BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1983—1989 (1968)

Hydrolysis of Uranium Monocarbide and Oxidation Potentials

Yoshio HORI and Takashi MUKAIBO

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Tokyo

(Received February 6, 1968)

The hydrolysis of UC with 1 N H_2SO_4 was carried out in the presence of various oxidants at 80°C. The amount of gaseous products was measured by means of a gas chromatograph; the dissolved, carbon-containing compounds, and the insoluble residues produced in the reaction were analyzed for carbon. Analyses of the uranium and oxidants consumed were also made by volumetric and gravimetric methods. The results may be summarized: (1) The hydrolysis of UC with 1 N H_2SO_4 proceeds by an electro-chemical mechanism. (2) The hydrolysis products fundamentally depend upon the oxidation potential of the oxidants in the solution. (3) The oxidation potential at which the hydrolysis of UC with 1 N H_2SO_4 proceeds can be explained in terms of the partial ionic character of UC. (4) The application of this experimental method to other carbides would serve to clarify the chemical reaction and the bond character of the carbides.

Reactions between carbides and aqueous solutions containing oxidants have been studied by several authors. According to these studies, the hydrolyses of some carbides, such as uranium and actinides with nitric acid, yield products with different compositions from those obtained from aqueous solutions without any oxidants.[1-5] Others, such as CaC_2, give rise to products of the same composition whether containing nitric acid or not.[6] The present study seeks to clarify the mechanism of the hydrolysis of uranium monocarbide, which has not been discussed by previous authors.

Experimental

Experimental Procedure. About 250—500 mg of a UC sample was placed in a reactor. The reactor (volume: *ca.* 200 m*l*) consists of a glass tube 40 mm in diameter, connected with two vacuum stop cocks. After evacuation through one of the stop cocks, 35 m*l* of an aqueous reagent solution was introduced into the reactor as fast as possible in order to prevent air dissolution. Then it was immersed in a thermostated water bath at 80±0.1°C or placed in an air bath at the same temperature; in the latter case the reaction had to continue for more than ten hours. After the reaction, the reactor was cooled to room temperature, and the products were analyzed as will be described below.

Materials (1) Uranium Monocarbide. The same powdered sample as had been used in a previous work[7] was employed in this study.

Materials (2) Aqueous Reagent Solution. The solutions were prepared by dissolving oxidizing reagents into 1.1 N H_2SO_4, which had been flushed with purified nitrogen before the reaction. In order to control the oxidation potentials of the reactant solutions, the following reagents were employed (the standard oxidation potentials at 25°C are shown in parentheses): $FeSO_4\cdot7H_2O$(Fe^{2+}/Fe −0.44 V), JIS GR grade reagent. $CoSO_4\cdot7H_2O$(Co^{2+}/Co −0.277 V), JIS GR grade reagent. $NiSO_4\cdot7H_2O$(Ni^{2+}/Ni −0.250 V), JIS GR grade reagent. $SnSO_4$ (Sn^{2+}/Sn −0.140 V), the reagent solution of Sn^{2+}, was prepared by dissolving a ten-fold excess of Sn metal, 99.9% purity, into GR grade $CuSO_4$ and an H_2SO_4 aqueous solution in a purified nitrogen atmosphere. The resultant solution was analyzed to ascertain the absence of Cu^{2+} and Sn^{4+} concentrations. By the use of a KI and starch solution, Cu^{2+} was not detectable. The concentration of Sn^{2+} was equal to the total concentration of Sn ions within 1%; this indicates the absence of Sn^{4+} in the solution. $CuSO_4\cdot5H_2O$ (Cu^{2+}/Cu +0.377 V), JIS GR grade reagent. Ag_2SO_4 (Ag^+/Ag +0.799 V), the Ag_2SO_4 was obtained as a precipitate by the addition of H_2SO_4 to a GR grade $AgNO_3$ solution. The precipitate was filtered and then washed with alcohol and ethyl ether. NO_3^- was not detectable in the compound. $Fe_2(SO_4)_3\cdot xH_2O$ (Fe^{3+}/Fe^{2+} +0.771 V), JIS GR grade reagent.

