A QUALITATIVE STUDY OF THE CATALYTIC HYDROGENATION OF THE OXIDES OF CARBON.

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The possibility of synthesizing some such valuable products as methyl alcohol or formaldehyde from hydrogen and carbon monoxide has held the interest of many chemists. Despite the recent successful syntheses of the former product under high pressures in Europe, there still remains, no doubt, considerable speculation as to the possibility of uniting these two gases at lower pressures in the presence of various catalysts. With this in view, there are recorded below the results of experiments in which metallized silica gels were used as catalysts with mixtures not only of carbon monoxide and hydrogen but also of carbon dioxide and hydrogen.

Previous Work.—The rather meager literature on the subject was, until quite recently, confined largely to a discussion of the conditions under which methane, and in some cases ethylene, could be obtained with various catalysts. Among the few who have reported formaldehyde among the products may be mentioned Bach (1), Chapman and Holt (2), Jahn (3), and Calvert (4). Practically all of their reports are lacking either in details or in satisfactory evidence of the presence of formaldehyde. The recent work by Patart and the Badische Company on the synthesis of methanol under high pressures has been reviewed by Lormand (5).

Materials Used.—The catalysts employed in the present work were metallized silica gels prepared by the method of Latshaw and Reyerson (6). While the temperature of the original reduction by this method is about —20°C., the higher temperatures prevailing during their use as catalysts also exerts an influence on the state of the metals in the gels.

The carbon dioxide and electrolytic hydrogen used were of the usual commercial variety, and were sent through the customary purification processes. The carbon monoxide was generated by allowing formic acid to drop slowly into hot concentrated sulfuric acid. It was bubbled through concentrated solutions of potassium hydroxide and of sulfuric acid before being stored in a gasometer.

Analytical Tests Employed.—As is apparent from the statement of the object of the investigation, a satisfactory method for the detection of formaldehyde was highly desirable. For this purpose the resorcin ring test was most commonly used. When complications began to develop, however, in the use of this test, an investigation of several of the other methods discussed by Allen (7) was undertaken. Of these,

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the phenol test alone seemed to be of sufficient value to justify its being used in the present work.

The resorcin ring test is stated to be also available for methanol, the procedure being to oxidize the alcohol to formaldehyde by means of a hot copper wire as a preliminary step. In the absence of a better method, this test was often made, although it cannot be said to be free from objection in the case of low concentrations of the desired products. The molybdic acid test for alcohols was found to be of no service whatever. Not until the latter part of the investigation was it discovered that the modified Sanglé-Ferrière-Cuniasse (7) test could be used to advantage in testing for methanol.

Experimental Data.—The results of the first series of experiments will be mentioned but briefly. In these, the gases, after passage over the catalyst, were sent through water, which was expected to remove any formaldehyde or methanol formed. This water was then tested for the latter two substances. A large number of combinations of catalyst, temperature and reaction mixture were tried in these early experiments. Much of the work on carbon monoxide was with palladium as a catalyst. Platinum, which is poisoned by the monoxide, appeared to be the most favorable catalyst for a study of the carbon dioxide systems. Entirely negative results were obtained in many of the tests, others were doubtful, while still others gave evidence of being more or less positive. It should be mentioned that the pink rings, when obtained in the resorcin test, were always rather faint. The best tests appeared to result when use was made of mixtures of carbon dioxide and hydrogen in the presence of a new platinized gel.

With the hope of increasing the yield of the desired products, a means of recirculation of the gases was next adopted. A mercury circulator, constructed after the model described by Menzies, Collins and Tyson (8) was inserted into the system. The gaseous mixture, after passage over the catalyst, was, by means of this device, continuously but slowly returned to its original container.

Typical results obtained from the use of this apparatus with a platinum catalyst and an approximately equi-molecular mixture of hydrogen and carbon dioxide are shown in table I.

