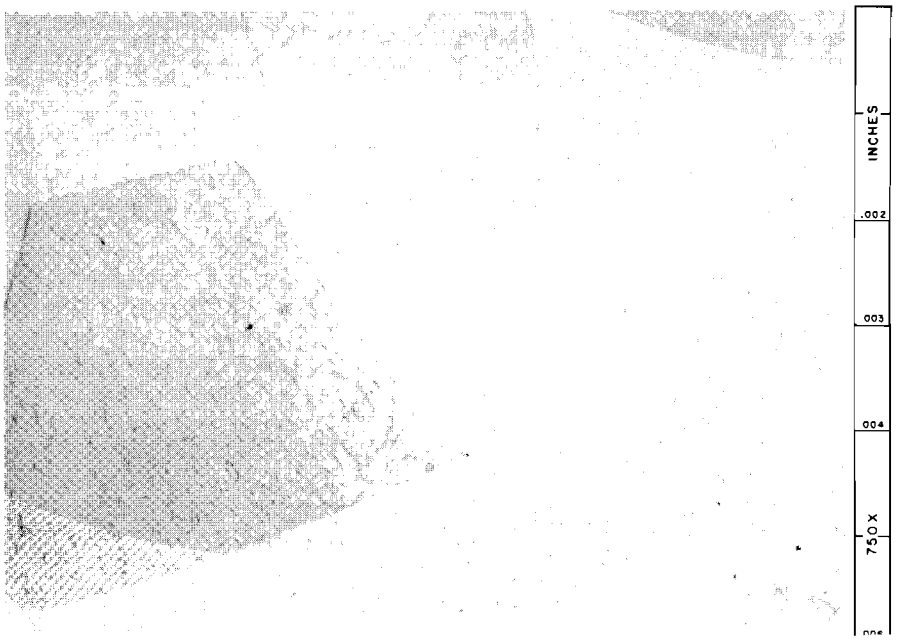

Fig. 1. Photomicrograph of specimen 2C showing UC as the primary phase with a trace of U metal (the white areas at the grain boundaries) and a higher carbide (the dark needles).

Fig. 2. Photomicrograph of specimen 6B showing UC as the primary phase with uranium metal both at the grain boundaries and inside the grains (the large white spots) and possibly a trace of a third phase (the dots within the grains).