Chemical Analysis (1). The aqueous systems which involved Fe^{2+} and Co^{2+} were not analyzed for the corresponding metal after the reaction, because no metal deposit was found in these systems after the reaction had been completed. Ni^{2+} was weighed as nickel dimethyl glyoxime.[8] Sn^{2+} was determined as follows. A known amount of $FeCl_3$ solution was added to the test solution, and the Fe^{2+} reduced by Sn^{2+} was titrated

---

[1] J. L. Drummond, B. J. McDonald and H. M. Ockenden, *J. Chem. Soc.*, **1957**, 4785.

[2] P. L. Pausen, J. McLean and W. J. Clelland, *Nature*, **197**, 1200 (1963).

[3] D. M. Donaldson, K. Hartley, P. Lees and N. Parkinson, *Trans. AIME*, **227**, 191 (1963).

[4] F. H. Pollard, G. Nickless and S. Evered, *J. Chromatog.*, **15**, 223 (1964).

[5] L. M. Ferris and M. J. Bradley, *J. Am. Chem. Soc.*, **87**, 1710 (1965).

[6] M. B. Sears and L. M. Ferris, *J. Inorg. Nucl. Chem.*, **29**, 1255 (1967).

[7] Y. Hori and T. Mukaibo, This Bulletin, **40**, 1878 (1967).

[8] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," Macmillan, New York (1952).

by 0.05 N $K_2Cr_2O_7$ using sodium diphenyl amine sulfonate as an indicator. An Sn metal, precipitated during the hydrolysis of UC, was dissolved into a mixed solution of HCl and H_2SO_4; after conversion to Sn^{4+} by chlorine gas, Sn^{2+} was precipitated as SnS_2 by H_2S. It was weighed as SnO_2 after vigorous heating. The concentration of Cu^{2+} was determined by iodometry.[8] The Fe^{2+} concentration in the solutions was determined by titration with 0.05 N $K_2Cr_2O_7$, and the total Fe was treated similarly after having been passed through a Jones reductor. Ag^+ was weighed as AgCl as usual.[8] The uranium test solution was reduced by a Jones reductor after appropriate separations, and was titrated by 0.05 N $K_2Cr_2O_7$ after air-bubbling for 10 min.[9]

Chemical Analysis (2). The carbon which was initially included in the UC powder was found in the gaseous products, in the reactant solution, and in the solid products after the reaction. The total pressure of the gaseous products was measured by a conventional mercury manometer, and the volume at STP was obtained by the correction of the water vapor pressures at room temperatures. The analysis of the gaseous products was made for N_2, H_2, CO, CO_2, CH_4, C_2H_6, C_3H_8, C_3H_6, i-C_4H_{10}, 1-C_4H_8, and unidentified C_4 and C_5 products by means of a gas chromatography equipped with a thermal conductivity detector. They were separated by means of a 4 m-long column containing 38% dimethyl formamide - activated alumina with H_2 carrier gas, a 2.5 m-long column containing 2.5% squarene-silica gel, with H_2 carrier gas, and a 1 m-long column containing a 13X molecular sieve, with H_2 and N_2 carrier gas. All these four operations were carried out at room temperature, and all gave accurate and reproducible results concerning the composition of the gaseous products. The carbon - containing compounds in the solutions were analyzed for carbon by persulfate oxidation.[10] The solid products were treated in warm hydrochloric acid in order to dissolve the deposited metals, and the insoluble residues were burned to CO_2, which was then weighed in a usual way.

Results

Table 1 presents the products of reactions between UC and various aqueous systems.

Aqueous Systems Which Contain Fe^{2+}, Co^{2+}, Ni^{2+}. Apparently from Table 1, the products and the compositions obtained for the systems containing Fe^{2+}, Co^{2+}, and Ni^{2+} (columns 4 to 6) are virtually equal to those without any oxidant (column 2). No metal deposition was observed for any of these systems. For comparison a reaction between UC powder mixed with *ca.* 20 mg of Ni powder and Ni^{2+} solution was also carried out. The result (column 7) differs a little from that obtained for the system without Ni powder (column 6). The difference between the solutions with and without nickel metal (columns 6 and 7) may be attributed mainly to the nucleation overpotential of nickel. It indicates that the hydrolysis of UC is influenced by the oxidant at the oxidation potential of −0.26 V for $Ni^{2+}+2e \rightarrow Ni$ (concentration 0.10 M and at 80°C). The uranium ion was found to exist as U^{4+} in all the solutions.

