in aqueous solution has been investigated. The photochemical decomposition has been formulated in a manner similar to the thermal decomposition which takes place above 30°, namely, $K_2S_2O_8 + H_2O = 2KHSO_4 + {}^1/_2\ O_2$, but no evidence of any intermediate reaction could be obtained.

2. Analytical methods for following the reaction were studied and a method, capable of yielding precise results in the extremely dilute solutions used, was developed which depended upon the reduction of the remaining persulfate with ferrous sulfate.

3. New methods of photochemical technique were developed including the stirring of the exposed solution and temperature control.

4. The photochemical decomposition was found to proceed according to a zero or linear order in the more concentrated solutions with a limited light intensity and according to a unimolecular order in the very dilute solutions. The order for the intermediate solutions is an accelerated unimolecular one, the value of the constants depending upon the light intensity and upon the concentration. An explanation of this phenomenon is given.

5. The effect of gases and of the aging of the lamp has been studied. Varying the concentration of the oxygen produces no change in the rate of the reaction; consequently, the reaction is not reversible. Hydrogen and nitrogen appear to accelerate the reaction.

6. Solid potassium persulfate has been found to decompose under ultraviolet radiations.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 34]

A REPORT OF ATTEMPTS TO ACTIVATE COPPER FOR CATALYTIC HYDROGENATION BY OXIDATION AND REDUCTION

BY ROBERT N. PEASE AND C. W. GRIFFIN

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In connection with our studies of the activity of copper in catalytic hydrogenation it was desired to devise methods of preparation which would allow control of the nature of the catalyst surface. In particular it was desired to prepare a catalyst which should have a low porosity (and surface area) but a high activity. For this purpose low-temperature oxidation and reduction of a well-sintered sample seemed to be the most promising method. Although we have not been able to prepare a permanently active catalyst by this method, the results are thought to be worthy of record.

The method used was as follows. A bulb containing a sample of copper oxide in wire form was sealed into the usual apparatus consisting of a manometer, gas buret and Töpler pump with suitable leads to gas supplies.

The oxide was reduced with purified electrolytic hydrogen at about 300° and the metal was then heated in hydrogen or in a vacuum to 500–550°. Previous work had shown that such treatment gave a catalyst without measurable activity at temperatures much below 150°, and one which was judged by its shrinkage to be relatively dense. This material was partially reoxidized at some fixed temperature and reduced. It was then tested with an equivalent mixture of ethylene and hydrogen at room temperature.

The net result of the experiments was that with sufficient oxidation a catalyst could be prepared which was highly active for a single run but whose activity thereafter was negligible. That the method of testing and general manipulation were not at fault was shown by preparing a catalyst from the same starting material by reduction at 150° without further treatment. This catalyst was shown to be permanently active.

In confirmation of the results of Wright and Menke[1] it was found that the extent of oxidation of a sample was chiefly a function of the temperature. At a given temperature, oxidation takes place up to a certain limit which is higher, the higher the temperature. For example, by passing a constant flow of purified air over the same sample of copper for a period of five hours, oxidations of 9.00, 11.11 and 17.30% were obtained at temperatures of 250°, 350° and 450°, respectively.

No appreciable oxidation in a stream of air took place below 100°. Oxidation at 100° was unmeasurable (in terms of weight of water absorbed by calcium chloride on reduction) though the copper was somewhat dulled. The catalyst, oxidized at 100° and reduced at 150°, caused a drop in pressure of 9 mm. in one-half hour at room temperature with an equivalent mixture of ethylene and hydrogen at one atmosphere. After heating to 500° the sample was reoxidized and reduced, both at 150°. Again the copper was somewhat dulled on oxidation (the extent was not measured) and caused a pressure drop of 15 mm. in one-half hour. Oxidation at 175°, after heating to 500°, yielded first the brilliant interference colors and then an even coating of oxide after eight hours' treatment. Reduction at 150° gave water equivalent to 3.0% oxidation and resulted in a catalyst which caused a pressure drop of 220 mm. in 15 minutes in the first run, indicating a very active catalyst. However, after the catalyst had been pumped out at 200° a second run showed almost complete inactivity. In order to show that the pumping out at 200° between runs was not responsible for this, the experiments were repeated except that the evacuation was done at room temperature. The results were the same except for a somewhat lower initial activity.

