HYDROLYSIS OF URANIUM MONOCARBIDE*

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The substoichiometric uranium monocarbide $UC_{0 \cdot 95}$ was hydrolyzed in acid medium at 80°C· The composition of the products of hydrolysis corresponds to published data, but it correlates better with the stoichiometric composition of the hydrolyzable carbide. The mechanisms of the hydrolysis reaction are discussed and a modified radical mechanism is suggested based on the concept of initiation of the radical process by $H^{\bullet}$ radicals formed owing to the nonstoichiometry of the substance. A relation is proposed for calculating the content of free hydrogen in the hydrolysis products of carbides of metal nature, for which a radical mechanism of their reaction with water can be assumed. Some effects occurring during the hydrolysis of uranium carbide, as described in literature, are explained in terms of the concept suggested, and the results obtained by the authors for carbides of manganese (Mn_7C_3) and for rare earth elements are discussed.

In view of the technological importance of uranium monocarbide, its hydrolysis has been studied extensively. Apart from the studies[1-3] performed before the introduction of gas chromatography, a number of investigations[4-11] have been aimed at a detailed analysis of the gaseous products of hydrolysis. The mechanism of the reaction, however, has received considerably less attention. Rather than pure methane, expected for the ideal $U^{IV}C$ stoichiometry, the reaction affords a mixture of methane, higher hydrocarbons, and hydrogen. The content of hydrogen is here even higher than as can be explained by the possible nonstoichiometry of the substance, UC_{1-x}. These facts are usually interpreted in terms of a radical mechanism of the reactions involved; intermediate formation of the $CH_3^{\bullet}$, $CH_2^{\bullet\bullet}$, and $CH^{\bullet\bullet\bullet}$ mono-, bi-, and triradicals and of $H^{\bullet}$ radicals is assumed [6,7,11,12], the final gas mixture resulting from their mutual recombination. Similarly, hydrocarbon radicals are supposed to react with molecular hydrogen[10]. In other publications, the radical species are not specified and the formation of the hydrocarbon mixture is referred to as "radical polymerization"[4,8] in general. Alternatively, higher uranium carbides (U_2C_3 and UC_2) and uranium metal are thought to be present in the monocarbide (prepare from the metal and carbon), compensating for the deficit to give the overall UC composition.

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In order to prevent the possible formation of the recently studied[7,8,11] U-UC alloys, for which the origin of hydrogen in the hydrolysis products cannot be specified unambiguously, the carbothermal reduction of the oxide was used for the preparation of our samples.

Despite the ample and fairly reliable data of the hydrolysis of uranium carbide, we considered it necessary to verify the consistency of our method of the carbide preparation and the gas chromatographic (GLC) method of analysis of its hydrolysis products with the published data. Based on the results obtained, in conjuction with selected literature data, the mechanism of the hydrolysis reaction is then discussed from the point of view of the existing concepts as well as of our previous work in the hydrolysis of carbides[13-17].

EXPERIMENTAL

Synthesis of Uranium Monocarbide

A powder mixture of U_3O_8 of spectral purity (Laboratory of Uranium Industry, Příbram) and carbon (granulated black of 4N purity, Pramet, Šumperk) in the molar ratio of 1 : 11 was homogenized, pelletized, and sintered in the vacuum furnace of an Exhalograph EA-1 instrument (Balzers, Liechtenstein) in zirconium diboride crucibles at 1 800 and 1 900°C for 5 h under the final vacuum of $1 \cdot 3 \cdot 10^{-3}$ Pa.

Analysis of the Product

The content of total and free carbon was determined by coulometric titration of a barium perchlorate solution in which the carbon dioxide formed on the ignition of sample at 1 300°C in an oxygen stream had been absorbed. The free carbon was first released by decomposing the carbide with 50% sulphuric acid of reagent grade purity and trapped on a previously prepared and annealed asbestos filter in a Gooch crucible.

Powder X-Ray Diffraction Measurements

The records were taken on a Mikrometa 2E diffractograph (Chirana, Prague) equipped with a HZG 3 goniometer (Freiberger Präzisionsmechanik, GDR) and an RTF Sonde VA-H-289 proportional counter (RTF, Dresden, GDR). Filtered CuK_α radiation was used; entrance slit $1 \cdot 4 \times 9$ mm, exit slit $0 \cdot 4 \times 9$ mm.

