Trimethyl-β-methylxyloside has been prepared in two ways: (a) from pure crystalline β-methylxyloside and (b) from pure xylose, using the methyl sulfate and sodium hydroxide method. After purification by recrystallization, the crystals resulting from (a) had the following constants: m. p. sharp at 51°; $[\alpha]_D^{20}$ in $CHCl_3$, −69.5°; $[\alpha]_D^{20}$ in H_2O, −81.7, while those resulting from (b) showed $[\alpha]_D^{20}$ in $CHCl_3$, −59.6°. As this value, which is about 10° low, did not change appreciably on recrystallization, it is concluded that this method gives a less pure product. On hydrolysis both trimethyl-α-methylxyloside and trimethyl-β-methylxyloside yield the same crystalline trimethylxylose. It is therefore concluded that these two substances contain the same ring structure, forming an α- and β-pair. They have thus been definitely correlated for the first time and likewise the parent substances, α- and β-methylxylosides, from which they were derived. The properties of the purified trimethyl-α-xylose were m. p. 91 to 92°; $[\alpha]_D^{20}$ in $CHCl_3$ (final), + 24.2; $[\alpha]_D^{20}$ in H_2O (initial), 64.5°; (final), 17.7°. It is to be noted that for the most part the constants given above differ quite materially from those previously recorded.

WASHINGTON, D. C.

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

PROMOTER ACTION WITH OXIDE CATALYSTS FOR THE DECOMPOSITION OF ALCOHOLS[1]

BY HOMER ADKINS AND PAUL E. MILLINGTON

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It has been shown by experimental work described in a series of papers from this Laboratory[2] that the ratio of reaction products formed when alcohols are passed over solid catalysts is not primarily a function of the chemical nature of the catalyst mass but is determined by easily modifiable characteristics of the catalyst surface. Two explanations have been offered for this variation in the ratio of reaction products. Hugh Stott Taylor[3] in an extended discussion of our results among others stated that the oxides are dual catalysts, the metal part (metal ion) being dehydrogenating, and the oxygen part (oxide ions) being dehydrating. The ratio of the simultaneous reactions would then depend in part upon the ratio at the surface of active metal ions and active oxide ions. This latter ratio would depend upon the original distribution and upon the

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[1] The authors are indebted to E. I. du Pont de Nemours and Company for a fellowship held by Dr. Millington during the academic year 1927–1928.

[2] For references see Adkins and Lazier, THIS JOURNAL, **48,** 1671 (1926).

[3] Taylor, "Colloid Symposium Monograph," The Chemical Catalog Company, Inc., New York City, **1926,** Vol. IV, p. 25.

relative extent to which the two kinds of ions had been covered up by poisons. Upon the basis of this hypothesis the selective activation of catalysts observed in this Laboratory was dependent upon the relative occurrence in the catalyst surface of the two kinds of ions and upon selective poisoning of the one or the other kind of ions. Taylor further says that "the prediction can, therefore, be freely made that the presence of sulfate ion, and, for similar reasons, the anions of all the oxyacids, will cause an increase in dehydration ratio in the case of such predominantly dehydrogenating catalysts as uranium oxide, molybdenum oxide, ferric oxide and vanadium oxide." The adsorption of alkali ions will, on the contrary, favor dehydrogenation.

Adkins had previously suggested that the variation in the ratio of simultaneous reactions, was in part, a function of the space relationships of the active centers of the catalysts, *i. e.*, that the direction of distortion of an adsorbed molecule would be determined by the chemical nature of the catalyst and also by the relative position in space of the adsorbing centers which are close enough together to exert their influence simultaneously upon a single adsorbed molecule. Differences in spacings of the centers of activity might produce different molecular fragments just as the size and shape of fragments of a piece of paper would be in part determined by the relationship in space of the two hands which tore the original sheet. On the basis of this hypothesis small amounts of added materials might modify the ratio of reaction products through their effect in disturbing the spacial relations of the active centers on the catalyst surface. Such effects would presumably be highly specific and unconnected with the acidity or alkalinity of the added material and would vary from alcohol to alcohol, as a spacing favorable for a high dehydrogenation ratio of one alcohol would not be likely to be favorable for all alcohols.

A criticism of these hypotheses necessitates that there be available very accurate data over considerable intervals of catalyst life on the ratio of reaction products over a variety of pure and promoted catalysts. The experimental work described in this paper was carried out in order to provide such data.