Sn^{2+} Systems. The reaction proceeded as readily as in the non-oxidant solution. The gaseous products decreased with the Sn^{2+} concentration. The amount of hydrogen and methane considerably decreased. Ethane and the other higher hydrocarbons, the dissolved carbon-containing compounds, and the greenish-black insoluble residues increased. It is also significant that the quantity of the unsaturated hydrocarbons (C_8H_6 and 1-C_4H_8) became

TABLE 1. PRODUCT OF THE REACTION BETWEEN UC AND AQUEOUS SYSTEMS (80°C, 1.1 N H_2SO_4)

Oxidant	Non-oxidant	Au powder	Fe^{2+}	Co^{2+}	Ni^{2+}	Ni^{2+} and Ni	Sn^{2+}	Sn^{2+}	Cu^{2+}	Ag^+	Fe^{3+} and Fe^{2+}
Concn. (M)	—	—	0.30	0.30	0.30	0.10	0.025	0.100	0.191	0.118	1.94/1
Time (hr)	3.0	9.0	2.5	2.5	5.0	1.5	6.0	6.0	69	9.0	69
	ml/g	ml/g	ml/g	ml/g	ml/g	ml/g	ml/g	ml/g	ml/g	ml/g	ml/g
H_2	8.20	13.78	8.48	8.53	9.72	8.55	2.67	1.34	1.16	0.00	0.95
CH_4	85.2	76.7	84.1	83.0	82.4	76.0	64.9	42.3	9.00	0.17	2.17
C_2H_6	0.23	0.39	0.54	0.57	0.91	0.61	1.64	1.50	0.61	0.21	0.00
C_3H_8	0.07	0.21	0.09	0.14	0.20	0.12	0.42	0.42	0.00	0.00	0.00
C_3H_6	0.03	0.10	0.05	0.08	0.14	0.06	0.56	0.77	0.00	0.00	0.00
i-C_4H_{10}	0.00	0.00	0.00	0.00	0.00	0.00	0.18	0.25	0.00	0.00	0.00
n-C_4H_{10}	0.02	0.11	0.02	0.03	0.08	0.00	0.37	0.56	0.00	0.00	0.00
1-C_4H_8	0.02	0.07	0.05	0.03	0.07	0.00	0.07	0.17	0.00	0.00	0.00
C_5H_{12}	0.00	0.00	0.07	0.09	0.00	0.00	0.00	0.25	0.00	0.00	0.00
CO_2	0.00	0.30	0.00	0.00	0.00	0.00	0.00	0.22	17.4	5.15	14.9
	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g	mg/g
Solubles	0.00	0.29	0.00	0.00	0.00	1.54	1.52	3.78	68.7	2.74	7.05
Residues	0.20	3.72	0.21	0.57	0.25	0.72	1.05	8.75	35.9	48.8	30.2

---

9) I. M. Kolthoff *et al.*; "Volumetric Analysis," Vol. III (1957).

10) J. Katz, S. Abraham and N. Baker, *Anal. Chem.*, **26**, 1503 (1954).

more than that of the saturated hydrocarbons (C_3H_8 and C_4H_{10}, respectively). A gray sponge identified as metallic tin was produced.

Cu^{2+} Solution. The reaction was so slow that after 69 hr only 20% of the UC has reacted. Thus, the precision of the analysis of the products was lower than in the other systems. Though traces of hydrogen and methane were produced, the main products were dissolved, carbon-containing compounds and insoluble black residues. A small amount of CO_2 was also detected. A grain-like copper metal was produced, and some of the copper deposit was found to adhere to he carbide surface. The valence of uranium in the product solution was +6.

Ag^+ Solution. The reaction proceeded rather readily. Virtually no hydrogen and no methane were produced. The insoluble residues and carbon dioxide were obtained dominantly. Dendritic silver was deposited, and the uranium in the solution was in the +6 state.

