

THE MECHANISM OF CARBON OXIDATION IN THE PRESENCE OF CERTAIN METALLIC OXIDES

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A series of studies (1), involving the catalytic oxidation of carbon have been carried out in this laboratory, and others are in the process. The work completed thus far has furnished a method of preparing carbon of a good reproducible quality and also a method of oxidizing the carbon both in the absence and in the presence of several types of secondary substances which may be regarded as catalysts or inhibitors. The secondary bodies used thus far include (1) heavy metals, metallic oxides, chlorides, and sulfates.

These researches naturally gave birth to the question as to whether or not certain of these secondary bodies, particularly the heavy metals (or their oxides), were stoichiometric oxygen carriers or were contact catalysts in the accepted sense of the term. This research, therefore, is confined to this phase of the reaction mechanism, using the common oxide of iron, of copper, and of silver as the secondary substance in the carbon oxidation. It was believed that if carbon measurably reduced the oxide in an oxygen-free (e.g., nitrogen) atmosphere at the same temperature at which the carbon gave carbon dioxide in an oxygen atmosphere with the same metallic oxide present, that the oxide should be regarded as functioning in a stoichiometric capacity; and if the two oxidation temperatures were appreciably different, then the oxide was acting in a contact or other manner.

G. Charpy and S. Bonnerot (2) found that up to 950° C. solid carbon does not reduce ferric oxide. They used ferric oxide and graphite, previously purified, heated to $1,000^{\circ}$ C. in vacuo, mixed and strongly compressed. At 950° C. under pressures of .01, .1, 1, 2, 4, and 8 mm., the evolutions of carbon dioxide were .1, .14, .31, .56, 18, and 1.07 cc. per hour.

G. Tammann and A. Ya Zvoruikin (3) report that sugar carbon reduces copper oxide at 100° C. and graphite reduces copper oxide at 190° C. They also report that sugar carbon reduces ferric oxide at 625° C.

The reaction was made to take place in an electric furnace, and the temperature at which carbon dioxide was first evolved is herein known as the initial carbon dioxide temperature. This determination was made by passing nitrogen or oxygen through the furnace, thereby sweeping the carbon dioxide into a solution of barium hydroxide, and noting the first appearance of a white precipitate.

Two problems incident to the investigation were the calibration of a thermocouple and the obtaining of oxygen-free nitrogen.

The oxygen present in commercial compressed nitrogen was removed by the method of C. J. Van Brunt (4).

An iron-German-silver thermocouple was used. It was calibrated by keeping one junction of the thermocouple in boiling aniline and the other junction in melted paraffin. The paraffin was gradually heated and at ten degree intervals, the deflection on the scale was noted. Several of these determinations were made and then the difference in temperature was plotted against the average deflection and a graph obtained.

The precision in the measurement of the current was increased by the arrangement of the light and a lens in such a way that a ray of light was reflected from the mirror in the galvanometer. This scale was two meters long and a galvanometer deflection of one centimeter on this scale was equivalent to about one degree Centigrade.

Data

Initial carbon dioxide temperatures:

	N ₂ atmosphere	O ₂ atmosphere
CuO	273° C.	233° C.
CuO	275° C.	235° C.
Fe ₂ O ₃	280° C.	234° C.
Fe ₂ O ₃	284° C.	236° C.
Ag ₂ O	174° C.	175° C.
Ag ₂ O	173° C.	173° C.

It is noticed that the carbon dioxide appeared at a lower temperature with the copper and iron oxide reductions in an oxygen atmosphere than in a nitrogen atmosphere. This is probably due to the fact that the carbon of the pellet was uniting with the oxygen that was passing through. The reduction of silver oxide takes place at about the same temperature in an oxygen atmosphere as in a nitrogen atmosphere. This may be attributed to the fact that carbon unites with silver oxide at a lower temperature than this sample of carbon itself burns.

Conclusions and Summary

1. It was desired to find out whether or not silver oxide, copper oxide, and ferric oxide were stoichiometric oxygen carriers or adsorption oxygen carriers.

2. An apparatus was devised to remove traces of oxygen, water, and carbon dioxide from nitrogen.

3. A thermocouple was made and calibrated to indicate accurately the temperature of the furnace in which the reaction took place.

4. The test for initial oxidation was the formation of a white precipitate in a solution of barium hydroxide as the carbon dioxide was evolved.

5. The oxidation temperatures were found. They were the same for silver oxide in both an atmosphere of oxygen and an atmosphere of nitrogen.

6. The oxidation temperatures for copper oxide and ferric oxide were lower in an atmosphere of oxygen than in an atmosphere of nitrogen.

7. Since the oxidation temperature of carbon, using silver oxide as a secondary substance, is the same in oxygen as in nitrogen, silver oxide must be a stoichiometric oxygen carrier.

8. Since the oxidation temperature of carbon, using ferric oxide and copper oxide as secondary substances, is lower in an atmosphere of oxygen than in nitrogen, copper oxide and ferric oxide are adsorption oxygen carriers.

Bibliography

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