Apparatus and Method of Experimentation

The assembly of the apparatus used for this work is indicated in Fig. 1. The catalyst tube was of pyrex, of which the upper half, eighteen inches in length, was constructed of quarter-inch tubing and carried the male half of the ground-glass joint. The lower half was of half-inch tubing, fourteen inches in length. A Gooch filter plate was pressed against a slight constriction in the tube at a point which fell near the center of the furnace when the apparatus was assembled. The tube was indented for the entire length above the filter plate.

A fine capillary, drawn out at one end of a piece of ordinary capillary tubing, was connected by a section of rubber tubing to the female half of the ground-glass joint mentioned in the preceding paragraph, in such a way that the tip of the capillary extended well down into the wide part of the joint. Alcohol or other liquid, contained in a liter bottle, was forced through the capillary by means of compressed air, maintained at practically a constant pressure by a column of water confined in a rubber tube leading from a reservoir in an upper room to a storage bottle on the laboratory desk. This bottle carried a simple manometer and was connected through a sulfuric acid drying tower with the flask containing the alcohol. The lower part of the catalyst tube carried a rubber stopper over which was fitted a glass cup with an outlet for gases and condensed liquid. A small pyrex tube also projected through the cup, the tip of the tube pressing against the catalyst. Ordinarily this tube served only to hold the catalyst mass in place. If the temperature of the reaction was wanted, a thermocouple was inserted into the tube and the tip of the latter imbedded in the catalyst. Another potentiometer was connected to the thermocouple and the temperature read off as desired.

The liquid was vaporized in the upper part of the catalyst tube by means of a preheating device. This consisted merely of a fourteen-inch length of pyrex tubing wound with eighteen feet of No. 18 nichrome wire and covered with asbestos. A current of two amperes maintained a temperature of 170 to 180°. A multiple unit furnace was used to heat the catalyst tube. It was maintained at the desired temperature, plus or minus three degrees, by a Leeds and Northrup controller through the medium of a thermocouple mounted on the tube close to the catalyst mass.

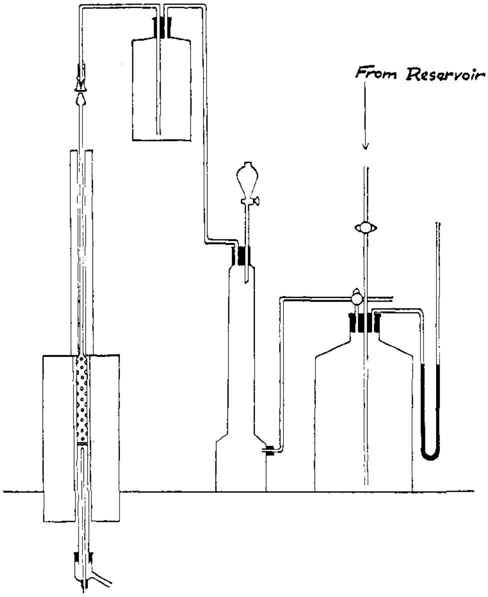

Fig. 1.—Apparatus for gas phase catalytic reactions.

Two forms of sampling apparatus were used. The first consisted of a 300-cc. calibrated bottle filled with saturated sodium bromide solution and fitted with a three-way stopcock. A second bottle served as a reservoir for the salt solution as it was displaced from the first bottle by the incoming gases. The second form provided for the condensation of the vapors issuing from the catalyst tube. The condensing system consisted of a 200-cc. round-bottomed flask fitted with a short glass coil, which served as the inlet, and a small upright coil condenser. The whole was immersed in an ice-bath and the uncondensed gases were collected over saturated sodium bromide solution in a calibrated three-liter bottle.

The charge of the catalyst, consisting of quartered tablets 6 mm. in diameter, was placed against the Gooch filter plate and held in place by a wad of glass wool. Air, partially dried and purified by bubbling through sulfuric acid, was slowly passed over the catalyst for fifteen minutes at the temperature maintained for the succeeding reaction.

