Conclusions

Simplified and accurate modified methods for micro-determination of sulfur and halogens in organic substances are described.

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THE REACTIONS OF THE ALCOHOLS OVER ZINC OXIDE CATALYSTS

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The attention of most investigators of catalytic reactions has been directed towards the study of the factors determining the amount of substance reacting rather than towards those which determine the ratio of the reaction products. It was first pointed out in this series of papers[1] that there were two phases to the problem and that there was apparently little relationship between the factors determining the amount of material undergoing reaction and those determining the path or paths followed by the reaction.

This paper is concerned with the variation in the proportion of the two simultaneous reactions of dehydrogenation and dehydration of alcohols over zinc oxide and with the significance of the experimental results in elucidating the mechanism of the reactions at the surface of solid catalysts. Six of the simpler alcohols and three zinc oxide catalysts have been used at temperatures of from 337° to 438°. A summary of the experimental results is presented in the figure.

The experimental methods were the same as those previously described. They involved the passage[1h] of 40 g. of the alcohols, per hour, over 1 g. of the catalyst held at a constant temperature. The temperatures recorded in the figure are those indicated by a thermocouple placed in the catalyst mass. All of the data are for catalysts that had been in use for at least an hour and so had reached a rather constant condition of activity. The alkene dissolved in the distillate during an hour's run was boiled out and mixed with the gases collected during the hour, and the whole analyzed. There were always small amounts of carbon dioxide and air in the gas collected but these were calculated out of the analyses and the alkene and hydrogen reported as though they represented 100% of the gas. The preparation of the catalysts has been previously described.[1e] Catalyst A was from the zinc hydroxide precipitated from a solution of zinc sul-

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[1] Earlier papers of this series by Adkins, Lazier, Bischoff and Nissen, THIS JOURNAL, (a) **44**, 386 (1922); (b) **44**, 2175 (1922); (c) **45**, 809 (1923); (d) **46**, 130 (1924); (e) **46**, 2291 (1924); (f) **47**, 808 (1925); (g) **47**, 1163 (1925); (h) **47**, 1719 (1925).

fate, B was the "dry process" commercial product, and C was obtained by the hydrolysis of zinc isopropoxide in moist air.

