Summary

By the use of allylmagnesium bromide the β-bromo ether synthesis of olefins has been extended to the preparation of 1,4-diolefins. 1,4-Pentadiene, 1,4-hexadiene and 1,4-heptadiene and the corresponding α-allyl-β-bromoalkyl ethers have been described.

The rule that unsaturated compounds with a double bond in the alpha position boil lower than the corresponding saturated hydrocarbons has been confirmed. It has been further shown that in any given family the continuous chain diolefins form a definite series with gradually increasing boiling points depending upon the relative position of the double bonds.

The 1,2,4,5-tetrabromo paraffins corresponding to the diolefins described have been prepared and found to show evidences of isomerism analogous to other polybromo aliphatic derivatives.

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE OXIDATION OF METHANOL WITH AIR OVER IRON, MOLYBDENUM, AND IRON-MOLYBDENUM OXIDES

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The oxidation of methanol with air over various metal and oxide catalysts at 300 to 700° results in the formation of varying amounts of formaldehyde, carbon monoxide and carbon dioxide. Sabatier and more recently Lowdermilk and Day have given a review of the literature on this oxidation to which little need be added at this time.[1]

In 1926 a catalyst containing equal amounts of iron and molybdenum was found to be very efficient for the oxidation of methanol to formaldehyde.[2] The investigation described in this paper was initiated in order to correlate the characteristics of the iron–molybdenum catalyst with those of the catalyst containing only iron or molybdenum, with the hope of throwing some light upon the mechanism of the oxidation.

Catalysts. Molybdenum Oxide.—Five grams of ammonium molybdate and 4.5 g. of malic acid were dissolved in water and made ammoniacal with ammonium hydroxide.

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[1] Sabatier–Reid, "Catalysis in Organic Chemistry," Van Nostrand Company, New York, 1922, pp. 90–97; Lowdermilk and Day, THIS JOURNAL, 52, 3535 (1930).

[2] Homer Adkins and Virgil E. Meharg, in an application for a U. S. Patent (1927) assigned to the Bakelite Corporation. The authors of the present paper are indebted to Mr. Meharg and the Bakelite Corporation for the design of the very efficient washing tower and for the design and construction of the catalyst chamber, which were used in this investigation. The senior author is also grateful to Mr. Meharg for many pleasant associations and very valuable and willing coöperation while the former was temporarily employed by the Bakelite Corporation during the summer of 1926.

To this solution was added 60 cc. of three-sixteenths inch steel ball bearings, previously pitted with dilute hydrochloric acid and washed with distilled water until free of all acid. The solution was slowly evaporated almost to dryness with stirring. The steel balls, covered with the paste, were then poured onto a watch glass in layers of one thickness. The catalyst balls were further dried by placing in an oven at 60° for several hours.

Iron Oxide.—Three grams of iron reduced by hydrogen was added to a water solution of 6 g. of malic acid. The iron was almost completely dissolved by gently boiling the solution for three or four hours and the undissolved iron removed by decantation. The solution of ferrous malate was made ammoniacal by the addition of ammonium hydroxide. Sixty cubic centimeters of pitted steel ball bearings was added and the preparation of catalyst continued as described above.

Iron–Molybdenum Oxide.—One and one-fourth grams of iron reduced by hydrogen was added to a water solution of 4.5 g. of malic acid. The iron was almost completely dissolved by gently boiling the solution for three or four hours and the undissolved iron removed by decantation. To this solution of ferrous malate was added with stirring a water solution of 3 g. of ammonium molybdate. The combined solution was made ammoniacal by the addition of ammonium hydroxide, steel balls were added and the catalyst prepared as described above.

The catalysts thus prepared were placed in the aluminum reaction tube and decomposed in a slowly moving current of air for an hour or more at 360–375°. They were then ready for use.