Samples of gas were ordinarily taken at atmospheric pressure in the 300-cc. bottles. The contents of the sampling bottle were well shaken to dissolve aldehyde and alcohol vapors, and to displace gaseous products from the condensate layer. When the condensate was extremely insoluble in the salt solution, this method was unreliable due to the comparatively large amounts of unsaturated hydrocarbons remaining dissolved in the condensate layer. In such a case the gases were first passed through the condensing system described above and collected in the calibrated three-liter bottle for a definite period. The condensing system was removed from the ice-bath without being disconnected from the gas holder, and the condensate refluxed under the short coil condenser until no more gas was evolved. The condensing coil, flask and reflux condenser were finally filled with boiling water to displace all of the gas they contained.

Gas Analysis.—The procedure used in determining the percentages of the constituents of the evolved gases was essentially that of Hempel. Samples were measured in a 100-cc. water-jacketed buret over water. Carbon dioxide, uncondensed acid and alcohol vapors were absorbed in 40% potassium hydroxide solution. Unsaturated hydrocarbons were removed by bromine water, oxygen by stick phosphorus and carbon monoxide by ammoniacal cuprous chloride. Hydrogen and methane were determined by combustion. When ethane was also present, hydrogen was absorbed in colloidal palladium[4] and the residue burned in an excess of oxygen.

Preparation of Catalysts

No. 1. Millington's zinc oxide *ex* sulfate was prepared by adding a 0.67 *N* solution of zinc sulfate dropwise to a well-stirred 0.67 *N* hot solution of sodium hydroxide. The precipitate was washed repeatedly with hot water and finally dried at 120° for twelve hours. There were traces of sulfate in the catalyst.

No. 2. Weston's zinc oxide *ex* sulfate was prepared by adding 0.5 mole of zinc sulfate dissolved in 400 cc. of water dropwise with rapid stirring to 1.5 moles of sodium hydroxide in a liter of cold water. The precipitate was washed twice with cold water, then twice by heating to 130° and dropping into boiling water. Traces of sulfate remained in the catalyst.

No. 3. Lazier's zinc oxide *ex* sulfate was prepared but was not used during the investigation reported on in 1926. The sodium hydroxide solution had been added to the zinc sulfate solution. The catalyst contained considerable sulfate.

No. 4. Lazier's zinc oxide *ex* sulfate "A" was the catalyst described under that symbol in 1926. It was prepared in the same way as No. 3.

No. 5. Zinc oxide *ex* acetate was made from the acetate; otherwise the procedure was the same as for No. 1.

No. 6. Zinc oxide *ex* zinc chloride was made similarly to No. 1.

No. 7. Zinc oxide *ex* zinc nitrate was made similarly to No. 1.

No. 8. Zinc oxide *ex* oxalate was prepared from zinc oxalate by heating to 400° for forty-five minutes. The oxalate was prepared by slowly adding a hot solution of 1.4 moles of oxalic acid in a liter of water to a vigorously stirred suspension or solution of 1.0 mole of commercial zinc oxide, zinc carbonate or zinc chloride. The mixture was then boiled for 0.5 hour, filtered and the oxalate washed several times with hot water, dried, powdered, heated to 130°, poured into boiling water, filtered and dried at various temperatures from 90 to 120°. The oxalate showed no test for sulfates or chlorides.

No. 9. Zinc oxide *ex* oxalate and chromic oxide was prepared by treating 50 cc. of a water suspension of 17.7 g. of zinc oxalate with 0.2 g. of chromic oxide. The mixture was heated to dryness and decomposed for forty-five minutes at 400° as in the case of No. 8; 0.01 mole of chromic oxide was calculated to be present for each mole of ZnO.

No. 10. Zinc oxide *ex* oxalate + B_2O_3 was the same as No. 9 except that 0.124 g. of boric acid replaced the chromic oxide; 0.01 mole of B_2O_3 per mole of ZnO.

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[4] Paal and Hartmann, *Ber.*, **43**, 243 (1910).

No. 11. Zinc oxide *ex* oxalate + WO_3 was the same as No. 9 except that 0.25 g. of commercial H_2WO_4 replaced the chromic oxide; 0.01 mole of WO_3 per mole of ZnO.

No. 12. Zinc oxide *ex* oxalate + V_2O_5 was prepared by grinding 0.182 g. of vanadium pentoxide with 17.7 g. of zinc oxalate and then heating to 400° as usual.

No. 13. Zinc oxide *ex* oxalate + ammonium vanadate was prepared similarly to No. 9 except that 0.234 g. of ammonium metavanadate, NH_4VO_3, was used instead of the chromic oxide.