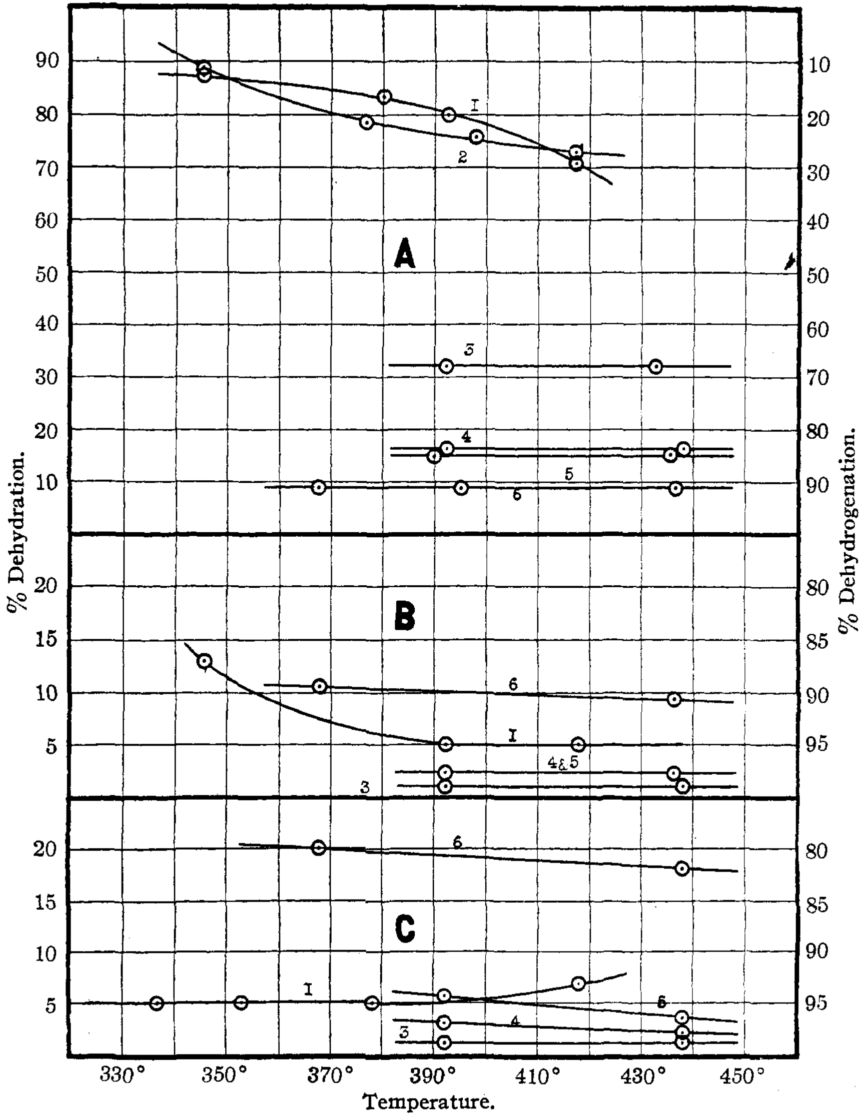

Fig. 1.—Behavior of alcohols over zinc oxide catalysts.

The percentage of dehydration and dehydrogenation over three zinc oxide catalysts, A, B and C at various temperatures, is shown for (1) *iso*propanol, (2) *sec.*-butanol, (3) *iso*butanol, (4) *n*-propanol, (5) *n*-butanol and (6) ethanol. Catalyst A was from precipitated zinc hydroxide, Catalyst B was from a "dry process" commercial zinc oxide, and catalyst C was from zinc *iso*propoxide.

The amounts of alkenes and hydrogen formed from the various alcohols, at the various temperatures, over the precipitated zinc oxide (A) have been previously reported.[1h] Similar accurate data for the other two catalysts are not available. These were not obtained because it had been previously demonstrated that the relative reactivities were independent of the type of catalyst and also because of the large amount of work necessary to obtain them. As previously pointed out, the reactivity varies with the way the pellets are placed in the reaction tube, the length of time the catalyst has been used, etc. Different preparations of the same type of catalyst give different reactivities; that is, two samples of precipitated zinc oxide may differ considerably in the amount of alcohol that they cause to react in unit time. In attempting to get the comparative reactivity of two alcohols, all of the above-noted conditions must be held constant and the experiments repeated many times. In contrast to the above, the relative rates of simultaneous reactions are very constant; that is, *iso*propanol with precipitated zinc oxide (A) at 418° will give, almost within the limits of error of gas analysis, 29% of hydrogen and 71% of propylene, in spite of very different reactivities due to different samples of catalyst, etc., as noted above.

It seems desirable to state the salient facts that have been disclosed in the experimental work.

1. The *relative* amounts of different alcohols undergoing reaction are independent of the catalyst within the limits of the experimental errors.[1h]
2. The ratio of dehydration to dehydrogenation is relatively independent of the structure of the alcohol as compared to its dependence upon the nature of the catalyst surface. For example, the order of the primary alcohols with respect to ease of dehydrogenation over precipitated zinc oxide is exactly the opposite of the order over the other two catalysts. With one of the catalysts (C), *iso*propanol, a secondary alcohol is dehydrated to a less extent than the primary alcohol, ethanol.
3. The above is further evidenced by a consideration of the extremely wide range over which selective activation of zinc oxide catalysts has been accomplished. The percentage of alkene formed at a given temperature has been varied from 5 to 88% for *iso*propanol, from 10 to 20% for ethanol, from 1 to 31.5% for *iso*butanol and from 2 to 15 or 16% in the case of *n*-propanol and butanol.
4. The ratio of dehydration to dehydrogenation, with the primary alcohols, is almost if not quite constant over the temperature range studied.
5. The ratio of the two reactions in the case of the secondary alcohols is markedly dependent upon the temperature. The extent of the change of ratio is a function of the catalyst and even the direction of change differs with the catalyst used. For example, *iso*propanol over Catalyst C gives more propylene at 418° than it does at 353°, while the reverse of this is true with Catalyst A.

6. It is obvious that, in general, Catalyst A is the best catalyst for dehydration, while Catalyst B is the best for dehydrogenation. However, these two catalysts give almost the same results with ethanol; while the C catalyst gives almost the same results as the B catalyst, except with ethanol.