Apparatus

The apparatus used in the experimental work is shown in Fig. 1. The air, which was supplied by a compressed air line A, was dried by passing it through a bottle B of

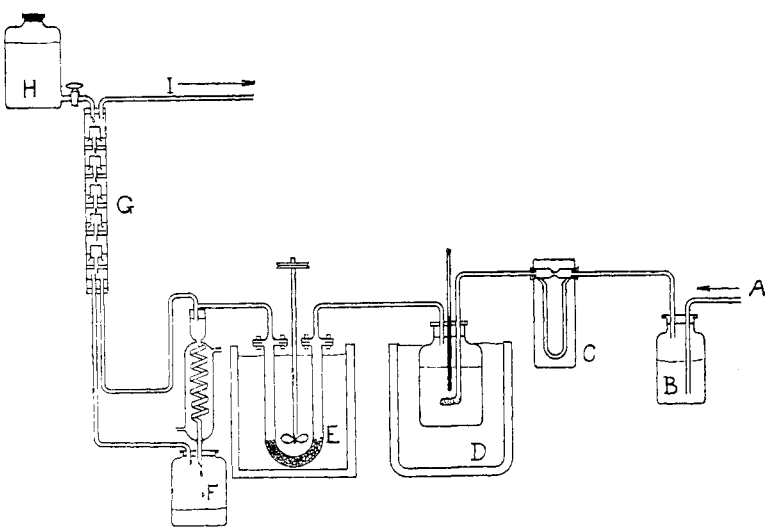

Fig. 1.—Apparatus for the oxidation of methanol.

concentrated sulfuric acid. The rate of flow of air was varied by means of a constant pressure valve. The flow of air was determined by means of a calibrated flowmeter C. The air was passed through a bottle D, containing the dried methanol. The vaporization of the alcohol was regulated by controlling the temperature of the vaporizer. The alcohol–air mixture was passed through a U-shaped aluminum catalyst tube. The U-

tube was made of a flattened piece of aluminum tubing 75 cm. in length and 50 × 6 mm. (I. D.) in cross section. It was filled in the bottom and inlet side with glass rod and balls. A 15-cm. depth of catalyst was placed in the outlet side. The catalyst tube was immersed in an electrically heated bath (E) of sodium and potassium nitrates. The temperature of the bath was controlled by means of a Leeds and Northrup potentiometer controller. The products of the reaction were passed through a water-cooled coil condenser and then through a bubbling tower G 60 cm. in length, down which water was passed at the rate of about 100 ml. per hour from the reservoir H. All the formaldehyde and methanol in the gases were collected in the wash tower and flowed back through the condenser into bottle F. I is an exit tube for gaseous products leading to an Orsat apparatus.

Examination of Products.—The water-insoluble gaseous products were analyzed in an Orsat apparatus. The carbon dioxide was determined by absorption in potassium hydroxide solutions. The remaining oxygen was removed by yellow stick phosphorus. The carbon monoxide was removed by bubbling through an acid solution of cuprous chloride. The water-soluble products collected in bottle F were analyzed for formaldehyde by the method of Haywood and Smith.[3] The unreacted methanol was determined by oxidation with chromic acid.[4]

The percentage efficiency as used in this paper refers to the percentage of oxygen used in the conversion of methanol to formaldehyde and was calculated from gas analysis data in the following manner

$$\% \text{ Efficiency} = \frac{\% \text{ oxygen used} - (1.5 \times \% \text{ carbon dioxide} + \% \text{ CO})}{\% \text{ oxygen used}}$$

The percentage efficiency so calculated agrees quite closely with the percentage efficiency calculated from the weight of formaldehyde obtained, the amount of methanol passed over the catalyst and the weight of methanol which was found unchanged in the distillate.