No. 14. Zinc oxide *ex* oxalate + MoO_3 was prepared the same as No. 9 except that 0.18 g. of ammonium molybdate was used.

No. 15. Zinc oxide *ex* oxalate + H_2SO_4 was prepared by evaporating to dryness and heating to 400° a mixture of 18.9 g. of hydrated zinc oxalate and 19.5 cc. of 0.1024 *N* sulfuric acid.

No. 16. Zinc oxide *ex* oxalate + NaOH was prepared the same as No. 15 except that 5 cc. of 0.2 *N* sodium hydroxide replaced the sulfuric acid.

No. 17. Iron oxide *ex* ferrous oxalate was prepared by heating ferrous oxalate for one hour at 400°. The oxalate was prepared by precipitation from solutions of ferrous sulfate and oxalic acid.

No. 18. Iron oxide *ex* ferrous oxalate + H_2SO_4 was prepared in the same way as No. 15 except that ferrous oxalate replaced the zinc oxalate.

No. 19. Iron oxide *ex* ferrous oxalate + NaOH was prepared similarly to No. 16.

No. 20. Iron oxide *ex* ferrous oxalate + B_2O_3 was prepared similarly to Nos. 9 and 10.

No. 21. Ferrous oxalate *ex* oxalate + CrO_3 was prepared similarly to No. 9.

No. 22. Titania *ex* tetra-butyl orthotitanate was prepared by allowing tetra-butyl orthotitanate to hydrolyze over water at 50 to 60° in a partially evacuated desiccator.

No. 23. Titania *ex* tetra-ethyl orthotitanate was prepared similarly to No. 22.

No. 24. Titania as in No. 23 + B_2O_3 was prepared by adding 20 cc. of an alcoholic solution containing 0.062 g. of boric acid to 4.0 g. of titania and then evaporating the alcohol during stirring.

No. 25. Titania from the hydrolysis of a mixture of tetra-ethyl titanate and sodium hydroxide was prepared by allowing a mixture of 50 parts of tetra-ethyl orthotitanate and 1 part of sodium hydroxide to hydrolyze as in No. 22.

No. 26. Titania *ex* tetra-ethyl titanate + NaOH was prepared similarly to No. 24.

No. 27. Alumina *ex* aluminum butoxide was prepared similarly to No. 22 except that the partially hydrolyzed material was heated to 80 to 90° from time to time during the hydrolysis.

No. 28. Alumina *ex* aluminum butoxide + CrO_3 was prepared by the hydrolysis of a mixture of chromic oxide and aluminum butoxide.

No. 29. Alumina *ex* aluminum butoxide + sodium hydroxide was obtained similarly by allowing a butanol solution of the butoxide and sodium hydroxide to hydrolyze.

No. 30. Alumina *ex* aluminum butoxide + H_2SO_4 was obtained by passing sulfur trioxide into aluminum butoxide and then allowing the mixture to hydrolyze.

At least two preparations of each catalyst were made and used except for some of the promoted iron and aluminum catalysts. For all catalysts which are claimed to be reproducible the gas analyses in the reaction products agreed within less than 1%. The promoted catalysts are qualitatively but not quantitatively reproducible; that is to say, chromium-promoted catalysts were always found to be more efficient for dehydration than were boron-promoted catalysts although the exact figures would vary somewhat. The data plotted in Figs. 2 and 3 are the results of two or more runs made on different samples of the same preparation of a catalyst. The points on the curve represent actual experimental determinations and are not averages. It is believed that differences in percentage of gases which are greater than 0.4% are significant of actual differences between the catalysts concerned. In the case of zinc oxide catalysts, from 0.0 to 2.5% of carbon dioxide was found to be present in the gases of reaction. This has been calculated out of the results and the alkene and hydrogen calculated as though they constituted 100% of the gas. There seems to be no adequate explanation of the variation in the formation of carbon dioxide over zinc oxide catalysts. Catalysts usually decrease on standing with respect to the formation of carbon dioxide. Therefore there seems to be some easily modified characteristic of the catalyst surface which determines the formation of carbon dioxide.

Summary of Experimental Results

A study of the effect of promoters demands the selection of a standard catalyst which can be readily reproduced and which is not modified in activity by the operations necessary for the incorporation with it of the promoter. Precipitated zinc oxide is not such a catalyst, as may be seen from the data given in Fig. 2 for the behavior of ethanol over a number of precipitated zinc oxides.

