CHEMISTRY LETTERS, pp. 1351-1354, 1980. © The Chemical Society of Japan 1980

DEOXYGENATION REACTION OF NITROBENZENE WITH CARBON CATALYZED BY POTASSIUM CARBONATE

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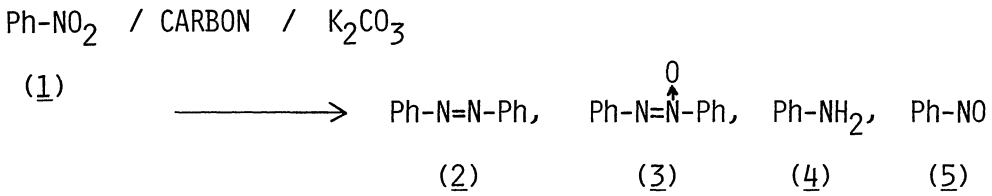
Nitrobenzene was deoxygenated by carbon to give azobenzene. Impregnation of K_2CO_3 on the carbon markedly lowered the temperature required for the reaction. The catalytic activity of K_2CO_3 was correlated to the oxidation behavior of the carbon observed by TGA and DTA in air.

Carbon has been used for the reduction of many inorganic compounds, but its use in the reduction of organic compounds has not been explored. In general, the reduction of metal oxides are carried out at high temperature. The reaction conditions are too drastic for thermally labile organic substrates. It is considerably difficult to conduct deoxygenative reduction of oxygen-containing organic compounds by use of carbon. Alkali salts are good catalysts for the Boudouard reaction,$^{1,2)}$ water-gas shift reaction,$^{3)}$ gasification of coal,$^{4)}$ and reduction of nitrogen oxide by carbon.$^{5)}$ We carried out the K_2CO_3-catalyzed reduction of organic compounds by carbon, with expectation that it would provide a new method for deoxygenation from oxygen-containing compounds and give some informations on surface properties of carbon and on its gasification reaction. In this letter we describe the reaction of nitrobenzene with carbon impregnated with potassium carbonate.

The impregnated carbon was prepared by mixing carbon (CAL)$^{6)}$ with a known amount of aqueous potassium carbonate. The slurry was evaporated to dryness at 100-110 °C in air. The impregnated carbon (abbreviated as K_2CO_3-CAL) was calcined at 400 °C under nitrogen stream for 3 h just before use. A fixed-bed flow reactor was used with 4 g of the carbon. The reactor was kept at the reaction temperature in an electric furnace. The vapor of nitrobenzene (24.1 mmol except for run 8) was carried through the catalytic bed at a rate of 0.2 mmol/min (except for run 5 and 6) by using nitrogen as a carrier gas. After the addition of nitrobenzene the reactor was kept at the reaction temperature for 1 h. The effluent was condensed at 0 °C. The products adsorbed on the carbon were extracted with dichloromethane in a Soxhlet extractor. The combined products were analyzed by gas chromatography using naphthalene as an internal standard. The results are summarized in Table 1.



$$\underset{(\underline{1})}{\text{Ph-NO}_2} \;/\; \text{CARBON} \;/\; \text{K}_2\text{CO}_3 \longrightarrow \underset{(\underline{2})}{\text{Ph-N=N-Ph}},\ \underset{(\underline{3})}{\text{Ph-N=}\overset{\overset{\text{O}}{\uparrow}}{\text{N}}\text{-Ph}},\ \underset{(\underline{4})}{\text{Ph-NH}_2},\ \underset{(\underline{5})}{\text{Ph-NO}}$$

Nitrobenzene (1) was deoxygenated with carbon to give the reduced products (2)-(5). Below 300 °C, most of the fed nitrobenzene on CAL was recovered unchanged, accompanied by a trace amount of the products (run 1). At 350 °C, a considerable amount of nitrobenzene was consumed, and a small amount of azobenzene was obtained by column chromatography as the only isolable product (run 2). Impregnation of potassium carbonate on the carbon lowered the temperature required for the deoxygenation of nitrobenzene. Four grams of K_2CO_3(5.0%)-CAL contains 2.90 mg-atom of potassium. The reaction of the carbon with nitrobenzene at 300 °C afforded 7.28 mmol of azobenzene (run 5). Thus, the deoxygenation proceeds catalytically with respect to K_2CO_3. It is worthwhile to note that practically no reaction took place when nitrobenzene was allowed to react with potassium carbonate at 300 °C. At the early stage of the reaction, the eluate was greenish-yellow, indicating the formation of nitrosobenzene (5), of which presence was confirmed by GC-MS analysis. The yield of azoxybenzene (3) was increased at lower temperature (run 10). The products (3 and 5), therefore, seem to be the initial

Table 1. K_2CO_3-Catalyzed Reduction of Nitrobenzene with Carbon (CAL)[a)]

Run	K_2CO_3 (wt%)	Nitrobenzene mmol	mmol/min	Temp. (°C)	Conv.[b)] (%)	Yield[c)] (%)	Products[b)] 2(%)	3(%)	4(%)
1	0	24.1	0.20	300	4.1	–	tr	–	tr
2	0	24.1	0.20	350	45.3	29	13.1	–	tr
3	5.0	24.1	0.20	300	45.8	45	20.4	–	tr
4	5.0	24.1	0.20	350	94.1	30	25.9	–	2.6
5	5.0	24.1	0.13	300	55.7	43	24.0	–	tr
6	5.0	24.1	0.08	300	60.4	42	25.3	–	tr
7	10.4	24.1	0.20	300	66.9	45	30.2	tr	tr
8	10.4	48.2	0.20	300	41.9	39	16.5	tr	tr
9	10.4[d)]	24.1	0.20	300	42.2	34	14.5	tr	tr
10	21.6	24.1	0.20	250	30.7	39	9.1	2.9	tr
11	21.6	24.1	0.20	300	73.3	34	23.9	–	1.4
12	21.6	24.1	0.20	350	99.6	21	19.9	–	1.3

a) K_2CO_3-CAL (4 g) was calcined at 400 °C under nitrogen stream for 3 h just before use. b) Mol-% based on the fed nitrobenzene. c) Total yields of the products based on the converted nitrobenzene. d) Re-used catalyst.