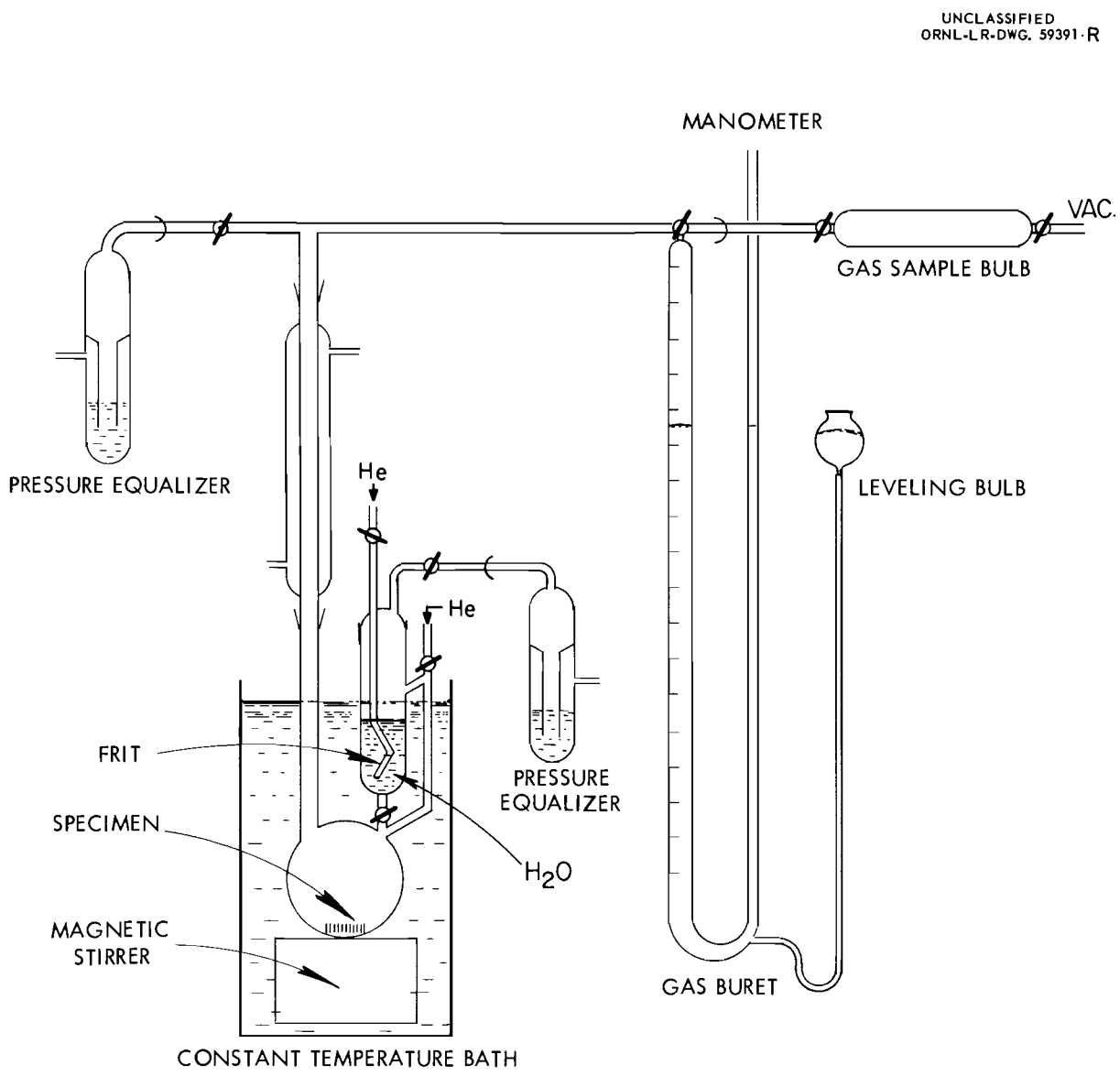

Fig. 3. Apparatus for measuring the volume of gas evolved in the reactions of uranium carbides with aqueous reagents.

connected to the condenser. The pressure equalizer was then isolated from the rest of the system, which was thereafter maintained at atmospheric pressure by continually adjusting the leveling bulb. 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 collected by using the gas buret as a Toepler pump. The gelatinous residue was dissolved in either 6 M HCl or 12 M H_3PO_4 and analyzed for both total and tetravalent uranium. The magnetic stirrer was used only during the uranium dissolution step.

Gas volumes were converted to $0^{\circ}C$. and 760 mm. Hg pressure, 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 v/o and frequently less than 0.1 v/o.

Analytical. - Gas samples were analyzed by a gas-chromatographic technique by a Burrell Kromo-log K-2 instrument modified with a Gow-Mac thermister detector. Hydrogen, oxygen, nitrogen, methane, and ethane were determined on a 5-A Molecular Sieve column (6), while Burrell di-2-ethylhexylsebacate,

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(6) A. D. Horton, ORNL Analytical Chemistry Division, personal communication.

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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 (7). Nitrogen was determined by dissolving the sample in a sulfuric

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

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 reacted with water at temperatures between 25° and 99°C., yielded an insoluble, gelatinous, greenish-brown colored uranium(IV) compound and 93 ml. (STP) of gas per gram of carbide, consisting chiefly of methane (86 v/o) and hydrogen (11 v/o) (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 v/o were found between the saturated butanes and pentanes, and between the pentanes and hexanes. No ethylene or acetylene was ever detected.

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 tetravalent hydrous oxide of uranium. No insoluble organic material remained after dissolution of the hydrous oxide in 6 N HCl.

TABLE II

PRODUCTS OF THE URANIUM MONOCARBIDE-WATER REACTION AT VARIOUS TEMPERATURES

Composition of specimens given in Table I

Specimen	Temp., °C.	Total Volume of gas, ml./g.	Total Carbon, mmoles per gram	Total Hydrogen, mmoles per gram	Volatile Products: Composition of Gas Evolved,[a] v/o								
					H_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}[b]	iso-C_5H_{12}	n-C_5H_{12}	Branched C_6H_{14}	n-C_6H_{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

[a] In addition, 0.001 v/o n-heptane and about 0.02 v/o of unidentified compounds were present.