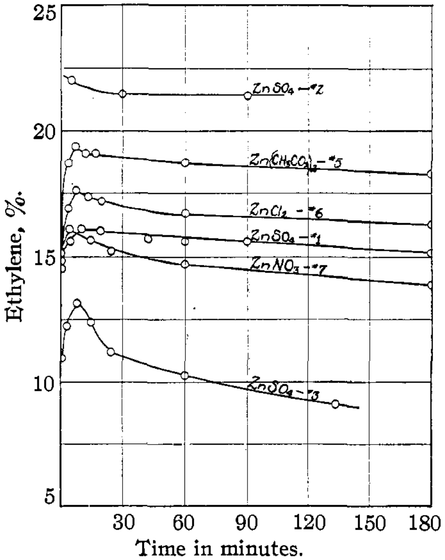

Fig. 2.—Percentage of ethylene in gaseous products from ethanol over various precipitated zinc oxide catalysts.

Zinc oxide obtained by the ignition of zinc oxalate seemed to be an excellent standard catalyst. Several different preparations from zinc oxide and oxalic acid, from zinc chloride and oxalic acid, and from basic zinc carbonate and oxalic acid gave practically identical ratios of ethylene and hydrogen. The percentages of ethylene in two typical experiments are given below: 5 min., 25.7 and 25.8%; 20 min., 24.7 and 25.0%; 45 min., 24.0 and 24.3%; 90 min., 23.2 and 23.6%; 120 min., 23.3 and 23.7%. It is not feasible to incorporate promoters with zinc oxide through the use of water solutions because this treatment in itself modifies the ratio of dehydrogenation and dehydration shown by the catalysts. However, alcoholic solutions may be used for the addition to and removal of alcohol from zinc oxide without modifying its catalytic effects. Promoters may be incorporated with zinc oxalate through the use of aqueous solutions or suspensions.

The effect upon the ratio of dehydration to dehydrogenation of ethanol of adding small amounts of various materials to zinc oxide *ex* oxalate is shown in Fig. 3. The effect of some of these same promoters upon the ratio of gaseous products from ethanol over titania is shown in Table II. The percentage of alkene formed from ethyl, *n*-propyl, *iso*propyl and *iso*butyl alcohols over nine different zinc oxide catalysts is shown in Table III. The percentage of hydrogen present in the gaseous products equals the difference between 100 and the percentage of alkene shown in the table for a given set of conditions. The data obtained in the use of the alumina catalysts are not given in a table because all of them except the one containing sodium oxide gave a gas containing 98 to 99% ethylene after the removal of alkali-soluble materials amounting to about 5%. The sodium oxide aluminum catalysts had a very low activity and showed about nine parts of ethylene for one part of hydrogen. This effect of sodium oxide in lowering activity and producing hydrogen is characteristic. The volume of hydrogen produced is small and is in all probability due in part to the catalytic action of sodium oxide as distinguished from its promoter action.

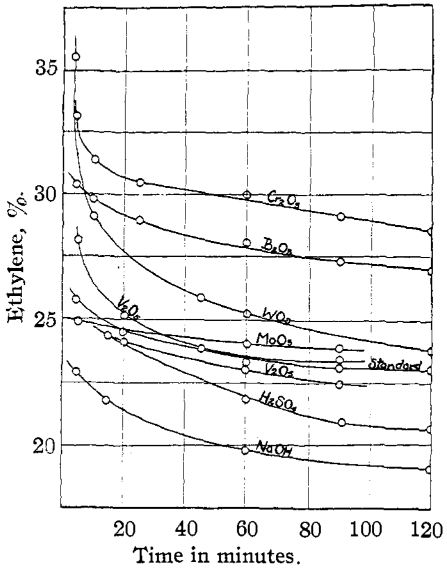

Fig. 3.—Percentage of ethylene from ethanol over "promoted" zinc oxide catalysts.

TABLE I

ETHANOL OVER IRON OXIDE CATALYSTS

Samples taken after 0.5 g. of catalyst had been used for one hour at 400°; rate of alcohol flow, 50 cc. per hour.