Gas Chromatographic Analysis

The carbide powder was hydrolyzed in vacuum in a glass ampoule with 50% sulphuric acid of reagent grade purity. At 80°C, the decomposition was complete in 5 h. The gas was analyzed on a Hewlett–Packard 5840A gas chromatograph fitted with a 18850 A terminal.

The program for analyzing the saturated hydrocarbons, hydrogen, air (if present), and carbon dioxide or monoxide was as follows: a 2 m column of 30% DC-200 on Chromosorb P (C_3, C_4, C_5 hydrocarbons), back flushing of the column (C_6 hydrocarbons and higher), a 2 m column of Porapak Q (CO_2, C_2 hydrocarbons), and a 5 A molecular sieve (H_2, O_2, N_2, CO, CH_4); temperature 70°C, carrier gas (helium) flow rate 20 ml/min, thermal conductivity detection (TCD). The unsaturated hydrocarbons were analyzed on the same chromatograph in an extra batch on a 2 m column of 0·19% picric acid on Carbopack C. Temperature 50°C, He flow rate 37 ml/min, TCD.

A qualitative evaluation of the records was carried out by employing standards of Linde. For the quantitative determination (in vol.%), the mass-specific correction factors were programmed for the TCD used *via* a model analysis of a standard mixture of saturated hydrocarbons, hydrogen, and carbon dioxide (Linde). The mass-specific correction factors for unsaturated hydrocarbons were taken from ref.[18] and converted to the molar correction factors for our TCD by relating them to the experimental factor of methane. The content of saturated hydrocarbons then was displayed by the chromatographic record, the contents of the additional components were calculated by means of the molar correction factors. Moreover, the content of hydrogen was verified by calculating it as the balance to 100%.

RESULTS AND DISCUSSION

Preparation and Analysis of Products

The carbothermal reduction of the oxide at 1 800 and 1 900°C gave phase-pure uranium monocarbide. The lattice parameter was $a = 0{\cdot}49583 \pm 1$ nm for the samples prepared at 1 800°C (8 measurements) and $a = 0{\cdot}49579 \pm 2$ nm for the samples prepared at 1 900°C (6 measurements). The stoichiometry as established from the dependence of the lattice parameter on the composition of UC according to Storms[19] corresponds approximately to $UC_{0.96}$, which agrees well with the chemical analysis giving $UC_{0.95}$. The presence of residual oxygen in a quantity comparable with the degree of nonstoichiometry, hence $UC_{1-x}O_x$, is not conceivable in view of the conditions of preparation[20,21] as well as the lattice parameter value; the latter is lower than as corresponds to the stoichiometric UC carbide, *viz.* $a = 0{\cdot}49605$ nm (ref.[19]), while the presence of oxygen would result in an additional transient increase in the cell dimensions, which is highest at[22] $x = 0{\cdot}027$.

Composition of the Products of Hydrolysis

The gas mixture from the hydrolysis of $UC_{0.95}$ contained 14 vol.% H_2, 83·2 vol.% CH_4, at least 2·6 vol.% alkanes whose concentrations decreased in the homologous series, and at least 0·22 vol.% alkenes. The atomic H/C ratio in the gas mixture, the GLC determination of which has been suggested[7] as a method of analysis of UC-U alloys (accuracy of 2%), indicates that the composition of the hydrolyzable fraction of the sample is completely identical with that revealed by chemical analysis, the value of $H/C = 4{\cdot}212$ corresponding to $UC_{0.95}$.

Mechanism of the Hydrolysis Reaction and the Relation Between the Carbide Structure and the Composition of the Hydrolysis Products