The Formation of Methylal.—Under certain conditions of operation formaldehyde reacts with methanol in the catalyst chamber with the formation of the methyl acetal of formaldehyde. The compound is only partially condensed with the other liquid products and some escapes with the gaseous products of the reaction. This acetal is not at all readily hydrolyzed. The method of Lowdermilk and Day[5] for the determination of unchanged methanol may give quite inaccurate results because methylal would appear with methanol in their procedure for analysis. The presence of methylal among the reaction products may be suspected if there is a 0.5 to 2% reduction in the volume of the effluent gas when bubbled through sulfuric acid, or if there is a discrepancy between the efficiency as calculated from the gas analysis and from the formaldehyde and methanol in the distillate. Methylal was formed in considerable quantities in one series of experiments, apparently due to the accumulation of alumina on the walls of the catalyst chamber. No further difficulty was experienced after the chamber had been thoroughly cleaned with a sodium hydroxide solution and with hydrochloric acid. Methylal was also formed when rather completely oxidized aluminum turnings were used as a support for the catalysts.

General Procedure.—The catalyst was put in place and decomposed and methanol and air passed over it continually (except for the removal of samples) for several days or weeks. Two or three times during each twenty-four hours the passage of the reactants was stopped and the amount of methanol which had been passed over the catalyst de-

[3] Haywood and Smith, This Journal, **27**, 1185 (1905).

[4] Blank and Finkenbeiner, *Ber.*, **39**, 1327 (1906).

[5] Lowdermilk and Day, This Journal, **52**, 3537 (1930).

termined by weighing the methanol left in the vaporizer. The condensate was taken out of the receiver and made up for analysis. Gas analyses were made from time to time on the effluent gases. The temperature of the catalyst and amount and ratio of air and methanol were changed as desired. After a given variation in the conditions of reaction had been studied, the conditions were again made standard, *i. e.*, 93 liters of air and 9 g. of methanol per hour at 373° and assurance was obtained that the catalyst had not been permanently modified. In this way a given sample of catalyst could be used for several weeks for the study of a variety of experimental conditions. Duplicate preparations of catalyst were used in the testing of all important points. The catalyst can be readily and precisely duplicated. Preparations made and tested independently by the two authors gave results which agreed almost as well as the data for the three typical experiments given below: 1–2–3. Iron–molybdenum oxide, 373°, 93 liters of air, 8.9, 9.38, 8.97 g. of methanol per hr., % converted to formaldehyde as actually obtained, 91.5, 91.8, 90.3%; % recovered methanol, 5.03, 6.47, 5.6 g. Gas analysis: % CO_2, 0.1, 0.1, 0.1; % oxygen, 18.0, 18.0, 17.5; % CO, 0.1, 0.1, 0.2; % efficiency based on gas analysis, 93, 93, 91.

Statement of Experimental Results

Space is not available for the tabulation of the complete data of the more than a hundred experiments upon the oxidation of methanol over oxide catalysts which have been carried on in the course of this investigation. It must suffice to give the following abstract of these data.

The characteristics of a molybdenum oxide catalyst as concluded from a study of its behavior toward oxidation of methanol with air to formaldehyde were found to be as follows.

1. The catalyst was highly efficient as evidenced by the fact that all of the methanol which was oxidized was converted into formaldehyde with no formation of the oxides of carbon.

2. The activity of the catalyst decreased during the first twenty-four hours of use, after which a steady state was reached in which its activity was approximately constant for several days. For example, a molybdenum oxide catalyst was capable of causing the oxidation of 6.8 g. of methanol (57.8% yield) to formaldehyde per hour during its first five hours of use; 5.17 g. of methanol (48.6%) to formaldehyde per hour for three and one-half hours after being used for five hours; and 4.73 g. of methanol (45.9%) to formaldehyde per hour the next three and one-half hours as compared to a 35.5% yield under comparable conditions after the steady state was reached.

3. The amount of methanol oxidized to formaldehyde per hour was a *linear* function of the rate of passage of the methanol over the catalyst. When 2.26, 5.28, 12.95, 18.4 and 20.0 g. of methanol per hour was passed over the catalyst with 50 or 93 liters of air, 1.58, 2.25, 3.72, 4.93 and 5.36 g. of the methanol, respectively, was converted into formaldehyde. However, the amount of methanol oxidized to formaldehyde per hour did not increase (over the range investigated) with increase in the rate of passage of the air over the catalyst. When 6.17 g. of methanol and

136 liters of air were passed over the catalyst in an hour, 2.31 g. of the methanol was converted into formaldehyde, as compared to the conversion of 2.41 g. of methanol when 6.67 g. of methanol in 50 liters of air were passed over the catalyst.