[b] Includes isobutane; concentration of isobutane varied from less than 0.001% to 0.03%.

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 mmoles of carbon (3.58 mmoles in methane and 0.31 mmole in C_2 to C_7 hydrocarbons) and 16.09 mmoles of monatomic hydrogen (0.92 mmole as H_2, 14.32 in methane, and 0.85 in C_2 to C_7 hydrocarbons). The original monocarbide contained 3.87 mmoles of carbon, as determined by chemical 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. 4). The time required to hydrolyze completely a 3- to 4-g. 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 there was an induction period during which extensive powdering of the sample occurred without much gas evolution. In one experiment at 25°C., the specimen disintegrated completely to a -20 mesh powder in 23 hr., yet only 50% of the carbon had been evolved as gaseous products.

Uranium Monocarbide - Uranium Metal Dispersion. - Hydrolysis, at 80°C., of specimen 6B, containing uranium metal (17 m/o) 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 v/o hydrogen, 60 v/o 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. 4). The hydrogen concentration increased from 20 v/o in the first 20% of the gas

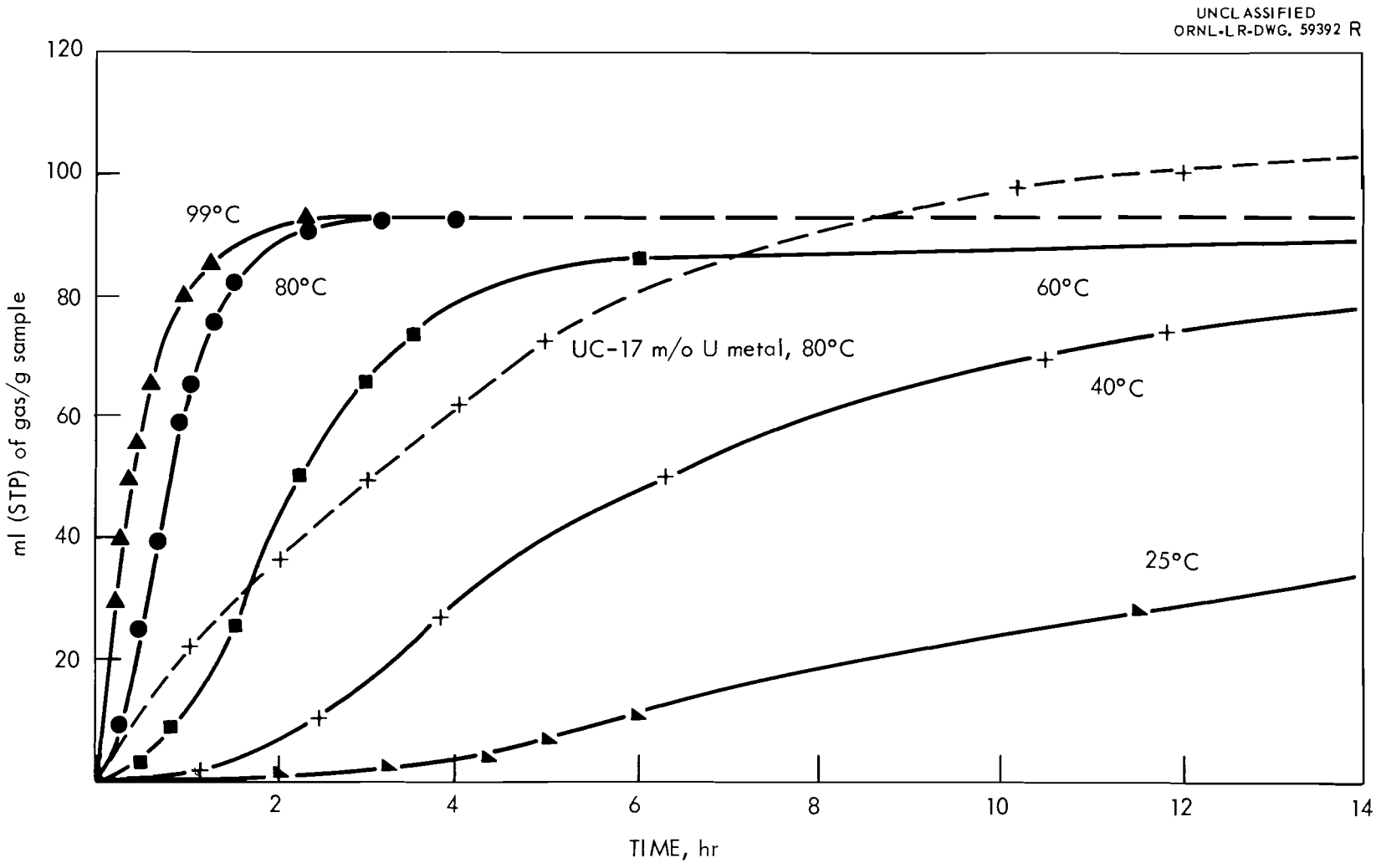

Fig. 4. Rates of gas evolution on hydrolysis of 3- to 4-g. uranium monocarbide and UC-U metal specimens.

evolved to about 50 v/o in the final 40% of the gas with a corresponding decrease in the methane concentration from 80 to 50 v/o. These results indicate that uranium metal reacts more slowly with water than uranium monocarbide.

TABLE III

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

Specimen 6B composition given in Table I

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] v/o						
				H_2	CH_4	C_2H_6	C_3H_8	C_4H_{10}	iso-C_5H_{12}	n-C_5H_{12}
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

[a]In addition to the values shown, 0.073 v/o of branched hexanes, 0.042 v/o of n-hexane, and 0.16 v/o of unidentified compounds were evolved.

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 insoluble. 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 m/o uranium metal was soluble in boiling 12 M H_3PO_4. 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 mmoles of U and 3.33 mmoles of C) yielded 3.31 mmoles of