The radical mechanism[6,7,11,12] suggested for the hydrolysis of uranium carbide involves the formation of $CH^{\bullet\bullet\bullet}$, $CH_2^{\bullet\bullet}$, and $CH_3^{\bullet}$ radicals by hydrogenation of carbon by the H$^{\bullet}$ radical. The first stage is assumed[12,23] to be the decomposition of the adsorbed water molecules, specified[12] as

$$H_2O + e^- \rightarrow H^{\bullet} + OH^- . \qquad (A)$$

$$UC \rightarrow U^{4+} + C + 4e^- . \qquad (B)$$

As a matter of fact, process (*A*) is reduction of water. According to ref.[12], the reductant is the UC structure

$$U^{x+}C^{x-} + 2H_2O \rightarrow UO_2 + C + 4H^{\bullet} . \qquad (C)$$

Oxidation of C^{x-} with water to carbon is highly unlikely (otherwise it would have to occur, with all the consequences, also during the hydrolysis of CaC_2, Be_2C, *etc.*), and so the first step of the hydrolysis reaction should rather be regarded as a reaction of water with the uranium structure containing interstitial elemental carbon. In fact, such a structure does not occur even in the so-called "interstitial" carbides, in which intensive covalent metal–carbon interactions take place[24]. Nevertheless, let us assume that hydrocarbon radicals are really formed so that a H$^{\bullet}$ radical reacts first with carbon[6,7,11,12]. The initial H$^{\bullet}$ radical-to-carbon ratio, or better, the ratio of the "activated particles of the given composition", then for UC equals 4 : 1, irrespective of the way in which water is reduced. After the freely mobile hydrocarbon radicals have formed, a reaction should take place referred to[6,7,11,12] as "recombination", in which all the activated particles are ultimately combined to give hydrogen and hydrocarbons.

However, with the same ratio of 4 H$^{\bullet}$ to a C, it is not clear why the Al_4C_3 or Be_2C carbides do not yield a number of hydrocarbons instead of methane solely[25]. The cause of the fact that these carbides are hydrolyzed analogously as other salts of weak binary acids (such as $NaNH_2$, Mg_3N_2, Al_2S_3, *etc.*), while the hydrolysis of other carbides has to be interpreted in terms of radical reactions, is to be sought in the qualitative difference between the two groups of carbides. Clearly, then, the factor responsible for the different behaviour will not be the degree of the ionic nature because this difference is quantitative only. The difference sought should account for the change in the nature of the bond from the state 0 in one group to a state different from 0 in the other group. One of the manifestations of such a difference may rest in the formation of hydrogen. While the stoichiometry of carbides of pre-transition metals does not allow for the formation of free hydrogen during their hydrolysis, transition metal carbides yield hydrogen as a rule. The formation of hydrogen is determined by the difference between the formal oxidation numbers of the metal in the carbide and in the inorganic hydrolytic residue, and follows formally from stoichiometric relations which can be evaluated[7,26,27] also as the H/C ratio in the gas mixture. The cause of the formation of hydrogen during the hydrolysis of uranium "monocarbide" lies in the nonstoichiometry expressed in our case by the composition $UC_{0.95}$.

In all instances the hydrogen and the hydrocarbon corresponding to the kind of the carbon group within the carbide structure are supplemented by a number of additional hydrocarbons.

Now, let us discuss the possible mechanism of the gas mixture formation in detail. Assume, again, the consecutive formation of $CH^{\bullet\bullet\bullet}$, $CH_2^{\bullet\bullet}$, and $CH_3^{\bullet}$ radicals by hydrogenation of carbon by $H^{\bullet}$ radicals, and consider them equally mobile. The probability of their collision then approaches that of the combination of pairs from an infinite set of particles. The probability of stabilization of the pairs by removal of energy through collisions with any other molecule or with the solid phase is the same for the pair of the collided activated particles as for any other pair, regardless of whether the reaction occurs in a thin gas film at the surface or in an adsorbed layer. Further, consider only the probability of combination of a pair of $H^{\bullet}$—$H^{\bullet}$ activated particles. For Mn_7C_3, the products of hydrolysis contained[16,17] about 40 vol.% hydrogen, which allows the considerations of the pair combination to be based on the concept of a mixture of freely mobile $H^{\bullet}$ and both $CH_3^{\bullet}$ and $CH_2^{\bullet\bullet}$ particles in the corresponding stoichiometric ratio, and so, the published concept of radical recombination or polymerization can be adopted for this carbide. In contrast to this, uranium monocarbide yields as little as 10–14% hydrogen, which is deeply below the value of 30% corresponding to the combination of pairs from a mixture containing 1·21 $H^{\bullet}$ per $CH_3^{\bullet}$ (Table I), let alone a mixture containing also bi- and triradicals. There are two

