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THE HYDROLYSIS OF THE COMPOUND OF POTASSIUM
WITH IRRADIATED GRAPHITE

by

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ABSTRACT

Potassium, the reaction product of graphite with potassium, and the reaction product of irradiated graphite with potassium were subjected to hydrolysis. The gases evolved from the respective samples were analysed mass spectroscopically. Hydrocarbons (methane and a trace of ethane) were found in the gas evolved from the irradiated graphite compound only, and the quantity was about that which would have been expected from the number of non-aggregated displaced atoms. The result was obtained for a single set of experiments and must be considered suggestive rather than conclusive.

INTRODUCTION

The heat of reaction of potassium and graphite was determined by Quarterman and Primak.¹ They then determined the heat of reaction of irradiated graphite and potassium² and found that the excess heat of reaction (due to irradiation) did not correspond to the excess heat of combustion. It was obvious that the explanation was that the compound formed from the irradiated graphite was different from the compound formed from unirradiated graphite. It was decided to investigate the compounds chemically. The first experiments undertaken were studies of the products of hydrolysis.

EXPERIMENTAL

Apparatus: The apparatus in which the hydrolytic products were prepared consisted of the four interconnected vacuum systems shown in Figure 1. Figure 1A shows the apparatus used to prepare the gas-free water sample. Triply distilled water was introduced into the flask and the tubulation sealed off. The water was boiled under vacuum until it froze in the flask. Then the stopcock S_1 was closed while the rest of the systems

¹L. A. Quarterman and W. Primak, J. Am. Chem. Soc. **74**, 806 (1952).

²L. A. Quarterman and W. Primak, ANL-4749 (January, 1952).

Figure 1

A schematic diagram of apparatus used to prepare the hydrolytic products of graphite-potassium.

were flamed and while the potassium compound was prepared. After this the stopcock was opened and a sample of solid gas-free water was collected in the spherical liquid air trap in high vacuum. When enough had collected, the stopcock S_1 was closed again and the water could be introduced into the reaction chamber by permitting it to melt and flow through the tube ③. Figure 1B shows the reaction chamber, nearly identical to the calorimeter described by Quarterman and Primak.² Figure 1C shows the system used to prepare pure potassium as described by Quarterman and Primak.³ Figure 1D shows the drying and gas collecting system. The first part was a large bulb whose walls were coated with sublimed P_2O_5 formed by heating the P_2O_5 in the tube below it. This bulb was separated from the second part, the gas sample bulb, by means of a stopcock. The manometers were used to determine the pressures in the reaction chamber, the drying bulb, and the sample bulb.

Procedure: The potassium-graphite compound was prepared in the same manner used in the calorimetric work except that no thermal measurements were made and some helium was present in the calorimeter chamber to facilitate heat transfer. Only several samples were dropped into the potassium at one time, the calorimeter cup never being permitted to rise above $90^\circ C$ during preparation of the potassium-graphite. After the potassium-graphite had been prepared, the helium was withdrawn. The gas-free water sample was then condensed on the spherical liquid air trap. The evacuated calorimeter cup was isolated from the pumps, and the frozen water was permitted to melt and drip into the calorimeter cup until the latter was immersed. After the system had cooled to room temperature, the pressure was read. The cock leading to the evacuated drying bulb was opened and the pressure read again. The cock was now closed. After the gas had remained in the drying bulb for 2 hours, the manometer in this part of the system was read. The cock leading to the evacuated sample bulb was opened and the manometer read again. The sample bulb was then sealed off and submitted for mass spectrographic analysis.

Samples: Four experiments were performed in which the materials subjected to hydrolysis were, respectively, (1) potassium to which no graphite had been added; (2) potassium to which graphite (unirradiated) had been added; (3) potassium to which graphite irradiated for 240 Units* had been added; and (4) potassium to which graphite irradiated for 202 Units* had been added.

*These Units are defined by Primak⁴ and by Primak, Fuchs, and Day.⁵

³L. A. Quarterman and W. Primak, J. Am. Chem. Soc., 72, 3035 (1950).

⁴W. Primak, Phys. Rev. 95, 837 (1954).

⁵W. Primak, L. H. Fuchs, and P. Day, J. Am. Ceramics Soc. 38, 135 (1955).

Results: The results of the experiments are given in Tables I and II. The hydrolysis data are given in Table I. The weight of potassium was computed from the volume of evolved hydrogen. The latter was computed from the volume of the P_2O_5 chamber (determined to be 1.2 liters) and the pressures which are given. The mass spectroscopic data are given in Table II.

Table I

HYDROLYSIS DATA

Run	Subject	Room Temp. (°C)	Pressure		Wt. Potassium (g)	Wt. Graphite (g)
			After Hydrolysis (mm Hg)	After Introduction into P_2O_5 Chamber (mm Hg)		
1	Potassium	30.6	418	354	7.0	-
2	K, graphite unirradiated	26.8	330	271	7.6	3.79
3	K, graphite 240 Units	28.8	397	333	10.6	2.66
4	K, graphite 202 Units	28.1	339	283	8.6	3.03

Table II

MASS SPECTROGRAPHIC ANALYSES OF
THE HYDROLYTIC PRODUCTS

Run	Analysis
1	~ 100% H_2
2	~ 100% H_2
3	99.53% H_2 0.38% CH_4 0.09% C_2H_3
4	93.26% H_2 6.65% N_2 0.08% A

DISCUSSION

It is seen that the potassium and the mixture of potassium and the compound of potassium and unirradiated graphite gave nothing but hydrogen on hydrolysis. The hydrolytic products formed in Run 4 must have become contaminated with air from which the oxygen was removed (as indicated by the proper ratio of argon) and this result must therefore be discarded. This leaves but a single result for the composition of the hydrolytic products of irradiated graphite-potassium.

The percentage of carbon atoms in the graphite yielding hydrocarbons (assuming the graphite to have been their source) can be computed as follows: there was formed 0.135 mole H_2 ; hence, from the percentages in Table II $5.1(10^{-4})$ gram atom C as CH_4 and $2.4(10^{-4})$ gram atom C as C_2H_6 ; these were formed from 0.22 gram atom C as graphite, and hence $2.3(10^{-3})$ was the fraction of atoms giving CH_4 and $1.1(10^{-3})$ the fraction of atoms giving C_2H_6 . This result may be compared with the result reported by Hennig and Smaller⁶ who found that upon irradiation under conditions similar to the ones used for the samples reported here, the paramagnetic resonance saturated at $1.2(10^{-3})$ paramagnetic center per carbon atoms in graphite, a result not far different from the fraction of atoms yielding methane in the present experiments.

While it is tempting to associate the CH_4 with single carbon atom interstitials originally present in the irradiated graphite and the C_2H_6 with double carbon atom interstitials, it must be pointed out that (a) there is but a single unconfirmed result and (b) even if the graphite was the source of the hydrocarbon gases, the possibility that they formed from a surface deposit (like carbon oxygen polymers) has not be excluded.

The complexity of the reaction product of irradiated graphite and potassium is indicated by the results. If there is formed a K_4C or K_6C_2 interstitially, and if the difference in the heat of reaction of these compounds and the recombination of holes and interstitial carbon atoms or the combination of carbon interstitials is several electron volts per atom, the contribution (or subduction) to the heat of reaction would amount to some 20 cal/g, a considerable fraction of the excess heat of reaction reported by Quarterman and Primak.²

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⁶G. R. Hennig and B. Smaller, ANL-5385 (January, 1955).