Conversion of Carbon and Alkali Metal Carbonates to Hydrocarbons Containing Aromatic Hydrocarbons by the Reaction with Copper Oxides and Aqueous Alkaline Solution

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Reaction of activated carbon and copper(II) oxide in the presence of aqueous potassium carbonate solution at 380 or 400 °C gave mainly carbon dioxide, accompanied by the formation of hydrocarbons containing aromatic hydrocarbons such as benzene and toluene. The similar reaction of copper(I) oxide gave mainly methane, accompanied by formation of smaller amounts of carbon dioxide, benzene, and toluene than the reaction of copper(II) oxide. Although the reaction of copper(II) oxide with aqueous potassium carbonate solution did not give hydrocarbons in the absence of activated carbon, the reaction of copper(I) oxide with aqueous potassium carbonate solution gave hydrocarbons even in the absence of activated carbon.

Attention has been focused on prebiotic syntheses of organic compounds from inorganic compounds.[1—4] In these researches, amino acids or organic compounds having a nitrogen atom have been synthesized using electric discharge, laser beam, or high energy protons from a mixture of inorganic compounds such as carbon dioxide, nitrogen, and water. It has been reported that an inorganic compound such as carbon or metal carbonate was converted to methane by thermochemical reaction. Activated carbon was converted to methane by the reaction with hydrogen using various catalysts at temperatures higher than 500 °C.[5,6] Metal carbonates were converted to hydrocarbons by heating with hydrogen at a temperature as high as 800 °C.[7] In the present report, two new findings will be reported. One finding is that activated carbon can be converted to hydrocarbons containing aromatic hydrocarbons such as benzene and toluene by heating with a mixture of aqueous potassium carbonate solution and copper(II) oxide or copper(I) oxide at lower temperature than 500 °C. The second finding is that alkali metal carbonates can be converted to a mixture of hydrocarbons containing methane as a main component and aromatic hydrocarbons as minor components by heating with a mixture of water and copper(I) oxide even in the absence of carbon at temperatures lower than 500 °C.

Experimental

General Procedure. Activated carbon was obtained from Nacalai Tesque Co. The elemental analyses of the activated carbon was as follows: C, 92.46%; H, 0.74%; ash, 1.86%; O (by difference), 4.94%. Gaseous products were analyzed by means of gas chromatography and mass spectroscopy. Instruments used were explained in the preceding paper.[8] Gas formed by the reaction was transferred to stainless steel gas storage, the temperature of which was kept at 110 °C so that toluene or benzene might not condense, and the gas was analyzed by means of gas chromatography and mass spectroscopy. Qualitative and quantitative analyses of aliphatic hydrocarbons were performed using GLC columns of Unipak S and Porapak Q. Formation of benzene and toluene was confirmed by ^{1}H NMR measurement, retention time of GLC, and mass spectroscopy: The gas formed by the reaction was introduced into $CDCl_3$, the ^{1}H NMR spectra of which showed the existence of benzene and toluene; mass spectra of the compounds assigned as benzene and toluene by the retention time of GLC had peaks of 78 and 92, respectively. Carbon dioxide was analyzed using GLC column of Unibeads C. Neither hydrogen nor carbon monoxide was formed.

Reaction of Activated Carbon with Aqueous Potassium Carbonate Solution and Copper Oxide. A 100 ml stainless steel (sus 316) autoclave equipped with a mechanical stirrer was charged with 10 g of copper(II) oxide or copper(I) oxide, 0.058 mol of potassium carbonate, and 40 ml of water. Inside of the autoclave was replaced by nitrogen gas (7 MPa) as described in the preceding paper.[8] The autoclave was heated at 380 or 400 °C for 6 h with constant stirring.[9]