4. The percentage conversion of methanol to formaldehyde rose with decrease in the rate of passage of the methanol over the catalyst. When 20.0, 10.2, 6.67 and 2.57 g. of methanol were passed over the catalyst with 50 liters of air, the yields were 26.9, 33.3, 36.2 and 54.2%, respectively.

5. The conversions of methanol to formaldehyde at 373, 390 and 400° were approximately the same. However, at 361° lower conversions were obtained. When approximately 9.5 g. of methanol in 93 liters of air was passed over the catalyst at 361, 373, 390 and 400°, yields of 23.8, 31.5, 32.1 and 32.4%, respectively, were obtained when the catalyst had reached its "steady state."

The characteristics of an iron oxide catalyst, as concluded from a study of its behavior when methanol mixed with air was passed over it, were found to be as follows.

1. The catalyst was very active, the methanol being oxidized almost wholly to carbon dioxide. When the amount of methanol passed over the catalyst was varied from 11.2 to 33 g. per hour (373°, 93 liters of air per hour), there were only traces of formaldehyde and this only with a catalyst that had been in operation for several days and with more methanol passing over the catalyst than could be oxidized to carbon dioxide by the available oxygen.

2. The activity of the catalyst became less as the temperature of the reaction was lowered and increased as the temperature was raised. At 310°, with 20 g. of methanol and 93 liters of air, 9.4% of the methanol passed over the catalyst was converted to formaldehyde; 81.0% remained unreacted, the remaining 9.6% having been converted into carbon dioxide. At 340° approximately 18% of the methanol was converted into formaldehyde, with about 68% remaining unreacted; the remaining 14% was converted into carbon dioxide. At 400 or 443°, no formaldehyde was formed, 4.92% of the methanol remained unreacted, the remainder having been lost as oxides of carbon.

3. An iron oxide catalyst that has been used at a low temperature (340°) when raised to 373° was less active toward oxidizing methanol and produced more formaldehyde than it formerly did at 373°. It gradually recovered its original activity, giving results identical within experimental error with those obtained previously at 373°. Previous to the lowering of the temperature, the results obtained at 373° showed the formation of 1.3% of formaldehyde with very little methanol (5.1%) remaining unreacted. After raising the temperature again to 373°, the results obtained for the first two experiments showed conversions

of methanol to formaldehyde of 4.67 and 4.16%, respectively; the amounts of methanol remaining unreacted were 21.9 and 7.88%, respectively.

The characteristics of an iron–molybdenum oxide catalyst, as concluded from a study of its behavior when methanol was oxidized with air on the surface of the catalyst, were as follows.

1. The activity and efficiency of the catalyst increased during the first few hours of use, after which a steady state was reached in which its activity was constant for weeks. During the first twelve hours of use, the average conversion of methanol to formaldehyde was 82.0%. During the next five hours, the average conversion was 88.5%, and for the next six and one-half hours, the average conversion was 90.8%. The air flow was kept at 93 liters per hour, while the passage of methanol varied from 8.8 to 10.1 g. per hour in these experiments.

2. More carbon monoxide than dioxide was produced from methanol over molybdenum–iron oxide catalysts.

3. The iron–molybdenum oxide catalyst was relatively inactive toward formaldehyde. A 5-cm. depth of catalyst produced the same yield of formaldehyde as did a 15-cm. depth of catalyst using 93 liters of air per hour carrying approximately 10 g. of methanol per hour. The efficiency for the 5-cm. depth of catalyst was 92.3% and for the 15-cm. depth 85.6%. The above conclusion may also be drawn from the results obtained by passing alcohol and air in the same ratio but at different rates over a 15-cm. depth of catalyst. Considering air flows of 93 and 136 liters per hour, the efficiencies were found to be 90.7 and 93.8%, respectively. However, with an air flow of 50 liters per hour, the yield (80.8%) as well as the efficiency (66.5%) decreased considerably. The "space-time-velocities" in passing 136 and 50 liters of air over a 15-cm. depth of catalyst were the same as for the passage of 93 liters of air over 10.3 and 27.9-cm. depths of catalyst, respectively.