monatomic carbon (2.83 in CH_4 and 0.48 in C_2 to C_6 hydrocarbons) and 16.06 mmoles of monatomic hydrogen (3.43 as H_2, 11.34 in CH_4, and 1.29 in C_2 to C_6 hydrocarbons).

DISCUSSION

Although methane is the principal gaseous product evolved on hydrolysis of the uranium carbide specimens, $UC + (2+x)\ H_2O \longrightarrow UO_2 \cdot xH_2O + CH_4$, significant amounts of hydrogen and C_2 to C_7 hydrocarbons were also produced. Hydrogen is a product of the reaction of uranium metal with water, $U + (2+y)\ H_2O \longrightarrow UO_2 \cdot yH_2O + 2\ H_2$; however, more hydrogen was obtained than expected on the basis of the uranium metal content. For example, hydrolysis of 1 g. of the high-purity uranium monocarbide produced a total of 0.92 mmole of monatomic hydrogen whereas only 0.54 mmole would be expected from the uranium metal content (3.4 m/o based on the chemical analyses). Similar results were obtained with the uranium metal-uranium carbide dispersion. There are at least two plausible means by which hydrogen and the higher hydrocarbons could have been formed from the monocarbide specimens. Both hydrogen and hydrocarbons could arise from the polymerization of free radicals produced during hydrolysis. Allowing for the hydrogen yield from 3.4 m/o uranium metal in the specimens, the H/C atom ratio from the remaining hydrogen and the hydrocarbons was 4/1, as required by the polymerization mechanism. The higher hydrocarbons could also have resulted from the presence of U_2C_3 as an additional impurity in the samples. The H/C atom ratio in the higher hydrocarbons was 2.7 as required: $U_2C_3 + (4 + 2z)\ H_2O \longrightarrow 2\ UO_2 \cdot zH_2O + C_3H_8$. If the higher hydrocarbons were formed in this manner, hydrogen would necessarily result strictly from uranium metal in the samples. About 5 w/o of both U_2C_3 and uranium

metal would be required to account for the results obtained.

The results of this study differ markedly from those obtained by Litz (4), who found 12% hydrogen at 83°, 22% at 90°, and 37% at 100°C. in the gaseous products from the uranium monocarbide-water reaction.

ACKNOWLEDGMENT

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Oak Ridge, Tennessee

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