TABLE 1. Recirculation Experiments with Carbon Dioxide and Hydrogen

Temperature	Length of Run	Color of Resorcin Ring Test for HCHO	Test for CH_3OH
110-115°C	23 hr.	Distinct pink	Distinct pink
185°	23	Very faint	Very faint
110°	24	Very faint	Very faint

Since the results appeared to be the same both before and after the attempted oxidation with a hot copper wire, the presence of any alcohol was not demonstrated. The third run was made to verify a suspected poisoning of the catalyst at the higher temperature of 185°, This poisoning was later shown to be attributable to sulfur compounds previously adsorbed by the platinized gel. New samples of the catalyst gave results similar to those shown above.

The tests made for formaldehyde after operation at 110-115° with a carbon dioxide system were the most favorable of any obtained throughout the investigation. Not only were the rings of the proper pink color, but there developed upon standing the cloud of white material which is characteristic of a satisfactory test.

Representative results obtained from the application of the recirculation apparatus to mixtures of hydrogen and carbon monoxide are shown in table II. The catalyst designated as Cu No. 2 was reduced at a much higher temperature than was Cu No. 3. A two to one ratio of hydrogen to carbon monoxide was adopted for this work. Such a ratio is the theoretical one required for the formation of methanol, as is indicated by the following equation:

$$2\ H_2 + CO = CH_3OH$$

TABLE II. Recirculation Experiments with Carbon Monoxide and Hydrogen

Catalyst	Temperature	Length of Run	Color of Resorcin Ring Test for HCHO	Test for CH_3OH
Pd	115-120°	20 hr.	Faint pink	Faint pink
Pd	185	24 hr.	Colorless	Colorless
Pd	30	29 hr.	Not pink	
Pd	100	12 hr.	Colorless	Colorless
Cu. No. 2	185	16 hr.	Green	Deeper green
Cu. No. 2	95	19 hr.	Colorless	Green
Cu. No. 2	160	20 hr.	Faint pink	Green
Cu. No. 3	300	22 hr.	Brownish pink	Yellowish green
Cu. No. 3	190-210	18 hr.	Green	Deeper green
Cu. No. 3	160-170	16 hr.	Yellowish pink	
Cu. No. 3	150	45 hr.	Yellowish pink	Yellowish brown

The phenol test, which was applied after certain of the runs with a copper catalyst, generally yielded the expected pink ring. Only in the last run shown in the above table was the color of the ring of sufficient intensity, however, to approach classification as a satisfactory test.

The appearance of a variety of colors when applying the resorcin test led to an investigation of the results obtained with this test when used with very dilute solutions of various organic substances. Methanol was found to give a pinkish brown ring, which developed a cloud of white material upon standing, while acetaldehyde yielded a brownish green ring. Formic acid and ethyl alcohol both gave faintly pink rings, which did not, however, develop a white cloud. It was also observed that methanol, when oxidized with a hot copper wire, gave rings varying in color from brown to green, and did not give the expected pink one. This observation is worthy of mention in view of the results shown in the last column of table II. The results of tests made when copper was the catalyst tend to indicate, in fact, the strong possibility of more than one substance among the products.

It should also be mentioned that the effluent gases generally had a very pleasant odor. While this odor was not identified, it should not be overlooked, in view of the fact that Fischer and Tropsch (9) have also observed a pleasant odor during similar experiments in which they synthesized various homologues of methane. That such products were being obtained in the present work is not improbable. During the course of a subsequent quantitative study it was demonstrated, in fact, that both saturated and unsaturated hydrocarbons are produced.

After the completion of the work at atmospheric pressure an entirely different apparatus was assembled for the purpose of investigating the same reactions under pressures of from eight to 27 atmospheres. Although the catalyst, temperature, pressure and reaction mixture were varied considerably during this work, better tests than those resulting from experiments at atmospheric pressure could be obtained.

SUMMARY.

1. Attempts to synthesize formaldehyde or methanol at atmospheric pressure have been followed by means of qualitative tests for these substances.

2. The most favorable tests for formaldehyde were obtained when using a platinized gel as catalyst with mixtures of hydrogen and carbon dioxide.

3. With hydrogen and carbon monoxide and a copper catalyst, the evidence seemed to point towards a mixture of products.

4. Pressures varying from 8 to 27 atmospheres gave no indication of being more favorable than one atmosphere for these syntheses.

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