Three hypotheses have been offered to account for the variation in the ratios of competing or simultaneous reactions. The first hypothesis presupposes differences in the relative adsorbing powers of the catalyst for the products of the reaction. The second depends upon differences in the spacing of the active points of the catalyst, wider spacings being supposed to catalyze one reaction and narrower spacings another. The third hypothesis postulates differences in the degree of unsaturation of the atoms (or groups of atoms) of the catalyst, one degree of unsaturation producing one reaction and another degree of unsaturation another reaction.[2] In their original form, all three of these hypotheses would lead one to expect that the best catalyst for the dehydrogenation of one alcohol would be the best for the dehydrogenation of all alcohols. The data presented in this paper shows that this is not in accord with the experimental findings.

Since the previous papers from this Laboratory have apparently not made clear the senior author's conception of the role of the catalyst in these reactions, it seems advisable to state explicitly the hypothesis which has been advanced. It is based on the idea of Langmuir[3] that the catalyst adsorbs the reactant and thereby produces a shifting of the electrons of the adsorbate so that further reaction may follow.

When an alcohol molecule, for example, is being adsorbed (or is adsorbed) it is attracted or acted upon by the forces (affinity) located in the active points or reaction centers of the catalyst. The direction of distortion of the electrons of the alcohol molecule (or, better, the direction of the shifting of the electron orbits) will of course be determined by the chemical nature of the catalyst (that is, whether the adsorbing material is platinum or alumina, for example), but it will also be determined, it is believed, 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. It would then follow that differences in the spacings of these active points would produce different distortions of the electron orbits and hence result in different reactions, just as the shape of the fragments of a

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[2] Bancroft, [*J. Phys. Chem.*, **21**, 602 (1917)]. Bancroft formulated the first hypothesis but he no longer considers it tenable although it is still held by numerous other chemists. The second hypothesis, suggested by Adkins, has been somewhat misunderstood because of his ill-advised use of the phrases "space lattice" and "spacing of the molecules" in the original paper. Later papers, however, pointed out that the "spacing" referred to was that of the relatively few "active points" of the catalyst. H. S. Taylor [*Proc. Roy. Soc.*, **108A**, 105 (1925)] advanced the third hypothesis noted above.

[3] Langmuir, *Faraday Soc.*, **17**, 617 (1922).

piece of paper would be in part determined by the relationship in space of the two hands which tore the original sheet.

As suggested above, there is no evidence that there is any particular spacing of points that, irrespective of the structure of the organic compound, will always produce dehydration or dehydrogenation or decarboxylation, and to that extent the original hypothesis of 1922 must be considered in error. It is believed that the way in which one of the "alcohol-catalyst" compounds will break up will be determined by the chemical nature and spacial configuration of the organic compound and by the chemical nature and spacial configuration of the catalyst. In what has been said above, reference is made to those reactions in which a single organic molecule breaks up into different sets of reaction products. In some cases where two organic molecules are involved it is necessary, as pointed out by Langmuir, that the adsorbing points be sufficiently close together so that this interaction may occur.[1d]

Taylor[2] has pointed out good reasons for believing that there are atoms of the metal in various degrees of unsaturation on the surface of copper and nickel catalysts. There is no evidence for believing that these variously unsaturated atoms would produce different ratios of simultaneous reactions, although the more unsaturated atoms will certainly adsorb molecules that the less unsaturated will not. It seems probable that the temperature at which a catalyst will begin to cause reaction is determined by the affinity of the active points. The greater this affinity the lower, possibly, will be the temperature at which the distortion of the molecule will be sufficient to permit reaction. Since the lower the temperature the less the tendency of these unsaturated atoms to rearrange to more stable configurations, it is readily seen why, the lower the temperature of reduction of a metallic oxide, the greater would be the proportion of these highly unsaturated atoms. This would result in a more powerful catalyst. It may well be that this explains why an alcohol-reduced nickel catalyst is more effective in splitting alcohol into methane, carbon monoxide and hydrogen than a hydrogen-reduced nickel catalyst; for, as Taylor has pointed out, the *real* temperature at the surface of the atoms in the reduction of nickel oxide by alcohol is lower than that with hydrogen because of the energy absorbed in splitting hydrogen out of the alcohol molecule. The *apparent* temperature of reaction is, of course, much higher for the alcohol reduction. Taylor's hypothesis offers a reasonable explanation for the fact that the activity of a catalyst for alcohols does not run parallel with its activity for acids, for example. It would seem that there may be a number of points on a titania catalyst that are unsaturated enough to react with acetic acid, but not enough so to react with ethanol.