4. Increasing the rate of passage of methanol increased the grams of methanol oxidized to formaldehyde, but there was also a decrease in efficiency if the methanol passage became too high. With 93 liters of air carrying 9.38 g. and 15.0 g. of methanol per hour, the weight of methanol converted to formaldehyde was 8.61 and 12.8 g., respectively. The efficiencies were 90.7 and 85.5%, respectively.

5. The maximum activity was obtained when equimolecular proportions of iron and molybdenum were present in the oxide mixture. A high percentage of iron oxide in the catalyst showed more of the carbon dioxide forming properties of an iron oxide catalyst, while a high percentage of molybdenum oxide in the catalyst showed properties intermediate between those of an iron–molybdenum oxide catalyst and a molybdenum oxide catalyst, that is to say, the efficiency was higher and the conversion of methanol to formaldehyde was lower than for the mixed oxide catalyst.

6. Lower conversion of methanol to formaldehyde was obtained at 353 than at 373 and at 400°. The efficiency was less at 400 than at 373 and 353°. With 93 liters of air and approximately 9 g. of methanol passing over the catalyst per hour, the conversions of methanol to formaldehyde at 353, at 373 and at 400° were 85.2, 91.8 and 91.9%, respectively, and the efficiencies were 90.0, 90.7 and 85.3%, respectively.

Discussion of Results

The catalyst surface of these oxide catalysts was constantly undergoing change as measured by the amount of oxidation of methanol or by the ratio of products. For example, in the case of molybdenum oxide a new catalyst rapidly decreased in activity for several hours until a steady state was reached for the particular temperature, rate and ratio of methanol and air involved. The new iron and iron–molybdenum catalysts showed a change in the ratio of products during several hours before a steady state was reached. When the experimental conditions were changed the catalysts rather slowly shifted in activity until a new steady state was reached. The former steady state could be slowly regained if the experimental conditions which produced it were reproduced. The constant change and renewal of the active surface was also indicated by the fact that the catalysts are active for weeks and months of continuous use. It is extremely unlikely that any surface would remain active for any such lengths of time unless it was being continually renewed. Thus the relationship between an effective catalyst and the reactants must not only be such that the former brings about the reaction of the latter, but the reactants must maintain the state of the catalyst which is favorable to the desired reaction.

A desirable catalyst for the oxidation of methanol to formaldehyde would therefore be one that required only a low concentration of methanol in the effluent gas stream in order to maintain it in the optimum state of reduction; in other words, a desirable catalyst would be one which would stay reduced without an excess of methanol. It should not be active toward formaldehyde, that is, it should desorb it rapidly. Molybdenum oxide is an efficient but undesirable catalyst because too much methanol is required to keep it reduced to the active state. Iron oxide is an undesirable catalyst because it goes into such a high state of oxidation that any formaldehyde formed is not desorbed, but is oxidized to carbon dioxide. The mixture of iron and molybdenum oxide apparently requires no considerable excess of methanol to maintain it in the desired state of oxidation and has a low activity toward formaldehyde. The mixture of oxides differs from either of the pure oxides not only in these facts but in that the mixture produces the monoxide rather than the dioxide of carbon.

Langmuir[6] in his classical paper on the oxidation over platinum of carbon monoxide by oxygen, pointed out that there are three possible mechanisms for such an oxidation: (1) the oxygen may be absorbed by the platinum and then be struck by a molecule of carbon monoxide: (2) the carbon monoxide may be absorbed by the platinum and then be struck by a molecule of oxygen; (3) the two reactants may be adsorbed on adjacent active points on the catalyst surface sufficiently close together so that the reaction may ensue.