We had concluded at this stage that our ill success was due to a change in the catalyst in the course of the first test of its activity. This could be due either to poisoning by impurities or by secondary reactions, or to the

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[1] Wright and Menke, *J. Chem. Soc.*, **37**, 789 (1880).

shaking down of the hypothetical irregularities in the surface to which activity is currently ascribed, that is, to rearrangement of the surface atoms (amounting to crystal growth) as a result of their activities in promoting the catalysis. In order to test out the general method and settle the question of impurities, runs were carried out on a sample of metal prepared by reduction of the original oxide at 150° without further treatment. This showed permanent high activity—200 mm. pressure drop in three to five minutes in five successive runs. This appeared to settle the question of poisoning by impurities and presumably by secondary reactions also.

It was difficult to believe that sufficient oxidation of the sintered copper would not eventually give a catalyst similar to that described above. Accordingly, oxidation at a higher temperature was carried out. The greatest degree of oxidation which was attained was 17.3% at 450°. With this sample the first run gave a considerably higher activity than on previous oxidations, the second was about as high, but the third run showed almost complete inactivity.

Convinced that neither the degree of oxidation nor the temperature of evacuation of the catalyst bulb had any bearing on the sudden inactivity of the catalyst after the first or second run, it occurred to us that perhaps the temperature of reduction of the copper oxide might be the influencing factor. Accordingly, a sample of the copper was treated similarly to the others as to oxidation and sintering, but was reduced much more rapidly at a temperature of 200° instead of at 150°. However, this sample behaved as the others had, yielding a good first run, followed by a poor second run and a practically negligible third run.

Seeking to find any other possibility which might have been overlooked as an explanation of the peculiarity of this sudden inactivity, the idea occured that perhaps even repeated oxidation and reduction had been a case of setting and resetting of the crystals in the identical configuration from time to time without fixation of any additional active centers. In other words, perhaps upon reduction the surface fell again into its original configuration. Therefore, a sample was oxidized to an extent of 8.2% and then the *oxide* was heated for an hour at 500°. Reduction followed at 150° as usual. Two runs on this sample were made, the first showing an excellent activity of the catalyst, the second, however, complete inactivity.

It is to be remembered that the material underlying the oxidized and reduced surface is presumably well crystallized as a result of the sintering process. Our results appear to point to a reaction on the atoms on the metal surface as a result of catalytic action whereby they become labile for a moment and may subsequently become oriented to an underlying crystal. This action is apparently more violent than would be obtained by heating the catalyst to 450°.

Summary

A copper catalyst has been prepared which has a limited number of very active centers.

It has been shown that such a catalyst suffers sufficiently great loss of active centers in catalyzing the $H_2 + C_2H_4 = C_2H_6$ reaction, as to render it inactive after the first or second run, and that this deactivation is not due to the temperature of oxidation of the copper, to the temperature of evacuation of the catalyst bulb, to the temperature of reduction in preparation of the catalyst nor to fixation of surface crystals on the catalyst.

A catalyst unrestricted to a very few very active centers, prepared from the same original oxide, has been found to behave normally, giving permanent activity.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF WISCONSIN]

THE SPECIFIC HEAT OF GASEOUS NITROGEN TETROXIDE[1]

BY EDGAR D. MCCOLLUM

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Investigation of the heat capacity of gaseous nitrogen tetroxide makes an interesting study, because it involves a large absorption of heat caused by dissociation. Density measurements have shown that there are two gases in equilibrium, as given by the equation $N_2O_4 \rightleftarrows 2NO_2$. When the temperature is raised, heat is absorbed not only in increasing the kinetic energy of the molecules, but also in breaking down nitrogen tetroxide molecules into nitrogen dioxide. This heat of dissociation has been calculated from equilibrium measurements at different temperatures, and it was the purpose of this investigation to determine the specific heat over small temperature ranges.

The research was undertaken with the idea that the thermal measurements of a simple system of this type, in which the equilibrium conditions are known, might help in the interpretation of more complex systems. In a previous communication from this Laboratory[2] it has been shown that certain organic liquids exhibit irregularities in their specific heat-temperature curves due, in all probability, to a transformation of one molecular species into another as the temperature is raised. In some cases a negative temperature coefficient of specific heat was observed and an actual maximum in the specific heat-temperature curve for one liquid was located. The specific-heat measurements on nitrogen tetroxide

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[1] This communication is based on a thesis presented in 1925 at the University of Wisconsin for the degree of Doctor of Philosophy. The investigation was carried out under the direction of Professor Farrington Daniels.

[2] Williams and Daniels, THIS JOURNAL, **46**, 1569 (1924).