There is no reason for predicting that the methods used in this Laboratory for the selective activation of oxide catalysts would result in atoms or groups of atoms which differed in their degree of unsaturation. Even if they were produced, the temperatures used with the oxide catalyst would certainly result in rearrangement to less unsaturated states, which would result in changes in the ratio of the competing reactions. On the contrary, experience has shown that the relative rates of the reactions are quite constant for different samples of catalyst and for long periods of use, while the activity which is dependent upon the number of active centers varies greatly under the same conditions. The more unsaturated centers would certainly be poisoned first and this would result in changes in the ratio of reactions, which phenomenon has not been observed to an extent at all like that which has been observed with respect to the activity.

Taylor further suggests[4] that the selective activation observed in this Laboratory may have been due to "selective poisoning." Unquestionably, selective poisoning determines in many cases the ratio of simultaneous, or the number of successive, reactions. It seems improbable that it does so in these cases, for it is hard to explain why the ratio of reactions is so constant a value, as long as the catalyst is made from a certain solid compound, while the activity of the catalyst is so variable for different preparations of the catalyst. In other words, why is it that the ratio of alkene to hydrogen is so constant for different preparations of catalyst from zinc hydroxide, while the activity of the catalyst may vary 100%, depending upon the manner of precipitation of the hydroxide, the thoroughness of washing, and the temperature at which the catalyst was dried? These latter factors unquestionably determine the number of "active centers" and the amount of "catalyst poisons" but they do not affect, except in a very minor way, the characteristics of the catalyst which determine the ratio of the reaction products. A rather conclusive answer to the suggestion of "selective poisoning" is the fact that the same catalyst is produced by the action of water upon a xylene solution of aluminum ethoxide as is obtained by the reaction of ammonium hydroxide upon an aqueous solution of aluminum sulfate or nitrate or of aluminum amalgam on water, while the alumina resulting from the hydrolysis of *solid* aluminum ethoxide is a very different sort of catalyst.[1b]

A further conclusion should be drawn from the experimental results, in view of the numerous attempts now being made to measure the relative tendency of groups or compounds to enter into a given reaction. For example, the ease of ring formation for each of three compounds is desired. It has been assumed that if A gave a yield of 75% of the cyclic compound, B of 50%, and C of 25%, these figures represented the relative ease of ring formation for A, B and C. If the relation between the conditions of reactions and the proportion of products held in that case as they have been shown to hold in the case of the reactions of the alcohols over zinc

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[4] Taylor, *J. Phys. Chem.*, 30, 165 (1926).

oxide and the esters over alumina, then the conclusion as to relative tendency for ring formation would be false; for, if the ease of dehydration of *iso*propanol as compared with ethanol had been measured over a certain zinc oxide, the conclusion then would have been that ethanol is more readily dehydrated than *iso*propanol, which we know to be untrue. It is not safe, therefore, to determine susceptibility for a given reaction under conditions such that the product or reaction we are interested in is only one of two or more simultaneous reactions.

Summary[5]

The outline and results of the experimental work have been so concisely stated in the second and in the numbered paragraphs of the paper that they need not be repeated here.

It has been further demonstrated that there are two distinct and almost unrelated sets of factors having to do with the catalytic reactions of the type here considered. One phase of the problem has to do with the amount of material entering into reaction, and the other with the proportions of the competing reactions.

The hypothesis as to the importance of the spacial configuration of the catalyst surface in determining the proportion of reaction products has been concisely restated. The validity of this and other hypotheses has been considered in the light of recent experimental work.

The relative reactivity, even of the members of an homologous series, may not be determined by noting the amount of a given end-product when that product represents only one of two or more simultaneous reactions, for the proportions of this product may be more a function of the particular conditions of the reactions than it is of the compounds under comparison.

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ACYL DERIVATIVES OF ORTHO-AMINOPHENOL. I

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When certain di-acyl derivatives of *o*-aminophenol are prepared in which one acyl group is attached to the oxygen and a different acyl group is attached to the nitrogen, several products are possible, depending on the acyl groups used and the order in which they are introduced into the *o*-aminophenol molecule.

Introduction of two different acyl groups in reverse order does not usually result in an isomeric di-acyl derivative, but either may result in the derivative obtained when the first order of introduction was used, or the

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[5] The formation of carbon dioxide and of resins from alcohols over zinc oxides is discussed by the same authors in the June number of the *Journal of Physical Chemistry.*