TABLE I

Probability of combination of pairs from an infinitely high number of particles of $H^{\bullet}$ radicals and hydrocarbon radicals present in a ratio of $a : b$ as a result of hydrolysis of $UC_{0\cdot95}$

Pairs	Probability			
	formula	value, %, for the stoichiometric ratio		
		$CH^{\bullet\bullet\bullet} + 3\cdot21\ H^{\bullet}$	$CH_2^{\bullet\bullet} + 2\cdot21\ H^{\bullet}$	$CH_3^{\bullet} + 1\cdot21\ H^{\bullet}$
$H^{\bullet}$—$H^{\bullet}$	$a^2/(a+b)^2$	(H_2) 58·1	(H_2) 47·4	(H_2) 30·0
$H^{\bullet}$-hydrocarbon radicals	$2ab/(a+b)^2$	$(CH_2^{\bullet\bullet})$ 36·2	$(CH_3^{\bullet})$ 42·9	(CH_4) 49·5
Hydrocarbon radicals-hydrocarbon radicals	$b^2/(a+b)^2$	5·6	9·7	(C_2H_6) 20·4

explanations to this fact: either the mobility of the activated $H^\bullet$ particles in the hydrolysis of UC_{1-x} is somehow specifically limited as compared with Mn_7C_3, or the presumed stoichiometric ratio of the reacting particles does not hold true.

While the former concept has no rationale, the latter can be regarded as an evidence in favour of the hypothesis that the recombination of $CH_x^\bullet$ and $H^\bullet$ particles is not the primary reaction in the gas mixture formation. Two pathways can be proposed based on the asumption of the interaction between an activated particle (radical) and a molecule. The first of them, concerning the reaction of molecular hydrogen with a hydrocarbon radical as supposed for the hydrolysis of UC in ref.[10], can be expressed as

$$(H^\bullet + C) \rightarrow CH_3^\bullet + H_2 \rightarrow \text{hydrocarbons} + \text{hydrogen}\,. \qquad (D)$$

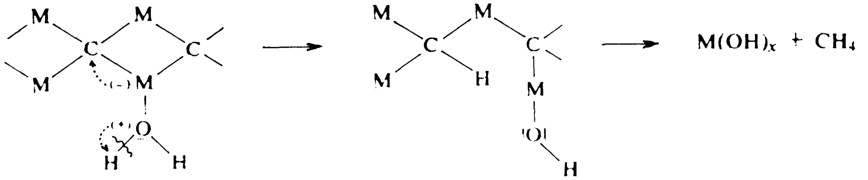
This concept, however, fails to account for the absence of hydrogen and higher hydrocarbons during the hydrolysis of carbides of non-transition metals. The second concept is based on the assumed primary reaction of methane with simultaneously created activated (nascent) hydrogen,

$$CH_4 + H^\bullet \rightarrow CH_3^\bullet + H_2 \rightarrow \text{hydrocarbons} + \text{hydrogen}\,. \qquad (E)$$

This reaction is consistent with the absence of hydrogen from the products of hydrolysis of carbides of non-transition metals, immediate formation of methane as the primary product of hydrolysis being assumed. Methane is formed on the attack of water on the bond between the metal and carbon. The actual course can be regarded as a combination of two limiting cases, *viz.* the ionic mechanism (*F*),

$$M_a^{(4/a)+}C^{4-} + 4\,H^+ + 4\,OH^- \rightarrow CH_4 + a\,M^{(4/a)} + 4\,OH^- \qquad (F$$

and the covalent mechanism (*G*), in which the metal atom in the carbide acts as a Lewis acid:



(*G*)

Carbides of transition metals exhibit, in addition, interactions of metal nature, manifesting themselves in the composition and in metal properties of the substances (uranium monocarbide is also, *e.g.*, a conductor of electricity[28].) Besides methane, hydrogen is formed on the "hydrolysis" of such structures, in analogy with the hydrogen formation in the reaction of any non-noble metal with water. Clearly, the hydrogen formation is again reduction of water, but it does not involve the entire structure of the carbide, including both the metal and carbon; instead, it only concerns the hypothetical fraction of the metal which is involved in the formation of metal interactions delocalized over the ion-covalent metal-carbon bonds. Stoichiometrically speaking,