Fe^{3+} and Fe^{2+} Solution. Although the reaction rate was not high, the reaction was completed after 69 hr. Virtually no hydrocarbons evolved. A large amount of an insoluble powder and/or sponge-like residue was found. The quantity of the dissolved carbon-containing compounds decreased. The evolution of CO_2 increased. A trace of CO was detected, but no quantitative analysis was made. After the reaction, Fe^{3+} was found to be reduced to Fe^{2+} quantitatively.[*1]

Au Powder System. The reaction between UC and 1.1 N H_2SO_4 in the presence of Au powder was studied in order to determine whether or not the reaction products differ when UC came into contact with non-reactive metal. About 250 mg of UC and 3 g of 325 mesh under Au powder were mixed in a mortar, and then charged into a reactor. There were more hydrogen and more insoluble residues, and less methane, compared with the non-oxidant solution (Table 1, columns 2 and 3). These results will be discussed in the following section.

Discussion

The Relation between the Oxidation Potentials and the Hydrolysis Reaction of UC. The hydrolysis of UC with 1 N H_2SO_4 is considered, on the basis of the experiment with Au powder to be discussed below, to proceed by the electrochemical mechanism:

TABLE 2. CARBON AND HYDROGEN BALANCE OF THE REACTION (80°C, 1.1 N H_2SO_4)

Oxidant	Non-oxidant		Au powder		Fe^{2+}		Co^{2+}		Ni^{2+}		Ni^{2+} and Ni	
Concn. (M)	—		—		0.30		0.30		0.30		0.10	
	mg atom/mmol		mg atom/mmol		mg atom/mmol		mg atom/mmol		mg atom/mmol		mg atom/mmol	
	C	H	C	H	C	H	C	H	C	H	C	H
H_2		0.183		0.307		0.189		0.190		0.217		0.191
CH_4	0.950	3.800	0.855	3.420	0.938	3.75	0.927	3.71	0.917	3.678	0.848	3.39
C_2-C_5	0.011	0.033	0.027	0.070	0.024	0.062	0.028	0.084	0.039	0.103	0.020	0.05
CO_2	0.000		0.004		0.000		0.000		0.000		0.000	
Solubles	0.000		0.006		0.000		0.000		0.000		0.032	
Residues	0.004		0.078		0.005		0.012		0.005		0.015	
Total	0.965*	4.016	0.970	3.797	0.967	4.00	0.967	3.98	0.961	4.00	0.915	3.63

Oxidant	Sn^{2+}		Sn^{2+}		Cu^{2+}		Ag^+		Fe^{3+}/Fe^{2+}	
Concn. (M)	0.025		0.100		0.191		0.118		1.94/1	
	mg atom/mmol		mg atom/mmol		mg atom/mmol		mg atom/mmol		mg atom/mmol	
	C	H	C	H	C	H	C	H	C	H
H_2		0.060		0.030		0.026		0.000		0.022
CH_4	0.724	2.89	0.471	1.883	0.100	0.400	0.002	0.008	0.024	0.096
C_2-C_5	0.096	0.251	0.133	0.317	0.014	0.042	0.005	0.014	0.000	0.000
CO_2	0.000		0.002		0.194		0.057		0.166	
Solubles	0.033		0.079		0.923		0.057		0.146	
Residues	0.023		0.182		0.745		1.018		0.625	
Total	0.876	3.201	0.867	2.230	1.976	0.468	1.075	0.022	0.961	0.118

* UC contained 0.968 mg atom/mmol of carbon, initially.

[*1] The valence of uranium was not determined. Titration with a $K_2Cr_2O_7$ solution is employed as a conventional volumetric analysis of uranium. As the direct oxidation of U^{4+} to UO_2^{2+} by $Cr_2O_7^{2-}$ proceeds slowly, it is recommended to add a Fe^{3+} solution first, then oxidize U^{4+} to UO_2^{2+}, and finally determine the resultant Fe^{2+} by titration. Therefore, uranium ions coexisting with Fe^{3+} can be regarded as UO_2^{2+}.