products in the deoxygenation reaction of nitrobenzene. Furthermore, the formation of aniline (4) indicates the presence of phenylnitrene intermediate (6). The deoxygenative coupling of nitrobenzene giving 2 and 3 may be explained as follows. The reaction of nitrobenzene with the carbon affords nitrosobenzene, which is further deoxygenated to phenylnitrene. Azoxybenzene is derived from nitrosobenzene dimer or the reaction of 5 and 6. Azobenzene is formed by deoxygenation of 3 and/or direct coupling of 6.

As shown in Table 1, the conversion increased generally with an increase in the potassium carbonate content of the carbon. However, the total yields of the products decreased with increasing the salt content. Also the increase in conversion observed at high temperature was accompanied by a decrease in the yields of the products (run 4 and 12). The conversion of nitrobenzene decreased with the reaction time (run 8). It may be caused by the adsorption of the

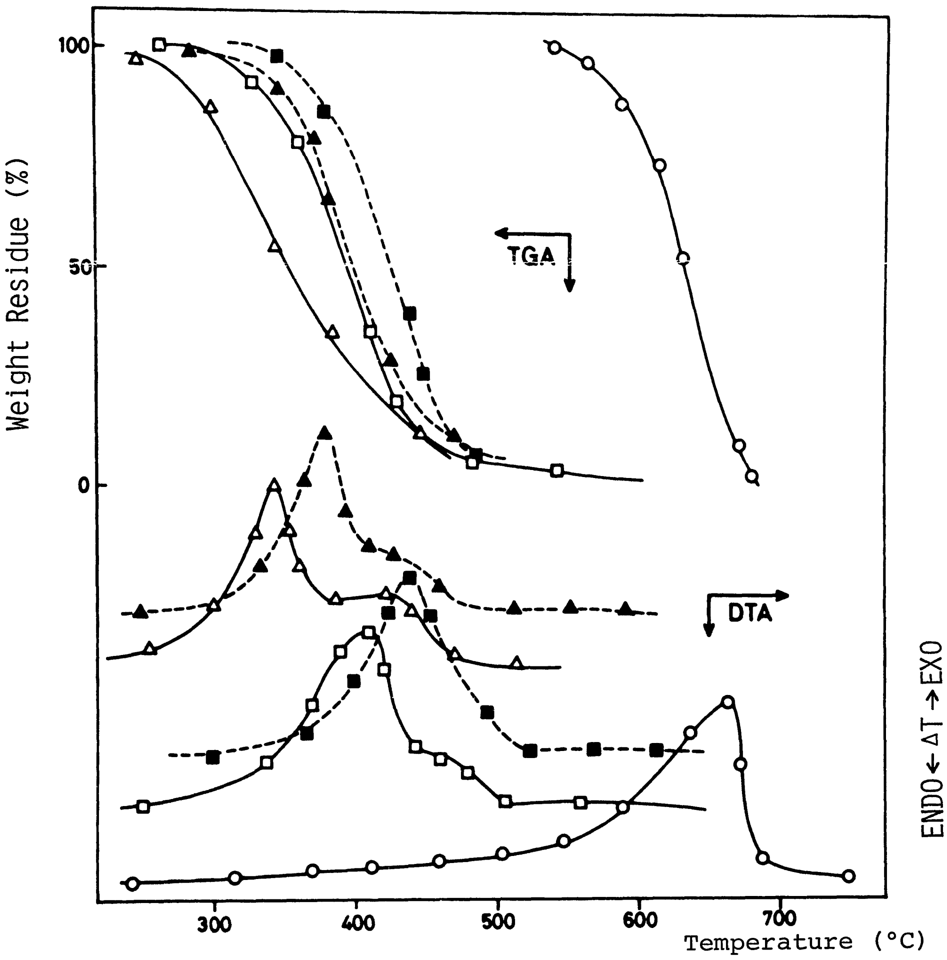


Figure 1. DTA and TGA of K_2CO_3-CAL
Heating rate 10 K/min, in air.
The K_2CO_3 content (%); ○ 0,
□ 10.4, ■ 10.4 (recovered),
△ 21.6, ▲ 21.6 (recovered).

products on the carbon surface. The carbon recovered by washing with dichloromethane could be re-used as a reagent, but the conversion of nitrobenzene was lower than that in the reaction with the fresh one (run 9). This may be due to the deposition of insoluble by-products on the carbon surface.

Behavior of carbon in air oxidation was studied by thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The thermograms over the range 250-750 °C are shown in Figure 1. The effect of potassium carbonate on the carbon is surprising. In the case of CAL, the DTA curve exhibited exothermic peak at 670 °C assigned to the oxidation of carbon, while the K_2CO_3(21.5%)-CAL showed two exotherms at 340 °C and 430 °C. It is obvious that potassium carbonate catalyzes the air oxidation of carbon. The recovered carbons, after washing with dichloromethane, are oxidized at higher temperature than the fresh ones. These observations are in accord with the decrease in the reactivity of the impregnated carbon.

Further studies on the use of carbon with impregnated alkali metal salts in deoxygenation of several organic compounds and the mechanistic aspects of the reaction are in progress.

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6) Manufactured from Pittsburgh coal in granular form (1-2 mm). The BET surface area is 1090 m^2g^{-1}.

(Received August 22, 1980)