$$\begin{aligned}
&(1/0{\cdot}95)\,\mathrm{UC}_{0.95} &&+\ (2/0{\cdot}95)\,\mathrm{H_2O} &&\rightarrow\ [\mathrm{CH_4} + 0{\cdot}21\,\mathrm{H}^\bullet] + (1/0{\cdot}95)\,\mathrm{UO_2}\\
&(1/3)\,\mathrm{Mn_7C_3} &&+\ (14/3)\,\mathrm{H_2O} &&\rightarrow\ [\mathrm{CH_4} + 0{\cdot}67\,\mathrm{H}^\bullet] + (7/3)\,\mathrm{Mn(OH)_2}\\
&\mathrm{LaC_2} &&+\ 2\,\mathrm{H_2O} &&\rightarrow\ [\mathrm{C_2H_2} + 1{\cdot}0\,\mathrm{H}^\bullet] + \mathrm{LaO(OH)}\ \text{(ref.[14])}
\end{aligned} \tag{H}$$

while

$$\begin{aligned}
&(1/3)\,\mathrm{Al_4C_3} &&+\ (4/3)\,\mathrm{H_2O} &&\rightarrow\ [\mathrm{CH_4}] + (4/3)\,\mathrm{AlO(OH)}\\
&\mathrm{Be_2C} &&+\ 2\,\mathrm{H_2O} &&\rightarrow\ [\mathrm{CH_4}] + \mathrm{Be(OH)_2}
\end{aligned}$$

The problem of the consecutive ractions of the hydrocarbon with activated hydrogen is rather intricate. The transfer reaction(*D*) of the alkyl with a hydrogen molecule is at least a hundred times slower than the transfer reaction (*E*) of the $\mathrm{H}^\bullet$ radical with a hydrocarbon molecule, and thus it can be ignored[29]. In the first stage of hydrolysis, the transfer reaction of activated hydrogen (*E*) can only be competed by the formation of H_2 by collisions of hydrogen atoms, (*I*), and by combination of the $\mathrm{H}^\bullet$ particles with the methyl radicals created (*J*):

$$\mathrm{H}^\bullet + \mathrm{H}^\bullet \rightarrow \mathrm{H_2} \tag{I}$$

$$\mathrm{H}^\bullet + \mathrm{CH}_3^\bullet \rightarrow \mathrm{CH_4}\,. \tag{J}$$

Successively, transfer reactions of activated hydrogen with higher alkanes (*K*) formed by dimerization (*L*) or, generally, by radical combination (*M*) can take place:

$$\mathrm{R\text{-}H} + \mathrm{H}^\bullet \rightarrow \mathrm{H_2} + \mathrm{R} \tag{K}$$

$$\mathrm{R} + \mathrm{R} \rightarrow \mathrm{R\text{-}R} \tag{L}$$

$$\mathrm{R} + \mathrm{CH}_3^\bullet \rightarrow \mathrm{R\text{-}CH_3}\,. \tag{M}$$

Radical disproportionations such as (*N*) or (*O*),

$$C_2H_5^\bullet + C_2H_5^\bullet \rightarrow C_2H_4 + C_2H_6 \qquad (N)$$

$$C_2H_5^\bullet + H^\bullet \rightarrow C_2H_4 + H_2 \qquad (O)$$

are reported[29,35] to be at least twenty times slower than the combination reactions, which is consistent with the observed presence of traces of unsaturated hydrocarbons in the gas resulting from the hydrolysis of uranium monocarbide.

With the exception of transfer reactions, reactions of radicals, or of energy-richer particles, require the presence of molecules for removing the excess energy from the products formed. A quantitative treatment of the consecutive reactions of activated particles during the hydrolysis thus poses a problem although a volume of kinetic data are available for radical reactions of $H^\bullet$ with lower alkanes and for the accompanying by-reactions[29-35]. These data concern largely gas phase systems at low pressures and elevated temperatures (cracking) in defined environments (walls), which are substantially different, as far as the activity is concerned, from the surface of the solid during the hydrolysis. Qualitatively, however, the results of the papers cited support the reaction pathways (*E*)–(*O*) considered.