Oxidation of methanol on the basis of cases (1) and (3) involves successive addition and removal of oxygen from the catalyst, the difference between the two cases being as to whether the methanol reacts from the vapor state or from the adsorbed state. The adsorbed oxygen postulated in both cases might be adsorbed on the catalyst or might be held as a so-called definite oxide. For the purpose of the discussion that follows, it is immaterial which is the case.

If either case (1) or (2) holds for the oxidation of methanol over molybdenum oxide, then it should be possible by using a proper ratio of reactants either to consume almost all of the oxygen or convert almost all of the methanol to formaldehyde. The experimental results very definitely show that this is not true, as the percentage conversion of methanol to formaldehyde cannot be raised very high no matter how much the excess of oxygen or how long the time of contact, *i. e.*, how slowly the reactants are passed over the catalyst. The amount of methanol oxidized per hour is a linear function of the amount of methanol passed over the catalyst for a 10-fold increase in rate of passage. No more than 10% of the total available amount of oxygen could be consumed no matter how large the excess of methanol. It is probable, therefore, that the two reactants must both be adsorbed on adjacent active points on the surface of the catalyst before reaction may ensue.

Summary

The characteristics of molybdenum oxide, iron oxide and a mixed iron–molybdenum oxide catalyst as displayed in the catalysis of the oxidation of methanol with air have been described. In brief it may be said that molybdenum oxide was 100% efficient for the oxidation of methanol to formaldehyde, since this is the only reaction which occurred. However, only about 38% of the methanol could be converted to formaldehyde. Iron oxide was a very active catalyst but it induced the formation of carbon dioxide almost exclusively. A catalyst containing equal atomic amounts of iron and molybdenum converted over 90% of the methanol passed over it into formaldehyde, the other product being carbon monoxide. It is thus by far the best catalyst, so far described, for the oxidation

[6] Langmuir, *Trans. Faraday Soc.*, **17**, 3, 653 (1922).

of methanol. The catalyst was quite stable and may be used continually for months.

At least in the case of molybdenum oxide there is evidence that the reaction between methanol and oxygen takes place when both reactants are on the surface of the catalyst.

Evidence has been presented which indicates that the catalyst surface of these oxide catalysts is continually renewed during use; therefore the relationship between an effective catalyst and the reactants must not only be such that the former brings about the reaction of the latter, but the reactants must maintain the catalyst in the state of oxidation which is favorable to the desired reaction.

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[A COMMUNICATION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

THE EFFECT OF COPPER UPON THE YIELDS OF GRIGNARD REAGENTS

BY GEORGE JOHNSON AND HOMER ADKINS

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It is well known that the reaction of alkyl halides and magnesium results in the formation of Grignard reagents and of hydrocarbons, as indicated in equations I and II.

$$RX + Mg = RMgX \quad \text{(I)}$$
$$2RX + Mg = R_2 + MgX_2 \quad \text{(II)}$$

There has been in progress for some time in this Laboratory a study of the factors which determine the ratio of these two competitive reactions. During the course of this investigation some observations have been made in regard to the effect of copper upon the ratio of the reaction products which are of such practical importance that it seems desirable to publish them in advance of a more comprehensive paper, especially in view of the results of Gilman, Peterson, Schultz and Heck,[1] who reported that magnesium in certain copper–magnesium alloys reacted more rapidly with alkyl halides than did pure magnesium. Upon the basis of these findings it seemed that the use of the alloy might be advantageous in the preparation of Grignard reagents and this practice has been followed by a number of investigators.

The determination of the effect of various experimental conditions upon the ratio of the Grignard and Wurtz reactions was made in the following manner. The apparatus used was essentially of the type and size described and used by Gilman and Meyers for the preparation of ethyl-

[1] Gilman, Peterson and Schulze, *Rec. trav. chim.*, **47**, 22 (1928); Gilman and Heck, *Bull. soc. chim.*, **45**, 250 (1929).