TABLE 3. THE MATERIAL BALANCE FOR OXIDATION AND REDUCTION

Oxidant	Non-oxidant		Au powder		Fe^{2+}		Co^{2+}	
Concn. (M)	—		—		0.30		0.30	
Oxidation* potential					−0.455		−0.292	
	mg eqv/mmol		mg eqv/mmol		mg eqv/mmol		mg eqv/mmol	
	Oxid.	Red.	Oxid.	Red.	Oxid.	Red.	Oxid.	Red.
$UC \rightarrow U^{n+}$	4.00		4.00		4.00		4.00	
$C \rightarrow CO_2$			0.01					
$H^+ \rightarrow H^0$								
H_2		0.183		0.307		0.189		0.190
Hydrocarbon		3.833		3.49		3.81		3.790
Oxidant consumption						0.00		0.00
Total	4.00	4.02	4.01	3.80	4.00	4.00	4.00	3.98

Oxidant	Ni^{2+}		Ni^{2+} and Ni		Sn^{2+}		Sn^{2+}	
Concn. (M)	0.30		0.10		0.025		0.100	
Oxidation potential	−0.266		−0.260		−0.208		−0.187	
	mg eqv/mmol		mg eqv/mmol		mg eqv/mmol		mg eqv/mmol	
	Oxid.	Red.	Oxid.	Red.	Oxid.	Red.	Oxid.	Red.
$UC \rightarrow U^{n+}$	4.00		4.00		4.00		4.00	
$C \rightarrow CO_2$							0.01	
$H^+ \rightarrow H^0$								
H_2		0.217		0.191		0.060		0.030
Hydrocarbon		3.781		3.44		3.14		2.200
Oxidant consumption		0.00		0.00		0.566		1.384
Total	4.00	4.00	4.00	3.63	4.00	3.77	4.01	3.61

Oxidant	Cu^{2+}		Ag^+		Fe^{3+}/Fe^{2+}	
Concn. (M)	0.191		0.118		1.94/1	
Oxidation	+0.312		+0.711		+0.846	
	mg eqv/mmol		mg eqv/mmol		mg eqv/mmol	
	Oxid.	Red.	Oxid.	Red.	Oxid.	Red.
$UC \rightarrow U^{n+}$	6.00		6.00		6.00	
$C \rightarrow CO_2$	0.78		0.23		0.67	
$H^+ \rightarrow H^0$						
H_2		0.026		0.00		0.022
Hydrocarbon		0.442		0.022		0.096
Oxidant consumption		2.91		6.28		6.51
Total	6.78	3.38	6.23	6.30	6.67	6.63

* Oxidation potentials were calculated from thermochemical data (at 80°C).[11,12]

$$UC \rightarrow U^{4+} + (C + 4e)_{carbide}$$

$$(C + 4e)_{carbide} + 4H^+ \rightarrow CH_4$$

As UC is a good electric conductor, a part of the electrons liberated by the dissolution of U are able to migrate to Au powder, which is in contact with UC. Then the electrons will reduce protons to hydrogen radicals on Au particles.

Partially, $H^+ + e \rightarrow H\cdot$ (on Au particles)

Since there is no carbon atom available for the formation of methane on Au particles, these radicals will react with each other and will result in hydrogen molecules:

$$H\cdot + H\cdot \rightarrow H_2 \text{ (on Au particles)}$$

---

[11] W. Latimer, " Oxidation Potentials," Prentice Hall, Englewood Cliffs, N. J. (1952).

[12] A. J. deBethune, T. S. Licht and N. Swendeman, *J. Electrochem. Soc.*, **106**, 616 (1959).

As a result, carbon atoms which failed to react with hydrogen atoms would polymerize and precipitate, because the overall ratio of H to C remains 4.0.

$$C \rightarrow \text{insoluble residues}$$

Evidently the composition of the reaction products changes with the oxidation potential, as may be seen from Tables 1, 2, and 3. In solutions without any oxidant, the overall reaction will proceed as below:

$$(UC)_{carbide} \rightarrow U^{4+} + (C + 4e)_{carbide}$$

$$(C + 4e)_{carbide} + 4H^+ \rightarrow CH_4 + \text{a small quantity of higher hydrocarbons, and hydrogen.}$$