No.	Catalyst	CO_2, %	CO, %	C_2H_4, %	C_2H_6, %	H_2, %
17	Standard *ex* ferrous oxalate	10.2	1.1 to 1.7	6.1	7.5	76.2
18	Standard + H_2SO_4	4.8	1.1 to 1.7	7.0	7.5	80.8
19	Standard + NaOH	5.0	4.7	1.1	1.3	87.8
20	Standard + B_2O_3	6.2	1.1 to 1.7	10.8	18.9	64.0
21	Standard + CrO_3	8.4	1.1 to 1.7	7.1	8.8	75.6

A consideration of the data contained in the two graphs and the three tables brings out the following significant facts.

TABLE II

ETHANOL OVER TITANIA

Samples taken after 0.5 g. of catalyst had been used for five minutes at 400°.

No.	Catalyst	C_2H_4, %	C_2H_6, %	CH_4, %	H_2, %	Cc. of gas per min.
22	*Ex* $Ti(OC_4H_9)_4$ (a)	75.7	15.5	4.7	4.1	..
	(b)	75.6	16.4	5.2	2.7	..
	(av.)	75.6	16.0	5.0	3.4	..
23	*Ex* $Ti(OC_2H_5)_4$ (a)	64.8	27.1	4.6	3.5	..
	(b)	62.7	28.4	5.1	3.8	..
	(av.)	63.7	27.7	4.9	3.7	30.7
24	*Ex* $Ti(OC_2H_5)_4 + B_2O_3$	66.1	27.6	2.6	3.7	33.5
25	*Ex* $Ti(OC_2H_5)_4$ + NaOH	18.9	37.3	0.0	43.8	6.0
26	*Ex* $Ti(OC_2H_5)_4$ + NaOH	47.6	43.2	.0	9.2	30.0

TABLE III

PERCENTAGE OF ALKENE FORMED OVER VARIOUS ZINC OXIDE CATALYSTS

Samples taken after 0.5 g. of catalyst had been in use for one hour at 400°; alcohols passed over catalyst at the rate of 50 cc. per hour.

No.	Catalyst	Ethanol, %	Propanol, %	*Iso*propanol, %	*Iso*butanol, %
4	Lazier's "A"	9.5	16.0	..	31.5
2	Ppt. ZnO, Weston	21.6	..	..	1.4
3	Ppt. ZnO, Lazier	9.5	6.4	..	23.0
1	Ppt. ZnO, Millington	15.7	5.7	..	1.7
8	Standard, ZnO *ex* oxalate	23.6	4.1	7.4	1.2
11	Standard + WO_3	25.2	7.4	40.6	13.3
15	Standard + H_2SO_4	21.9	3.0	8.9	1.4
9	Standard + CrO_3	30.0	4.8	9.0	1.6
16	Standard + NaOH	19.9	1.6	5.0	..
10	Standard + B_2O_3	28.1	..	7.7	..

The proportion of ethylene to hydrogen is always lower for catalysts from the precipitated zinc hydroxides than for the zinc oxide *ex* oxalate (see Fig. 2). The ratio is dependent upon the exact method of precipitation and washing and varies very widely. This variation in catalytic effect is not due to the presence of a sulfate for the same variation is found with catalysts prepared from nitrates, chlorides and acetates. There is no evidence available to show that the variation may not be due to differences in the amount of sodium hydroxide adsorbed by the precipitated zinc hydroxide.

The use of 1% of chromium, boron or tungsten oxide in a zinc oxide catalyst markedly increases the proportion of ethylene formed. The percentage of ethylene in some cases is increased by 40% of the value of the unpromoted catalyst. Vanadium and molybdenum oxides have relatively little effect in changing the ratio of dehydration and dehydrogenation of ethanol while both sulfur trioxide and sodium oxide decrease the proportion of dehydration (see Fig. 3).

The effect of a given promoter is neither qualitatively nor quantitatively constant, but is specific for a given alcohol. For instance, a sulfate lowers the percentage of alkene from ethanol and propanol and raises it for *iso*propanol. Tungsten oxide, which shows but a slight promoter action for the formation of alkenes from ethanol and propanol, is a very active promoter for alkene formation from *iso*propanol and *iso*butanol. Chromium oxide, which is the most active of all the promoters used for ethanol, has very little effect upon the other alcohols. Boric oxide is a promoter for alkene formation from ethanol but in the concentration used is almost without effect upon *iso*propanol. These anomalous effects are even more marked in the case of some of the precipitated or *ex* hydroxide catalysts. For instance, Catalyst No. 3 gives only about 0.4 as much ethylene as the standard oxalate catalyst, yet it gives more propylene from propanol and almost 20 times as much *iso*butylene from *iso*butanol as does the standard oxalate catalyst. Lazier's "A" Catalyst and Millington's No. 1 Catalyst show similar divergent effects upon different alcohols.