A hydrocarbon mixture composition similar to that resulting from the carbide hydrolysis can be obtained experimentally, by radical reactions, only in a mercury-photosensibilized decomposition of hydrocarbon gas at room temperature. For propane[35], from which a mixture of C_3H_7 radicals and hydrogen atoms $H^\bullet$ primarily formed, a dimerization reaction of $H^\bullet$ leading to H_2 and a transfer reaction of $H^\bullet$ with propane giving additional $C_3H_7^\bullet$ radicals and molecular hydrogen took place. The $C_3H_7^\bullet$ radicals then either dimerized or disproportionated. Radical scissions to smaller particles, however, occurred at higher temperatures only.

The gas mixture formed by hydrolysis of uranium carbide can be considered as if part of the activated $H^\bullet$ particles recombined to molecular hydrogen, the rest of them being the source of hydrocarbon radicals by virtue of their reactions with methane or other hydrocarbons. Proceeding from a mole of $H^\bullet$, the former fraction be z mol, the latter fraction, $(1 - z)$ mol. The mole fraction of hydrogen in the mixture after the hydrolysis of MC_y carbide (containing C_1 groups in the structure and forming on the hydrolysis an inorganic residue in which the oxidation number of the metal is $+b$) then will be

$$x_{H_2} = (2 - z)(b - 4y)/(b - 2y)\,. \qquad (1)$$

In terms of the H/C ratio, used for expressing the stoichiometry of the hydrolysis reaction, the mole fraction will be

$$x_{H_2} = (2 - z)\,[(H/C) - 4]/[(H/C) - 2] \qquad (2)$$

if again the presence of C_1 carbon groups is considered.

In the calculations, all the hydrogen formed is assumed to result from the transfer reactions of $H^{\bullet}$ with hydrocarbon (*E*), (*K*), or from the combination reaction (*I*); this is also in agreement with the pathways of radical reactions occurring at elevated temperatures[29]. In addition, saturated hydrocarbons are assumed to form, their mixture having the property that the total number of mol remains unaltered by any exchange of the hydrocarbons formed:

$$m\,CH_4 = (m/n)\,C_nH_{2n+2} + m[1 - (1/n)]\,H_2\,. \qquad (P)$$

The z values for the hydrolysis of the substoichiometric uranium carbide UC_{1-x} prepared by us and by other authors were calculated by means of Eq. (*2*); the results are given in Table II. The z values calculated from the H/C ratio are found to be mutually consistent, the mean value is $z = 0{\cdot}46 \pm 0{\cdot}07$. (The z values calculated from the declared stoichiometric composition of the samples are in a poorer agreement, due to the incompleteness of the sample decomposition and to diverse errors of the chemical and GLC analyses.)

If the mean z value as calculated for UC_{1-x} is applied also to carbide of manganese, Mn_7C_3, Eq. (*2*) gives the content of hydrogen of $38{\cdot}5 \pm 1{\cdot}7\%$ H_2 (the experimental value[17] is $40{\cdot}6\%$ H_2); similarly, the carbide Mn_5C_2 should evolve $51{\cdot}3 \pm 2{\cdot}3\%$ H_2 (experimental value is not available) and Mn_3C should yield $77{\cdot}0 \pm 3{\cdot}5\%$ H_2 (experimentally[36], $75{\cdot}8\%$ H_2). Al_4C_3 and Be_2C, naturally, give 0% H_2.

Stoichiometric UC, however, should give also pure methane. This is not observed in reality owing to the fact that in the region of even slightly substoichiometric UC_{1-x} carbides, catenation of the C_1 groups in the carbide structure takes place[8,37]. The defect of the C_2 group formation in carbides[28] is manifested in the increased content of even hydrocarbons in the hydrolysis products at the expense of odd ones. This effect has been observed for uranium[4,8,11] and thorium[39] carbides. The presence of a C_2 group in place of two C_1 groups in the UC structure implies the formation of $(C_2H_2 + 6\,H^{\bullet})$ instead of two CH_4 molecules. In this manner, even more hydrogen atoms are produced per carbon atom than as was obtained from the substoichiometric carbide structure by reaction (*H*). In the UC structure with uniformly distributed catenation defects, the $H^{\bullet}$ atoms react (in addition to their mutual combination) both with ethyne from the C_2 groups and with methane from the C_1 groups. The hydrolysis products of such a carbide thus represent the combination of two hydrocarbon series with decreasing concentration order, *viz.* the even series and the natural series. This trend becomes more pronounced when the content of C_2 groups in the carbide is higher. This phenomenon can be illustrated also on alloys of uranium monocarbide and dicarbide or monocarbide and sesquicarbide[8,9,40], where the component