The same discussion holds also in the solution containing Fe^{2+} and Co^{2+}. At a potential higher than about -0.26 V of the oxidation potential (*i.e.*, Ni^{2+}/Ni solution), the composition of the reaction products is found to change with the potential. The overall reaction in the Sn^{2+}/Sn solution can be written:

$$UC + xH^+ + (4-x)/2\ Sn^{2+} \rightarrow U^{4+} + (4-x)/2\ Sn + CH_x$$

where x is the average ratio of H to C in the products. From Table 2, x is found to be $2.23/0.867=2.57$ in the 0.1 M solution of Sn^{2+}. The value of x decreases with the concentration of Sn^{2+}.

As is shown in Table 2 concerning the material balance, the total carbon exceeds 0.968 in the Cu^{2+}/Cu system, and the material balance for oxidation and reduction (Table 3) is not matched. The reason for this will be explained below. After the reaction, the insoluble residue was treated with warm hydrochloric acid in order to dissolve the unchanged UC. In this procedure, hydrogen probably evolved on copper metal adherent to the unchanged UC, and carbon atoms in UC were polymerized and precipitated by the mechanism described in connection with the Au powder system. The insoluble residues containing carbon which resulted from this procedure entered the product of the reaction in the Cu^{2+}/Cu system.

In the system of Ag^+/Ag and Fe^{3+}/Fe^{2+}, the overall reaction can be expressed:

$$UC + 2H_2O + 6Ag^+ \rightarrow UO_2^{2+} + 4H^+ + 6Ag + C^{*2}$$

Carbon atoms result in the insoluble residue, the dissolved compounds, and carbon dioxide in the above reaction.

The Production of CO_2. When the reactant solution did not include any oxidant, a substantial number of the carbon atoms in UC were converted to CH_4. As the oxidation potential becomes higher, C_2H_6, C_3H_8, C_3H_6, the soluble compounds, the insoluble residues, and CO_2 increase. Figure 1 presents the average oxidation number of the carbon atom. In its calculation a hydrogen atom bonded to a carbon atom is estimated at -1, and an oxygen, at $+2$. Obviously CH_4 is produced when no oxidation occurs, and the increase of C_2H_6, C_3H_8, C_3H_6, the soluble compounds, and the insoluble residues corresponds to partial oxidation, while CO_2 evolves as a result of full oxidation.

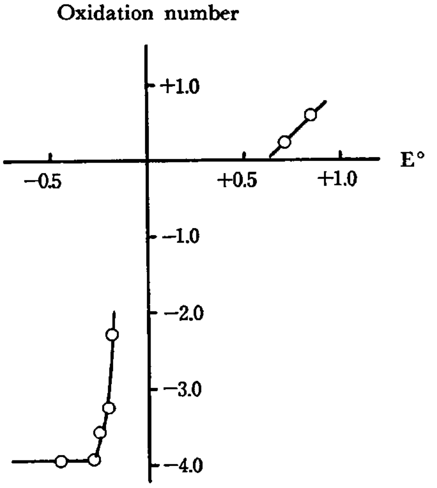

Fig. 1. Oxidation number of carbon *versus* oxidation potential.

The formation of CO_2 is interesting, since the oxidation potential for the reaction:

$$2H_2O = O_2 + 4H^+ + 4e$$

is about $+1.2$ V at 80°C.[11,12] It is impossible that CO_2 evolves through the oxygen molecules or atoms that come from the oxidation of water by such oxidants as ferric ions. CO_2 would be formed from the direct reduction of H_2O with the carbon atom which is recovered from the carbide lattice. Without presence of oxidants, the carbon atom will not react with H_2O to produce CO_2, because Coulombic repulsion will be caused between $\begin{matrix}{}^{\delta+}H \\ {}^{\delta+}H\end{matrix}\!\!>\!O^{\delta-}$: and the partially-ionic carbon atom, as will be discussed below. Accordingly, the carbon atom can reduce H_2O after losing some fraction of its electrons.