Trying of Isolation and Characterization of the Water Soluble Solid Products. After analyses of the gaseous products of the reaction, a resulting mixture of water, carbon, and copper oxide was transferred to a 300 ml beaker. A water soluble portion was filtered to give a pale greenish yellow solution. The aqueous solution was passed through ion exchange column DOWEX 50W-X4 to decompose carbonate and to remove metal ions. The solution flowing out was evaporated under reduced pressure to give 15-20 mg of pale yellow solid. ^{1}H NMR of this solid (in CD_3OD) showed only one signal at 7.9 ppm. When the aqueous solution before treatment by ion exchange resin was evaporated, a mixture of white solid containing metal salts was obtained. ^{1}H NMR of this solid (in CD_3OD) also showed a signal at 7.9 ppm. However, ^{13}C NMR measurement of the pale yellow solid obtained by treatment with the ion exchange resin did not show any signal, in spite of the long period (12 h) of measurement, although ^{13}C NMR measurement of the white solid obtained by evaporation of the aqueous solution before treatment by ion exchange resin gave one or two signals at 160—170 ppm which were considered to be signals of metal carbonates. Since the amount of the water soluble solid products was relatively small and these products did not give enough signal in ^{13}C NMR to assign structure, only the characterization of gaseous products was included in the present report.

Results and Discussion

When a mixture of activated carbon, copper(II) oxide, and aqueous potassium carbonate solution was heated at 380 °C for 6 h under nitrogen atmosphere, carbon dioxide, methane, benzene, and toluene were formed, accompanied by small amounts of C_2—C_6 aliphatic hydrocarbons, as shown in Run 1 of Table 1. When the reactions were carried out with addition of an appropriate amount of oxygen to nitrogen atmosphere of the reaction mixture, yields of hydrocarbons changed as shown in Runs 2—4 in Table 1. The yield of each hydrocarbon in Runs 1—4 of Table 1 was converted to that of methane by multiplying the yield by the number of carbons composing the hydrocarbon. The converted yields of all hydrocarbons formed were summed to give the total yield for each Run. The total yields of hydrocarbons varied with the change of oxygen content in the gas over the reaction mixture, as shown in Fig. 1. Although addition of small amounts of oxygen brings about slight increase of the yields, addition of large amounts of oxygen strongly suppresses the formation of hydrocarbons. The main reaction in the reactions shown in Table 1 is the formation of carbon dioxide. One reference reported that reduction of copper(II) oxide with carbon started at 250 °C.[10] In the course of the reduction of copper(II) oxide, an intermediate copper oxide (CuO_x) presumably forms. This intermediate CuO_x contributes to formation of the hydrocarbons.

$$2CuO + \frac{1}{2}C \rightarrow CuO_x \rightarrow\rightarrow Cu_2O + \frac{1}{2}CO_2 \qquad (1)$$

$$CuO_x + C + H_2O \xrightarrow{\text{alkali}} \text{Benzene} + \text{Methane etc.} + CuO \qquad (2)$$

Large amounts of oxygen added scavenge the intermediate CuO_x to bring about a decrease of the yields of hydrocarbons.

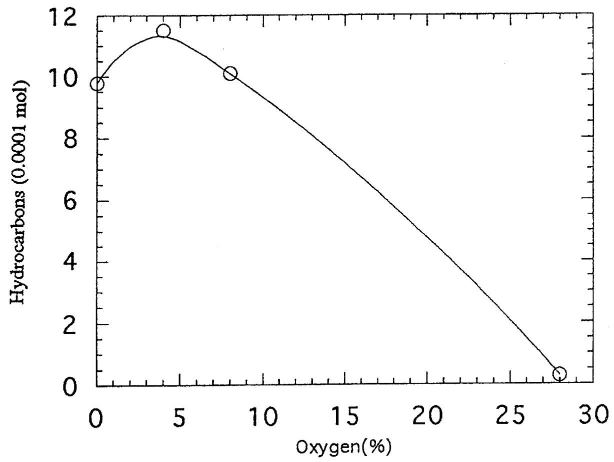

Fig. 1. Effect of oxygen content in the reaction atmosphere on the yields of hydrocarbons obtained by the reaction of activated carbon with copper(II) oxide and aqueous potassium carbonate solution at 380 °C for 6 h.