Small amounts of sulfuric acid, sodium oxide, boron and chromium oxides in iron oxide decrease the formation of carbon dioxide from ethanol (see Table I). Of these promoters only boric oxide materially increases ethylene and ethane formation at the expense of dehydrogenation. Sodium oxide increases hydrogen at the expense of hydrocarbon, but the change is accompanied by so great a decrease in the activity of the catalyst that the change in ratio of products is of doubtful significance.

Boric oxide has little effect upon titania but sodium oxide increases ethane at the expense of ethylene, at the same time doubling the hydrogen and eliminating the formation of methane (see Table II).

It is obvious that Taylor's hypothesis and prediction as to the effect of acidic and basic promoters upon the ratio of dehydration and dehydrogenation is not supported by all of the experimental results stated above. Two promoters so unlike as sulfuric acid and sodium hydroxide show the same effect upon ethanol; that is to say, they lower the percentage of ethylene. These two promoters show opposite effects upon *iso*propanol (*i. e.*, they behave as predicted). It is unsafe to predict that a catalyst which shows high comparative dehydration for one alcohol will do so for another, for quite the reverse is often true. Promoters may not be classified as promoting dehydration or dehydrogenation except with reference to a specific compound.

In view of the failure of this hypothesis in the simple cases it is perhaps not necessary to raise the question as to the number and kind of ions which must be assumed to be present in a surface in order that four distinct primary reactions may occur simultaneously, as is sometimes true.

In previous papers by Bischoff, Nissen, Lazier and Adkins numerous examples have been given of the modification of the ratio of simultaneous reactions through changes in the method of preparation of the catalysts.

In the case of several of these catalysts this difference in ratio of reaction induced was really dependent upon the presence or absence of traces of certain promoters or inhibitors. In several other cases there is a *possibility* that this was true; in still other cases it seems certain that the ratio of reaction products was modified other than by the presence or absence of a promoter or inhibitor.

This was first demonstrated by Adkins for the reactions of esters over alumina from various aluminum alkoxides. It was demonstrated in the second case by Bischoff for the reactions of alcohols and other materials over titania from various sources. Lazier next obtained similar examples of selective activation with alcohols over zinc and iron oxide catalysts. The first of these attempts may be criticized in that the reactions of the esters are rather complicated and especially in that the range of selective activation was not very great. Bischoff's work may be criticized in that at that time the importance of boiling out the gases from the condensate was not realized. Moreover, it was not determined with certainty whether the C_nH_{2n+2} found was really ethane or methane or a mixture of the two. Lazier's results may be criticized in that in no case was he able to distil or otherwise rigorously purify the compound from which the catalyst was prepared.

It was of the highest importance, then, to demonstrate conclusively that the ratio of two competing reactions could be modified without the influence of a promoter. To this end tetra-ethyl and tetrabutyl orthotitanates were prepared and repeatedly distilled until they were demonstrated to be free from the usual metallic and acidic impurities. These two titanates were then hydrolyzed and used as catalysts against ethanol, using the best technique that has been developed in this Laboratory for the determination of the ratio of gaseous reaction products. The results as given in Table II are in general agreement with those of Bischoff and show conclusively that the titania from the butoxide and from the ethoxide differ very considerably in the ratio of ethylene and ethane produced while they give almost identical percentages of methane and hydrogen. These experiments demonstrate conclusively that selective activation may be obtained other than through the effect of catalyst promoters or poisons.

It is clear then (1) that the direction of shifting of the ratio of two competing reactions is not always dependent upon the acidity or basicity of the promoter, (2) that both the direction and amount of change in the ratio is specific for the alcohol and the catalyst and (3) that the ratio of competing reactions may be modified by other means than through the addition or removal of a compound from the catalyst. Some of these facts are out of harmony with the first hypothesis given in the introductory paragraph, while they are entirely in harmony with the hypothesis previously advanced from this Laboratory with regard to the possible importance of spacial relationships of the catalyst surface in determining the ratio of competing reactions. It must be admitted, however, that Adkins' hypothesis in its present form is of no value for predicting experimental results, and does not lead to positive experimental verification.