Comparison with Other Studies. Damiens[13] studied the hydrolysis of cerium carbide with HCl solution which contained $FeCl_3$; the found that the products differed considerably from those obtained in a solution not containing an oxidant. The reaction between UC and HNO_3 has been studied by many authors in connection with the reprocessing of nuclear fuel.[1-5] Except for the report by Pollard

---

*2 The oxidation-reduction potential for the reaction
$$U^{4+} + 2H_2O \rightarrow UO_2^{2+} + 4H^+ + 2e$$
is $+0.264$ V at 80°C.[11]

13) A. Damiens, *Ann. chim.*, **10**, 137 (1918).

et al.,[4] most of their studies are in general agreement, showing that carbide carbon is converted to CO_2, oxalic acid, mellitic acid, other aromatic compounds, and free carbon in some papers. Pollard *et al.*, however, reported that most of the carbide carbon was found in hydrocarbons, the composition of which was virtually equal to that obtained in dilute acid not containing nitric acid. This discrepancy has not been explained. The formation of CO_2 and other organic compounds is consistent with the present experimental results, since the oxidation-reduction potential for the reaction:

$$NO_3^- + 4H^+ + 3e \rightarrow NO + 2H_2O \qquad E^\circ_{25^\circ} = 0.96\ \mathrm{V}$$

$$2NO_3^- + 4H^+ + 2e \rightarrow N_2O_4 + 2H_2O \qquad E^\circ_{25^\circ} = 0.80\ \mathrm{V}$$

Baudin[14] *et al.* reported the hydrolysis of UC with 3 N HCl - 0.25 N $K_2Cr_2O_7$. According to them, hydrogen decreased markedly (11.2%→1.1% of total gases), compared with a non-oxidant solution, and C_3, C_4 ethylenics evolved (C_3H_6 1.65%, C_4H_8 1%). Their report, however, indicates that the composition of products of a 0.25 N $K_2Cr_2O_7$ solution is rather equal to that for the nonoxidant solution, since more than 90% of the carbide carbon is converted to methane. In our preliminary 1 N HCl-0.25 N $K_2Cr_2O_7$ experiment, the reaction rate was rather low; about half of the reacted carbide carbon was found in CO_2, and the other half in insoluble residues. A more critical comparison of these marked differences between the two cannot be made since their experimental procedures were not reported in detail by Baudin *et al.* Greenwood and Osborn[15] described the hydrolysis of LaC_2 and La_2C_3 with 4 N H_2SO_4 and 2 N HNO_3. According to them, hydrogen was markedly lessened in 2 N HNO_3, but most of the carbide carbon was converted into C_2H_2, C_2H_4, and free carbon in both 2 N HNO_3 and 4 N H_2SO_4. Pollard *et al.*[16] reported the hydrolysis of LaC_2, CeC_2, NdC_2, GdC_2, and $YC_{1.6}$ with 4 N HNO_3. The hydrolysis of carbides with 4 N HNO_3 gave results virtually equal to those for water and 4 N H_3SO_4, in spite of the considerable evolution of nitric oxides. This problem cannot be further discussed critically, however, since the experimental details were not described.

Sears and Ferris[6] studied the reactions of CaC_2 and BaC_2 with different concentrations of nitric acid. The reactions of CaC_2 with 0—16 M HNO_3 and BaC_2 with 0—8 N HNO_3 yielded C_2H_2 as the only carbon-containing product, but when reacted with 10—16 M HNO_3, BaC_2 gave rise to free carbon and carbon oxides by the partial oxidation of carbide carbon simultaneously with the production of acetylene.

The Potential at Which UC Reacts with Aqueous Acid. On the basis of the present experiment, E_H, the oxidation potential at which the hydrolysis of UC proceeds really may be said to be near −0.26 V since the Ni^{2+} ion has the basest oxidation potential among any oxidants that show the oxidant effect. As an extreme case, the reaction:

$$UC = U^{4+} + 4e + C(\beta\text{-graphite}) \qquad E^\circ = -1.2\ \mathrm{V} \qquad (1)$$

can be interestingly compared with the present one. In this case the reaction:

$$4H^+ + 4e + C(\beta\text{-graphite}) = CH_4 \qquad E^\circ = 0.13\ \mathrm{V} \qquad (2)$$