When varying amounts of carbon were used for the reaction, yields of the hydrocarbons changed, as shown in Runs 5—10 in Table 1. The change in the total yield of hydrocarbons with the amount of carbon used is visualized in Fig. 2. In Run 7, which gave maximum yields of hydrocarbons, 1.5 mol% of activated carbon were converted to hydrocarbons. As is shown in Run 10 of Table 1 and Fig. 2, a reaction carried out without addition of carbon does not give hydrocarbons. This result indicates that the hydrocarbons formed in the reactions carried out with addition of activated carbon are derived from the activated carbon. Addition of too much carbon brings about decrease of the yields of hydrocarbons, as shown in Fig. 2. Presumably the intermediate CuO_x is scavenged by large amounts of carbon to give Cu_2O or Cu. In the region where maximum yields of hydrocarbons are obtained, maximum yields of benzene and hexane are also obtained (see Run 7 in Table 1). In that region, main component of hydrocarbons formed is benzene considering that benzene consists of six carbon atoms. Therefore, formation of hydrocarbons having six carbon atoms is considered to be facilitated in that region. Hexane presumably is formed as a by-product during formation of benzene. Therefore, the

Table 1. Yields of Hydrocarbons Formed by the Reactions of the Activated Carbon with Copper(II) Oxide and Aqueous Potassium Carbonate Solution

Run	Temp	Carbon	$O_2/(N_2+O_2)$	Products (μmol)					
	°C	g		CH_4	C_2—C_5[a)]	n-C_6H_{14}	Benzene	Toluene	CO_2
1	380	1.0	0	200	0.34	0.17	115	12.4	4450
2	380	1.0	0.04	265	0.26	1.26	120	13.2	6140
3	380	1.0	0.08	286	0.29	0.1	106	11.8	6360
4	380	1.0	0.28	21	t[b)]	t	1.2	0.14	7390
5	400	2.0	0.04	160	0.17	t	19	1.2	10100
6	400	1.2	0.04	275	0.37	0.22	127	15	11000
7	400	1.0	0.04	276	0.27	0.54	132	18	7330
8	400	0.75	0.04	249	0.21	0.61	78	10	2060
9	400	0.2	0.04	4.2	t	0.12	2.1	0.22	94
10	400	0.0	0	t	t	t	t	t	0

a) The sum of yields of C_2, C_3, C_4, and C_5 aliphatic hydrocarbons. b) "t" means trace amount.

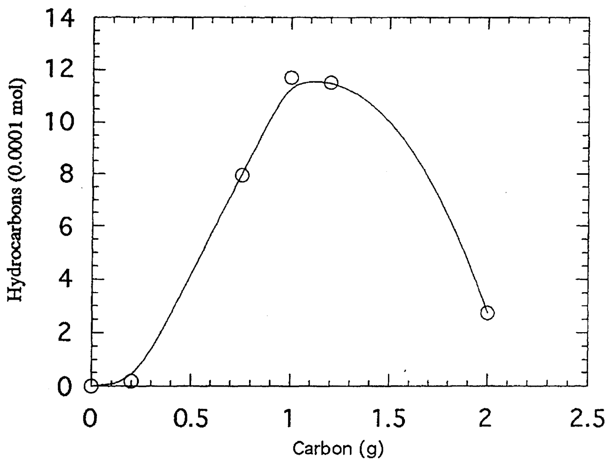

Fig. 2. Effect of amount of activated carbon used on the yields of hydrocarbons obtained by the reaction of activated carbon with copper(II) oxide and aqueous potassium carbonate solution at 400 °C for 6 h.

