RADIOCHEMICAL STUDY OF HYDROLYSABLE CARBIDES

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A simple radiochemical method has been developed for the phase analysis of hydrolysable carbides. The method is based on the radio gas chromatography of gaseous products of carbide hydrolysis with simultaneous mass and activity detection. The tritium-labelled hydrocarbons evolved (tritium oxide used for hydrolysis) are characteristic of the individual carbide phases. An application for Group III b carbide phase analysis is demonstrated.

The decomposition of Group III b dicarbides by water or water solutions leads to a mixture of hydrogen and hydrocarbons up to \( C_{12} \), while actinide carbides even give cyclic hydrocarbons up to \( C_{14} \). From the hydrolysis stoichiometry

\[
\text{LnC}_2 + 3\text{H}_2\text{O} \rightarrow \text{Ln(OH)}_3 + \sum_{n=2}^{12} (\text{C}_n\text{H}_{3n})
\]

the atomic H/C ratio of the evolved gaseous mixture should be 1.5 : 1. The results of our previous analyses, accomplished by gas chromatography with flame ionization detection combined with mass spectrometry, similarly as the results of other authors, e.g.,3,4 give varying H/C ratio of 1.46 up to 1.65.

It therefore seemed useful to investigate these differences of the H/C ratios (or their uncertainty). There are three possible reasons:

1. change of carbide phase composition of the sample, or presence of other carbides;
2. formation of hydrocarbons higher than \( C_{12} \);
3. errors in the quantitative analysis of the gaseous products.

The exact determination of the content of individual hydrocarbons is naturally important for determination of the hydrolysis mechanism. Apart from the analysis there is another factor seriously influencing the analytical results: the gaseous products change the composition by cold hydrogenation and polymerization. Quantitative evaluation is always influenced by the error of the detector. For the flame ionization detector use of Onkieshong's factor5 is recommended. A typical
analysis of a gaseous mixture after decomposition of LnC$_2$ with water is given in our previous paper.$^1$

To enhance the sensitivity of the determination of higher hydrocarbons rare earth carbides labelled with $^{14}$C were prepared and decomposition was carried out with water or tritium oxide. Samples of radioactive labelled hydrocarbons with hydrogen were analysed by radio gas-liquid chromatography (simultaneous detection of mass and activity). For the separation of hydrocarbons up to C$_6$ a 4 mm diameter column was used with 2 m 15% dimethylsulfolane and 4 m 10% v/v polypropylene glycol as stationary phase on Chromosorb W 60/80 at 35-50 °C, while for hydrocarbons up to C$_8$ a Porapak Q column was used at 190 °C. The analyses were carried out by means of a Packard 7409 gas chromatograph equipped with a flame ionization detector and gas flow proportional counter (splitting 1:1, without combustion).

As regards point (1), it was found that pure dicarbides decomposed by water give only even hydrocarbons. On the other hand, the sesquicarbides of Pu$_2$C$_3$ structure type give methane and allene. Trigonal hypocarbides of the type Ho$_2$C or Y$_2$C give hydrogen and methane with an H/C ratio of up to 6.

Point (2): In accordance with the scheme (Fig. 1) two experiments were carried out, to provide the following balance (Table 1). Loss in activity can be explained by error of the activity measurement of LaC$_2$ powder due to high self-absorption.

GLC and mass spectrometric analyses showed the same quantitative composition of the evolved gaseous mixture and the gas which was absorbed in the solution and in