would correspond to the cathodic one. The oxidation potentials for these two reactions, (1) and (2), can readily be calculated to be −1.2 V and +0.13 V, respectively from the thermochemical data.[11,17] E_H will depend upon the overpotentials for the evolution of methane and the dissolution of uranium. In general, the anodic dissolution of metals occurs at a rather low polarization; the cathodic evolution of gases, such as H_2 and O_2, is accompanied by rather high overpotentials. Accordingly, if it is assumed that the Reactions (1) and (2) actually proceeds in the hydrolysis of UC, E_H may be observed to be roughly equal to E_R,*3 the oxidation potential for (1), that is −1.2 V. Thus, the difference between the experimental E_H values near −0.26 V and E_R, −1.2 V would indicate the variation in the reactivity of the carbon in the carbide lattice from that in the graphite lattice.

From the behavior of CaC_2 and BaC_2 reported by Sears and Ferris,[6] the E_H value is estimated to be about 1.0 V for BaC_2 and higher than 1.0 V for CaC_2. The oxidation potential, E_R, for the (1)-type reaction.

$$BaC_2 = Ba^{2+} + 2e + 2C(\beta\text{-graphite})$$

may be said to be −2.62 V and that for CaC_2 −2.56 V on the basis of the thermochemical data.[11,18,19] $E_H - E_R$ is then, rather a large value of 3.6 V. CaC_2 is reported to be an ionic crystal, $Ca^{2+}C_2^{2-}$, on the basis of the neutron diffraction.[20] If it is tentatively assumed that the $E_H - E_R$ value becomes larger as the ionic character of carbides increases, the $E_H - E_R$ value of 0.9 V for UC may be

---

[14] G. Baudin, J. Besson, P. Blum and J. Spitz, *Compt. Rend.*, **254**, 4179 (1962).

[15] N. N. Greenwood and A. J. Osborn, *J. Chem. Soc.*, **1961**, 1775.

[16] F. H. Pollard, G. Nickless and S. Evered, *J. Chromatog.*, **15**, 211 (1964).

[17] M. H. Rand and O. Kubaschewski, "The Thermochemical Properties of Uranium Compounds," Oliver & Void, London (1963).

*3 Oxidation potential for reference reaction.

[18] R. H. Flowers and E. G. Rauh, *J. Inorg. Nucl. Chem.*, **28**, 1355 (1966).

[19] R. L. Faircloth, R. H. Flowers and F. C. W. Pummery, *J. Inorg. Nucl. Chem.*, **29**, 311 (1967).

[20] M. Atoji, *J. Chem. Phys.*, **35**, 1950 (1961).

said to be due to the partially ionic character of UC, *i.e.*, $U^{n+}C^{n-}$. The partial ionic character is also confirmed by the fact that the work function for U is about 3.5 eV,[21,22] while that for graphite is about 4.4 eV.[23] This suggests that electrons will be transferred from U atoms to C atoms in the UC crystal lattice. The reaction between UC and an acid aqueous solution would proceed as below:

$$U^{n+}C^{n-} \rightarrow U^{4+} + C^{n-} + (4-n)e_{\text{in crystal}}$$

$$C^{n-} + (4-n)e_{\text{in crystal}} + 4H^+ \rightarrow CH_4$$

As has been discussed above, the $E_H - E_R$ value would reflect the bond nature of carbide and could be employed as a parameter for the reactivity of various carbides.

Conclusion

1) The reaction between UC and 1 N H_2SO_4 proceeds by an electrochemical mechanism.

2) The hydrolysis products of UC with aqueous acid solution depend fundamentally upon the oxidation potential of the oxidant in the solution.

3) The potential, E_H ,where the hydrolysis proceeds is about −0.26 V for UC, and UC would be partial ionic crystal.

4) E_H can be employed as a parameter which expresses the reactivity of carbides.

The authors are grateful to Dr. K. Fueki for his valuable discussions during the course of this work.

---

21) J. C. Riviere, *Proc. Phys. Soc.*, **80**, 116, (1962).

22) R. K. Fry and A. B. Cardwell, *Phys. Rev.*, **125**, 471 (1962).

23) G. Montet, M. Hoch and G. Hennig, USAEC ANL-6804 (1964).