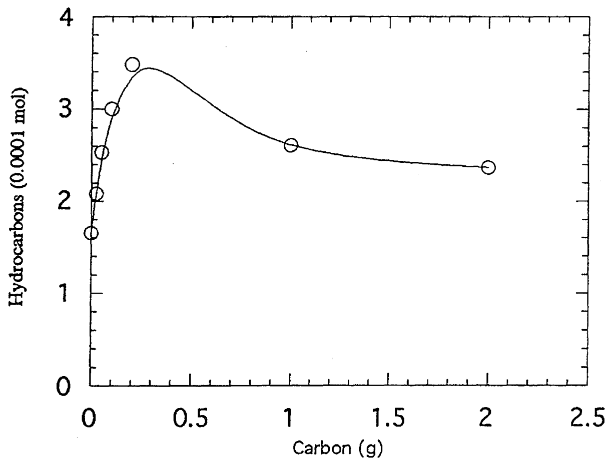

Fig. 3. Effect of amount of activated carbon used on the yields of hydrocarbons obtained by the reaction of activated carbon with copper(I) oxide and aqueous potassium carbonate solution at 380 °C for 6 h.

amount of hexane exceeds the sum of C_2—C_5 hydrocarbons in this region.

When a mixture of activated carbon, copper(I) oxide and aqueous alkali metal carbonate solution was heated for 380 °C for 6 h under nitrogen atmosphere, methane, benzene, and toluene were formed, as shown in Runs 11—17 of Table 2, in which varying amounts of activated carbon were used. Change of the yields of hydrocarbons with the amounts of activated carbon added is visualized as shown in Fig. 3. Although addition of large amounts of activated carbon gave carbon dioxide, as shown in Runs 11 and 12, addition of small amounts of activated carbon did not give carbon dioxide, as shown in Runs 14—17. Since copper(I) oxide has lower oxygen content than copper(II) oxide, carbon dioxide formed in the reactions of copper(I) oxide presumably reacts with carbonate to give hydrogencarbonate. The reactions of copper(II) oxide with carbon give enough amounts of carbon dioxide to exist as free carbon dioxide gas. Yields of benzene and toluene in the reaction of copper(I) oxide were less than those of the reaction of copper(II) oxide (compare Table 2 with Table 1). Presumably copper(I) oxide gives an intermediate CuO_y by the reaction with carbon.

$$Cu_2O + \frac{1}{2}C \longrightarrow CuO_y \rightarrow\rightarrow 2Cu + \frac{1}{2}CO_2 \qquad (3)$$

This intermediate presumably has lower ability to give aromatic hydrocarbons than the intermediate CuO_x formed by the reaction of copper(II) oxide. Since copper(I) oxide formed in Eq. 1 is reduced to give copper powder, reactions of both copper(I) oxide and copper(II) oxide with carbon showed deposition of metallic copper powder.

A surprising difference between the reaction behavior of copper(II) oxide and copper(I) oxide is that the reaction carried out using copper(I) oxide gives hydrocarbons (see Run 17 in Table 2) even without addition of activated carbon, contrary to the reaction of copper(II) oxide, in which hydrocarbons were not formed in the absence of activated carbon (see Run 10 in Table 1). Inspections of Figs. 2 and 3 indicate

Table 2. Yields of Hydrocarbons Formed by the Reactions of Activated Carbon with Copper(I) Oxide and Aqueous Alkali Metal Carbonate Solution[a)]

Run	Temp	Carbon	Additive	Products (μmol)					
	°C	g		CH_4	C_2—C_5	n-C_6H_{14}	Benzene	Toluene	CO_2
11	380	2.0	—	161	0.51	0.18	11.5	0.53	853
12	380	1.0	—	203	0.39	0.53	8.5	0.28	412
13	380	0.20	—	230	0.79	0.13	17	2.0	42
14	380	0.10	—	215	0.78	0.17	12.0	1.7	0
15	380	0.05	—	201	0.80	0.03	6.4	0.76	0
16	380	0.025	—	179	0.69	0.06	3.9	0.47	0
17	380	0	—	160	0.72	t	0.36	t	0
18[b)]	380	0	—	164	0.74	t	0.37	0.04	0
19	380	0	Cu[c)]	226	0.67	t	t	t	0
20	400	0	—	171	1.90	t	0.36	0.06	0
21	400	0	Cu[c)]	245	1.10	t	1.9	0.39	0

a) In the reactions shown in this table oxygen gas was not added. b) Cesium carbonate was used in place of potassium carbonate. c) 3 g of copper powder was added.