Lazier has suggested on the basis of unpublished work that the ratio of dehydration to dehydrogenation induced by a given catalyst is determined by the degree of hydration of the catalyst. Taylor called attention to this possibility in his address before the Colloid Symposium at Boston in 1926. The following facts would seem to have a bearing on the question. If a precipitated zinc oxide was brought up to reaction temperature (400°) and immediately used, there was first an increase in percentage of dehydration, followed by a slow decrease. This is clearly shown in Fig. 2. If, however, the catalyst was maintained at 400° in a current of dried air for fifteen minutes, there was no rise in alkene formation during the first few minutes of use (see Fig. 3). A prolonged preheating of an hour and a half increased ethylene formation by one per cent. or so over what it would have been after a fifteen-minute preheating and the rate of lowering of ethylene formation was decreased. Reheating a catalyst for thirty minutes in dry air after it has been in use for an hour or two restored the percentage of ethylene to approximately its former level. This reactivation may be repeated several times providing the catalyst has not become fouled. The passage of water vapor over the catalyst at 400° permanently impaired the dehydrating power of the catalyst, even when the catalyst was afterwards heated in dry air. These facts clearly show that the degree of hydration of the zinc oxide catalyst affects the ratio of dehydration and dehydrogenation of ethanol. It appears that the decrease in percentage of ethylene during the use of a zinc oxide is due to the accumulation of some volatile compound upon the catalyst. It seems questionable from a consideration of these facts whether the ratio of dehydration and dehydrogenation is a simple function of the degree of hydration of the catalyst.

Summary

The effect upon the ratio of simultaneous reactions of alcohols of the addition of small amounts of various acidic and basic oxides to zinc, iron, titanium and aluminum oxide catalysts has been experimentally investigated. The conclusions were reached (1) that the direction of the shift in the ratio of two competing reactions is not dependent upon the acidity or basicity of the promoter, (2) that both the direction and amount of change in the ratio is specific for the alcohol and the catalyst and (3) that the relative rate of competing reactions may be modified by means other than through the addition or removal of a compound from the

catalyst. These and other facts have been considered in their bearing upon the hypotheses which have been previously advanced to account for the variation in the ratio of competing reactions over various catalysts.

MADISON, WISCONSIN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BRYN MAWR COLLEGE]

THE SULFONATION OF PHENANTHRENE. I. A NEW MONOSULFONATE

BY LOUIS FREDERICK FIESER

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After a series of careful investigations, the results of which were published in 1902, Werner and his students[1] were able to show that three phenanthrene sulfonic acids may be obtained by the action of concentrated or fuming sulfuric acid on the hydrocarbon. Various methods of separating these isomers were elaborated and the compounds were all carefully identified and characterized. The yields, however, were poor, and the separation was a tedious process. In preparing large quantities of two of the acids according to Werner's methods, it has been found possible to introduce some improvements which render these substances more readily accessible and which also serve to cast further light on the course of the reaction.

Werner records that the best yields of the 2-acid (12%) and the 3-acid (18.6%) were obtained on heating phenanthrene with two molecular equivalents of concentrated sulfuric acid at a temperature of 120–130° for four and one-half to five hours. It was assumed that the greater part of the hydrocarbon was converted into disulfonic acids, and this conclusion has been confirmed by Sandqvist,[2] who found that disulfonic acids accompany the monosulfonic acids even when phenanthrene is sulfonated incompletely at room temperature. At a temperature of 100° or below, a third isomer, phenanthrene-9-sulfonic acid, which was not detected in the reactions carried out at 120–130°, is produced.

Before attempting to extend these observations, it seemed almost necessary to find some new method for the identification and the determination of the purity of the isomeric acids. Reactions such as the alkali fusion, or the preparation of the ester or the chloride, all require a fairly large sample of the dry salt, and they are all rather slow. A much more suitable derivative was found in the *p*-toluidine salt. With this amine, the phenanthrene sulfonic acids all form crystalline salts whose melting points are characteristic and fairly well separated. One can quickly

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[1] Werner, Frey, J. Kunz, M. Kunz, Löwenstein, Rekner and Wack, *Ann.*, **321**, 248 (1902).

[2] Sandqvist, "Studien über die Phenanthrensulfosäuren," Inaugural Dissertation, Upsala, **1912**.