TABLE II

Composition of the gas mixture (vol.%) from the hydrolysis of substoichiometric uranium carbides, as obtained by various authors

Component	Content for the carbide							
	$UC_{0·98}$[a]	$UC_{0·97}$[b]	$UC_xO_yN_z$[c]	$UC_xO_yN_z$[d]	UC_{1-x}[e]	UC_{1-x}[f]	UC_{1-x}[g]	$UC_{0·95}$[h]
H_2	9	13	11·4	10·4	11·2	11·7	12·1	14·0
CH_4	88	84	86·0	86·7	85·7	85·3	84·9	83·2
C_2H_4	0·03	0·04	—	—	0·3	0·2	0·25	0·06
C_2H_6	1·51	1·76	1·69	1·80	2·1	2·1	2·0	1·74
C_3H_6	—	—	—	—	—	—	—	0·04
C_3H_8	0·26	0·43	0·54	0·69	0·35	0·50	0·60	0·71
C_4H_8	0·14	0·10	—	—	—	—	—	0·12
C_4H_{10}	0·18	0·18	0·28	0·27	0·25	0·20	0·15	0·145
C_5H_{10}	—	0·01	—	—	—	—	—	—
C_5H_{12}	0·04	0·06	0·07	0·06	—	—	—	0·019
C_6H_{12}	0·02	0·02	—	—	—	—	—	—
C_6H_{14}	0·01	0·02	0·024	0·055	—	—	—	—
unidentified	0·13	0·13						
H/C^i	4·08	4·124	4·184	4·184				4·21
H/C^j	4·114	4·192	4·14	4·12	4·152	4·165	4·173	4·212
z^k	0·331	0·516	0·257[m]	0·163[m]	0·414	0·465	0·480	0·539
x_{H_2}, % ($z = 0$)	10·8	17·5	13·1	11·3	14·1	15·2	15·9	19·2
($z = 1$)	5·4	8·8	6·5	5·7	7·1	7·6	8·0	9·6

[a] Ref.[9], temperature during hydrolysis 80°C; [b] ref.[8], 80°C; [c] ref.[4], 60°C; [d] ref.[4], 80°C; [e] ref.[7], 80°C; [f] ref.[7], 90°C; [g] ref.[7], 100°C; [h] this work, 80°C; [i] from the stoichiometry given; [j] from the composition of the gas mixture; [k] from the composition of the gas mixture, relation (*2*); [m] not included in the calculation of the mean *z* value because of lacking analysis for unsaturated hydrocarbons.

containing C_2 carbon groups and increasing the concentration of activated hydrogen, $H^{\bullet}$, is present as a separate phase rather than defects. A mere mechanical mixture of the two carbides affords, as expected, hydrolysis products which are the combination of the hydrolysis products of the pure components[40], *e.g.*, UC_{1-x} and $UC_{1.86}$. In alloys, deviations from the linear combination of the composition of the products of hydrolysis of the pure components occur, less methane and more hydrogen being evolved. The deviations are the more marked the finer the starting alloy[40]. We suggest that the explanation is the same as in the case of the catenation defects in UC, which in fact is a limiting case of single-phase alloys of the monocarbide and dicarbide: the reactions of the activated particles are confined to the reaction surface, and so the activated hydrogen $H^{\bullet}$ from the $UC_{1.86}$ or U_2C_3 phase can react with methane from UC_{1-x}, reducing thus its concentration and enhancing the concentration of hydrogen, only if the two phases are in an intimate contact.

Thus, in terms of the suggested modification of the radical concept of the hydrolysis, the cause of the formation of the hydrocarbon mixture during the hydrolysis of the uranium monocarbide sample is sought in the nonstoichiometry of the latter, as expressed by the formula $UC_{0.95}$. Similarly as with other hydrolyzable carbides of transition metals, the formation of the series of hydrocarbons during the hydrolysis is related with the metal nature of the carbide, given by a structure or even stoichiometry such as requires the simultaneous formation of hydrogen in the reaction with water.

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