that the curve in Fig. 3 intersects on the ordinate at a point larger than zero, while the curve in Fig. 2 intersects on the ordinate at zero point. In order to make clear the tendency that the reactions of copper(I) oxide give hydrocarbons in the absence of activated carbon, several experiments under various experimental conditions, i.e., changing the reaction temperature, addition of copper powder, and use of cesium carbonate in place of potassium carbonate were performed, the results are shown in Table 2 (Runs 18—21). Although the reaction of cesium carbonate gives a result similar to that of the reaction of potassium carbonate (compare Run 18 with Run 17), increasing of the reaction temperature (compare Run 20 or 21 with Run 17 or 19, respectively) and addition of copper powder (compare Run 19 or 21 with Run 17 or 20, respectively) bring about increase of the yields of hydrocarbons. The fact that the reactions of copper(I) oxide with aqueous alkali metal carbonate solution give a mixture of hydrocarbons in the absence of carbon indicates that the following reaction takes place.

$$\mathrm{Cu_2O + M_2CO_3 + H_2O \rightarrow\rightarrow CH_4\ etc. + 2CuO} \qquad (4)$$

In the preceding paper it was suggested that potassium carbonate acted not only as a base but also as a carbon source for hydrocarbons, because the reaction of carbon with aqueous potassium carbonate solution gave higher yields of hydrocarbons than the reaction of carbon with aqueous potassium hydroxide solution for prolonged reaction time.[8)] Color of the copper salts in Runs 17—21 changed from bright red of copper(I) oxide to dark brown. A control experiment of these recovered salts with activated carbon in the presence of aqueous potassium carbonate solution gave the reaction products in a distribution which was intermediate between those of copper(II) oxide and copper(I) oxide with activated carbon. This fact indicates that the reaction of copper(I) oxide gives copper(II) oxide, as is explained in Eq. 4.

Another feature of the reaction of copper(I) oxide in the absence of carbon is that hydrocarbons formed mainly consist of methane compared to those reactions carried out in the presence of carbon (compare Runs 17—21 with Runs 11—16 in Table 2). The fact that the reactions of copper(I) oxide with alkali metal carbonate in the absence of carbon scarcely give aromatic hydrocarbons indicates that formation of methane by reduction of alkali metal carbonate with copper(I) oxide does not proceed through formation of carbon. Since copper(II) oxide can not reduce metal carbonate, the reaction of copper(II) oxide with alkali metal carbonate in the absence of carbon does not give hydrocarbons. The fact that addition of copper powder to the reaction mixture of copper(I) oxide brings about an increase of yields of methane indicates that copper powder reduces copper(II) oxide formed by oxidation of copper(I) oxide to give copper(I) oxide. Relatively low enhancement of the yields of methane by addition of copper powder presumably indicates that surface of copper powder is oxidized to turn to inactive form.

It is well known that reduction of alkaline-earth metal carbonate by hydrogen at a temperature as high as 800 °C gives carbon monoxide.[7)] Reduction of mixed alkaline-earth/transition metal carbonate with hydrogen gives a mixture of carbon monoxide and methane at around 700 °C. This report indicates that copper(I) oxide reduces alkali metal carbonate to give methane at lower temperature than 500 °C. There is a possibility that the yield of methane in this reaction can be improved by testing the experimental conditions. Improvement of experimental conditions of the reaction of copper(I) oxide with aqueous alkali metal carbonate solution is now under investigation.

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